NASA Conference Publication 3349

Second Aerospace Environmental Technology Conference

A.F. Whitaker, M. Clark-Ingram, and S.L. Hessler, Editors

Summary of a conference held
in Huntsville, Alabama
August 6–8, 1996

March 1997

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Marshall Space Flight Center • MSFC, Alabama

National Aeronautics and Space Administration
Marshall Space Flight Center • MSFC, Alabama 35812

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SOLID ROCKET MOTOR MANUFACTURING AND DISPOSAL TECHNOLOGIES

ELIMINATING THE USE OF OZONE DEPLETING SUBSTANCES IN SOLID ROCKET MOTOR MANUFACTURING

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ABSTRACT

Ozone depleting substances (ODSs) are used throughout the world in the manufacture of solid rocket motors. The primary ODSs used are TCA (1,1,1-trichloroethane) and CFC-113 (chlorofluorocarbon-113). These substances are used because of their excellent cleaning properties, low toxicity, chemical stability and non-flammability. The solid rocket motor industry has creatively and aggressively tested, verified and implemented a number of ODS elimination steps to reduce over 1.6 million pounds annual use. A handbook was prepared as a collaborative effort of four United States large solid rocket motor manufacturers to detail success stories to date. The Handbook serves as a resource to further reduce dependence on ODSs in solid rocket motor manufacturing internationally and in other industries with similar processes. Case studies and details of ODS elimination, technical challenges preventing ODS elimination, and descriptions of the corporate implementation steps that manufacturers used to accomplish the ODS elimination are discussed.

INTRODUCTION

Ozone depleting substances (ODSs) are targeted for phase out from production worldwide by the signatory nations to the Montreal Protocol. CFC-113 (chlorofluorocarbon-113) and TCA (1,1,1-trichloroethane) are ODSs traditionally used in the manufacture of solid rocket motors. Manufacturers have effected significant reduction in the use of these ODSs.

In the United States large solid rocket motors are used to launch a variety of payloads into space, including communication, navigational and scientific satellites and the manned Space Shuttle orbiter. The large solid rocket motor family includes the Titan IV solid rocket motor (SRM), the Titan IV solid rocket motor upgrade (SRMU), the Space Shuttle reusable solid rocket motor (RSRM), and the Minuteman III solid rocket motor.

A solid rocket motor design takes years to qualify after an expenditure of extensive resources. Past successes and failures in manufacturing solid rocket motors are critically important to the safety and reliability of the vehicle. Solid rocket motor success is assured through rigorous quality control and attention to detailed material specifications. Changes to manufacturing methods are accepted only after long-term testing and extensive

evaluation. Such testing and evaluation can involve numerous steps which may include multiple full scale static firings of a representative solid rocket motor.

Despite these technical safety and reliability challenges, the solid rocket motor industry has successfully tested, approved and implemented alternatives to ODS use. A handbook was written to detail the successful ODS reductions realized by the manufacturers of large solid rocket motors.(1) This information can be applied throughout the world's solid rocket motor and other manufacturing industries to assist in strategies to achieve complete elimination of ODS use.

BACKGROUND

ODSs are targeted for phase out from production worldwide by the signatory nations to the Montreal Protocol. The United States Federal Clean Air Act Amendments of 1990 require the Environmental Protection Agency to implement the produciton phase out in the United States. The Clean Air Act Amendments provide some limited exemptions to the production phase out schedule for specific ODSs for limited amounts of time. The exemptions are granted by authority established in the Montreal Protocol. Essential Use Exemptions are granted only if the parties to the Montreal Protocol approve the exemption request. An Essential Use Exemption may be granted after the following criteria are satisfied: 1) all feasible steps to eliminate ODS are being taken; 2) no remaining technically feasible alternatives exist; 3) storage and recycling are not available options; and 4) use is necessary for the functioning of human society.

NASA and Thiokol became aware that an Essential Use Exemption request was necessary for critical TCA uses to allow time to qualify alternatives for RSRM manufacturing.(2) Similarly, the Air Force developed an Essential Use Exemption request for critical TCA use in SRM manufacture.(3) Technical interchange meetings were held between NASA, Air Force and contractors to exchange and document lessons learned and to assure that every feasible step is taken to eliminate ODSs.

Solid rocket motor processing depends on the proven performance of past successes. Solvent compatibility is an issue and concern with the highly energetic materials and processes used to manufacture solid rocket motors. TCA and CFCs have a history of success due to their excellent cleaning properties, low toxicity, chemical stability and non-flammability. Changes to existing specifications require rigorous testing and evaluation.

The impending production ban was met with proactive corporate environmental policies which included integrated product/total quality management teams. This integrated approach is a proven key element to success. Some manufacturers approached ODS elimination from the corporate directive and organization level, while others approached the problem from a manufacturing process change level. Partnerships were formed with

teams from competing manufacturers. Production facilities were opened to scrutiny by international experts, i.e., the Solvents, Coatings and Adhesives Technical Options Committee of the Technology and Economics Assessment Panel to the Parties of the Protocol. Much of the initial cooperation was generated by the need to develop the NASA/Thiokol and Air Force Essential Use Exemptions for critical uses of TCA. At this juncture, the idea of documenting the manufacturers' successful ODS elimination resulted in the publication of the Handbook. The intent of the handbook is to extend the lessons learned from the United States solid rocket motor manufacturers to benefit the international community in developing strategies for total ODS elimination. The Titan Program office has funded and managed the Handbook effort with the direct cooperation of the involved manufacturers and the endorsement of NASA, the United States Environmental Protection Agency and the Industry Cooperative for Ozone Layer Protection (ICOLP).

ODS ELIMINATION

Solid rocket motor manufacturers were surveyed in detail on their past and present ODS use. Manufacturers of four large solid rocket motors were included: United Technologies Corporation/Chemical Systems Division (UTC/CSD) manufacturer of the Titan IV Solid Rocket Motor (SRM); Alliant TechSystems (formerly Hercules) manufacturer of the Titan IV Solid Rocket Motor Upgrade (SRMU); Thiokol Corporation manufacturer of the Space Shuttle Reusable Solid Rocket Motor (RSRM); and GenCorp Aerojet manufacturer of the Minuteman III. Each manufacturer replied to a survey on the following areas: corporate background and ODS elimination policy; solid rocket motor manufacturing technical constraints; past, current and future ODS usage; and ODS elimination, alternatives and recycling. Site interviews were conducted at each manufacturer by the handbook team consisting of Air Force, The Aerospace Corporation and support contractors. The manufacturers maintained review authority over the handbook content to ensure correctness of technical data and exclusion of proprietary information.

The handbook identifies manufacturing processes and quantities of ozone depleting substances historically used in the manufacture of solid rocket motors. Type of ODS, solid rocket motor manufacturer, and specific process hardware are described. ODS elimination efforts are discussed including strategies to identify criticality of use, screening and testing of alternatives, implementation of alternatives and resultant ODS reduction.

From 1989 through 1994, the four United States manufacturers of large solid rocket motors eliminated 1.6 million pounds of ODS use per year. Usage in 1996 is forecasted to be 10 percent of 1989 use. The four manufacturers are committed to elimination of

ODS use by 2002, if not earlier. Figures 1 and 2 illustrate the TCA and CFC reductions of the surveyed solid rocket motor manufacturers.

Elimination of ODSs was achieved through five general methods: 1) point of use inventory control and management: 2) personnel training; 3) manufacturing process and/or specification changes; 4) aqueous and semi-aqueous cleaning alternatives; 5) solvent capture and recycling.

Minimizing ODS use through inventory control is an effective strategy that can be applied to any manufacturing operation using hazardous materials. A single point of issue to distribute small quantities on an as needed basis eliminates excess quantities of materials occupying shop storage space, minimizes losses from excessive emission loss in large open containers and minimizes waste disposal quantities. An effective inventory control tied with employee training can effect large reductions in hazardous material usage.

Non-critical uses of ODSs were identified and eliminated through employee training and substitution of aqueous based cleaners. Employee ideas for ODS elimination and reduction were encouraged, accepted and awarded through company sponsored programs. Manufacturing and maintenance personnel were key members of integrated product teams to re-engineer methods to eliminate/reduce ODSs. Largest ODS reductions were realized through elimination of non-critical cleaning processes and replacement of TCA/CFC vapor degreasers.

Although ODSs alternatives were successfully implemented, elimination had some disadvantages. ODS substitutes increased the number and duration of manufacturing steps and caused an increase in waste stream volume. Aqueous and semi-aqueous cleaners may clean to the same or better level of cleanliness, however, they often require additional agitation with mechanical equipment with multiple rinse cycles and additional waste streams. For example, substituting an aqueous cleaner for TCA in one case resulted in increasing the liquid handled from 55 gallons of TCA that evaporated during use to 500 gallons of water and an aqueous cleaning solution that must be treated prior to disposal.

Manufacturers have implemented plans to achieve complete ODS elimination. However, critical solid rocket motor manufacturing processes remain which require Essential Use Exemptions for the continued use of TCA. These applications include critical bonding processes, propellant tool cleaning; cleaning of flight materials prior to bonding/sealing and dispersion of catalyst in the propellant formulation. Substitute materials or processes for these critical uses have not been qualified. Safety and reliability concerns restrict the use of non-qualified materials or processes.

Despite the technical challenges and potential for catastrophic failure, the solid rocket motor industry has aggressively tested, verified and implemented a number of ODS

FIGURE 1. TCA (1,1,1-trichloroethane) USAGE BY U.S. SOLID ROCKET MOTOR MANUFACTURERS

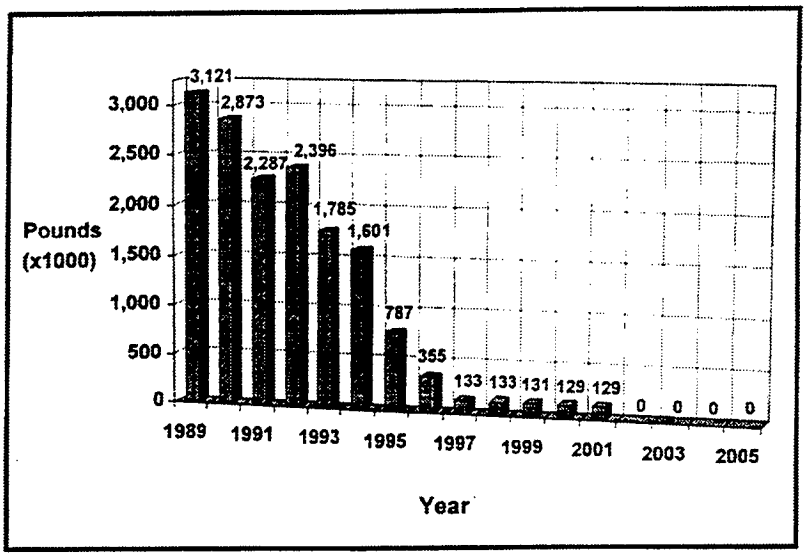
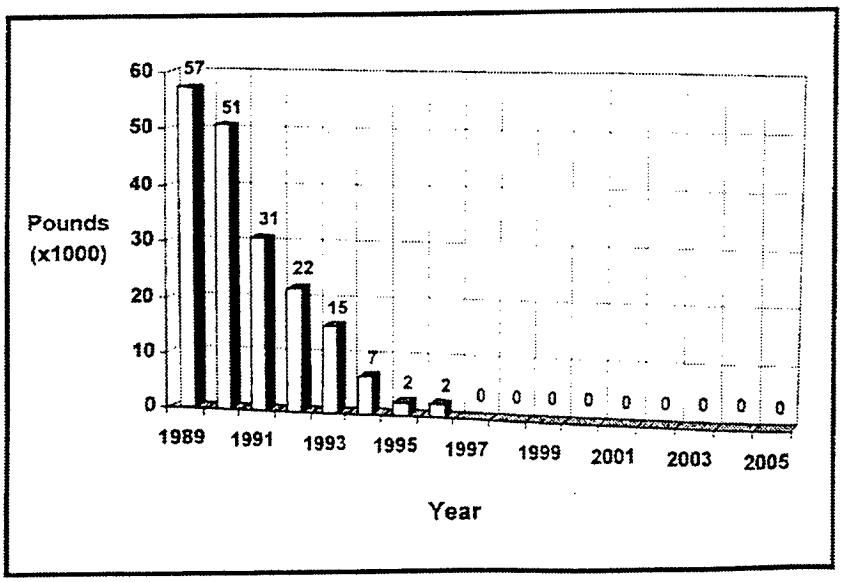


FIGURE 2. CFC-113 (Chlorofluorocarbon) USAGE BY U.S. SOLID ROCKET MOTOR MANUFACTURERS



elimination options. These steps led to elimination of more than 90% of ODS use over an 8-year period (1989-1996). Testing continues to further reduce the remaining ODS use.

MANUFACTURER EFFORTS/EXAMPLES

The four manufacturers surveyed for this project use a combination of corporate commitment and integrated product teams to achieve ODS elimination. This section of the paper will highlight corporate initiatives, ODS quantities eliminated, technical challenges and process/material change which resulted in a large ODS reduction.

Alliant TechSystems (formerly Hercules Aerospace Company).

Alliant TechSystems has implemented a number of corporate initiatives to aid in protecting and preserving the environment. These initiatives include:

- Responsible Care (established to improve chemical production, handling, use and disposal)
- We Care (award program for employees)
- 80/20 Program (air pollutant emission reduction program)
- 33/50 Program (EPA-17 reduction program)

A specific Pollution Prevention Management Practice was established which addresses ODS elimination projects. Environmental teams composed of different contributing offices within Alliant (Environmental Committee, Process Engineering, Project Offices, Manufacturing, Maintenance, Facilities Engineering, and Safety, Industrial Hygiene and Environmental Engineering) are trained to identify ODS use and maximize elimination.

In 1989, the primary ODS use was processing a TCA/methylene chloride-based sizing compound used to coat and protect the filaments in the manufacture of graphite fiber and case winding operations. Alliant's graphite fiber manufacture supports Titan IV solid rocket motor upgrade (SRMU), Delta and other commercial programs. In 1993, graphite filament production for the current buy of Titan IV SRMU cases was complete. In 1994, Alliant initiated the replacement of TCA/methylene chloride based sizing with a water-based substitute to support current customers and future hardware production.

Residual ODS use will be restricted to the small quantities of TCA requested in the Titan Program's Essential Uses Exemption.(2) Four small-quantity TCA uses are critical to the success of the Titan SRMU: surface activation at composite case/insulator bondline; surface activation of insulation for breather cloth attachment to ensure proper curing; surface activation at insulator/propellant bondline; and dispersing catalyst in propellant formulation. An intensive scientific effort, which includes detailed test plans, is ongoing to identify alternatives. Completion of the Air Force approved program, excluding any static test firings, is expected to approach $5 million.

Alliant has reduced a total of 1.5 million pounds of TCAuse from 1989 to 1995. By 1996, the use of TCA in the manufacture of the motor will be reduced to 1% of 1989 use.

United Technologies Chemical Systems Division (CSD)

CSD has an environmental policy that states "all environmental hazards can be controlled." The Consolidated Pollution Prevention Team aligns and drives the activities of three partner teams: Environmental Design Team, Environmental Technology Team, and Waste Elimination Steering Committee. This integrated team approach to pollution prevention with specific accountability to high levels of corporate management resulted in a large reductions of ODS use.

CSD reduced over 50% of their TCA use in one year (1989-1990) with a resultant decrease of 118,000 pounds. A key to this reduction was inventory control. Historical TCA issue was a 55 gallon drum delivered to a manufacturing area. Management made a key decision to restrict the purchase of TCA to limit and reduce usage. All 55 gallon drums were recalled and replaced with a 5 gallon container maximum issue. Training of the employees was tied with the minimizing strategy. Although the cost per gallon of TCA was greater in the smaller containers, less solvent was purchased and smaller quantities of TCA were used with less resultant waste. A net cost savings was the result.

In process manufacturing changes, elimination of TCA in vapor degreasing and solvent hand wiping operations effected the largest ODS reduction. CSD has reduced 98 percent of ODS use since 1988. A plan is in place to eliminate ODS use by the end of 1995.

Thiokol Corporation

Top management and corporate environmental leadership at Thiokol established a variety of policy setting directives as part of the overall corporation's pollution prevention policy. These directives include the following:

33/50 Program (EPA-17)
Hazardous Solvent Emission Reduction
Pollution Prevention

The ODS elimination problem was addressed by a joint NASA/Thiokol management team. All divisions using ODSs were surveyed followed by a solvent replacement tasks based on highest ODS usage. Training in recognizing, handling, controlling and proper disposal of ODSs and other hazardous substances was critical in reducing emissions. Cross-functional teams worked to identify and implement the elimination, reduction, or control of vapor emissions.

Although significant ODS reductions are effected, certain critical uses of TCA are necessary to avoid significant safety and reliability impacts to the Space Shuttle program. Thiokol/NASA requested and received approval for an Essential Use Exemption in recognition of continuing purchase requirements to meet critical needs. Thiokol requires an exemption of up to 125,000 pounds of TCA per year; emission levels are estimated at approximately 70,000 pounds per year. The request nomination was approved by Parties of the Protocol for 1996 and 1997. NASA/Thiokol has resubmitted the nomination for critical hand-wipe operations until the process can be eliminated by 1998-2001. Thiokol continues to take every technically and economically feasible step to reduce the amount of TCA use to accomplish the essential RSRM needs.

ODS reductions were implemented through the elimination of unnecessary use, reduction of the amount of preservative grease used to protect the steel case, and improvement of the vapor degreasing control system. A novel process change was instituted to transfer cleaned steel cases and domes between facilities using an enclosed environmental trailer. The use of the trailer eliminates the need for applying preservative grease for corrosion control during transport and subsequent hand-wipe cleaning operations using TCA.

From 1989 to 1994, Thiokol eliminated nearly one million pounds of TCA. Thiokol will reduce approximately 75% of historical use by 1996 with plans to reduce an additional 15% in 1997.

GenCorp Aerojet

A proactive environmental protection program is enforced by Aerojet corporate policies. Environmental incidents are mitigated through the Environmental Management Standards. Concurrent Product Development protocol involves early interaction between the program office, engineering manufacturing, quality, test and environmental support team to address all potential environmental issues as part of initial product development. Candidate ODS alternatives are approved through a New Product Evaluation process. Other corporate environmental initiatives at Aerojet include the following:

- Chemical Inventory Control System
- Community Awareness and Emergency Response Program
- Resource Recovery System
- Clean-Burning Solid Rocket Propellant
- Pollution Prevention Program and Solvent Replacement Policy

Aerojet reduced 37,000 pounds of ODS from 1989 to 1994. The elimination of vapor degreasing and solvent hand wipe cleaning resulted in the largest ODS reductions. Aerojet has a historical record of environmental vigilance. In 1987, Aerojet was one of the first aerospace companies to implement an aqueous wash system to replace vapor degreasers for metal parts.

SUMMARY/CONCLUSION

The cooperation exerted for this effort is unprecedented in the sharing of lessons learned among competing manufacturers and industry. ODS reduction efforts of the four large solid rocket motor manufacturers ultimately realized 1.6 million pound-per-year reduction from 1989 to 1994.

In conclusion, extracted is some select text of the Handbook foreward authored by Dr. Steve O. Andersen, Deputy Director EPA Stratospheric Protection Division. "*Rocket motor manufacturers and their customers decided to put protection of the ozone layer above concern for competitive advantages... It is too early to quantify the broader advantages of technical cooperation but it is significant that Air Force, NASA and their contractors all agree that it has been a win-win-win situation.*"(1)

ACKNOWLEDGMENTS

The Handbook project has truly been an integrated product team effort and there is not enough space in this small area to express gratitude to all the individuals who have personally contributed. I would like to acknowledge the contributions of the Handbook technical team (U.S. Air Force, The Aerospace Corporation, SRS Technologies, Kleinfelder and EA Engineering), and to re-emphasize the unprecedented cooperation and contributions of the solid rocket motor manufacturers and all the organizations which have reviewed and endorsed this project.

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ENVIRONMENTALLY BENIGN CLEANING AND DEGREASING METHODS FOR THE SOLID ROCKET MOTOR INDUSTRY

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Abstract

In response to impending environmental regulations on ozone-depleting chlorinated solvents and hazardous air pollutant emissions from other solvents, the propulsion industry is faced with the challenge to implement new environmentally acceptable solvents for use in manufacturing, maintenance, and other processing operations. Hardware cleaning and coating operations in particular, such as motor case and component degreasing, need to be addressed. While all industries face similar challenges, unique concerns such as case-insulation-propellant bonding characteristics in solid rocket motors and explosives safety issues regarding solvent/energetic material compatibility make transition to alternative processes more problematic in many respects for the propulsion industry. Considerable effort is being devoted to solving these problems. This paper briefly summarizes achievements by the solid rocket industry to identify alternative cleaning processes for flight hardware.

Introduction

1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113), 1,1,1-Trichloroethane (TCA), and methyl ethyl ketone (MEK) have been used as universal cleaning agents in the manufacture, refurbishment, processing, and maintenance of solid and liquid rocket propulsion systems. In the solid rocket industry, a critical application of these materials is to clean motor case, case insulation, propellant liner, and in some cases propellant surfaces that form critical bonded interfaces of the rocket motor structure. A cross section illustrating these interfaces for a representative motor configuration is shown in Figure 1. Two types of cleaning operations using these solvents are normally required: 1) vapor degreasing of the motor case using one of the chlorinated solvents to remove gross contamination, and 2) hand wipe precision cleaning of motor case and component surfaces. In addition, MEK is used to activate uncured insulator surfaces during insulator fabrication and installation. The production of CFC-113 and TCA has been prohibited under Title VI of the 1990 Clean Air Act Amendments (CAAA) as of 1 January 1996. The use of MEK for hand wipe operations will most likely be prohibited in the near future under another part of the CAAA, the Aerospace Manufacturing and Rework National Emission Standard for Hazardous Air Pollutants (NESHAP). This paper briefly summarizes achievements by the solid rocket industry to identify alternative environmentally acceptable cleaning processes for flight hardware. A more detailed review on implementation of alternative cleaning processes for solid rocket systems is also available (1).

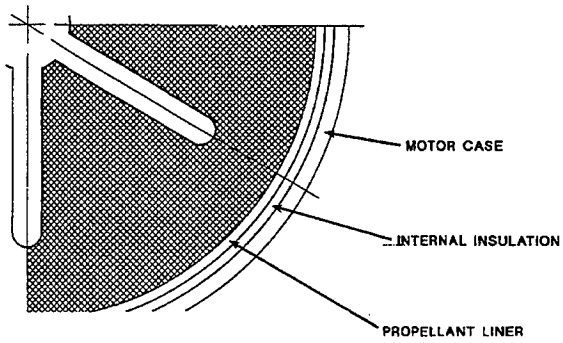

Figure 1. Critical Rocket Motor Bond Surfaces

Selection Methodology

For solid rocket motor applications, the most important quality of a potential alternative cleaning method is the resulting effect on the structural integrity of the motor case-insulation-propellant bonds. Bond integrity has been evaluated experimentally using variations of standard propulsion industry bondline tests such as the double plate tensile adhesion, 90° peel, and bond-in-tension "poker chip" tests. Many secondary factors important to the practical use of a technique must also be considered, however. Although a particular technology may provide effective cleaning, full scale implementation may be impractical due to environmental or occupational safety considerations, process integration issues, cost, or other factors. The experimental results on cleaning effectiveness/system effects can be used in a trade-off analysis against the other factors to select the best process or cleaner with presumably the least overall operational impact.

Results and Lessons Learned

In a program sponsored by the Phillips Laboratory, a team of investigators from Aerojet, United Technologies Chemical Systems Division (CSD), and Thiokol has performed a detailed assessment (not including experimental evaluation of technical viability) of commercial cleaning techniques for potential use in solid rocket motor manufacturing (2). Technologies recommended for laboratory and pilot scale evaluation/demonstration as replacements for vapor degreasing were aqueous spray cleaning, water jet blasting, and carbon dioxide pellet blasting. Likewise, methods recommended for testing as replacements for various hand wipe operations were:

1) precision cleaning of motor case prior to insulator application - aqueous cleaners, hydrocarbon cleaners, no clean after grit blasting, and carbon dioxide pellet blasting;

2) rubber activation during insulator fabrication - hydrocarbon cleaners, and no activation/wipe;

3) cleaning of rubber or phenolic insulation prior to liner application - aqueous cleaners, hydrocarbon cleaners, abrade and dry wipe, peel ply, and carbon dioxide pellet blasting;

4) cleaning of insulation or propellant prior to inhibitor application - aqueous cleaners, hydrocarbon cleaners, and no clean.

Several programs have investigated technologies identified in the Phillips Lab study.

Vapor Degreasing Alternatives

Thiokol and NASA Marshall Space Flight Center (MSFC) have conducted several studies to identify alternate methods to replace TCA vapor degreasing and precision cleaning of steel motor cases for the Space Shuttle Solid Rocket Motor (SRM) program.

In one program(3), five materials representing the major chemical variations of aqueous cleaners were evaluated as 10% solutions in a spray cleaning process at 155 °F, for removal of contaminants such as case preservative grease, hydrotest oil, and magnetic particle inspection solution residue. The cleaners evaluated were Brulin 815GD, Metalube 4U, Turco 3878 LFNC, Remoxide 32-M, and Detrex EC375d.

Fracture energy (for propagation of a crack through an adhesive bondline) tests with tapered double cantilevered beams (TDCB) according to ASTM D3433-75 and tensile adhesion tests with motor case-epoxy structural adhesive bond specimens showed that Brulin and Metalube appeared to perform as well as the TCA baseline, with Brulin performing slightly better than Metalube. Samples were also evaluated using tensile adhesion tests after accelerated aging at 135 °F and 70% relative humidity for four weeks. Again, Brulin performed slightly better than Metalube although both performed well. Thus, Brulin was down-selected as the aqueous cleaner of choice for use in a spray process.

In a concurrent NASA program(4), an agitated immersion process with the Brulin cleaning agent was demonstrated for removing preservative grease from steel case materials. The aqueous process demonstrated equivalent cleaning effectiveness to the baseline TCA process in tensile adhesion and peel tests (both bond strength and failure modes) of specimens fabricated using a variety of steel motor case materials with both butyl rubber and ethylene-propylene-diene-monomer (EPDM) rubber case insulation systems.

Additional work on aqueous cleaning was performed by investigators from Science Applications International Corporation (SAIC) and NASA/MSFC in support of the Space Shuttle Advanced Solid Rocket Motor (ASRM) program(5). Sample ASRM steel motor case coupons contaminated with metal case preservative grease were successfully cleaned (compared to TCA) using a spray process with either Brulin or Turco solutions, as determined by tensile adhesion and peel tests with specimens representing the steel motor case-Kevlar/EPDM internal insulation system. In addition, essentially no bondline degradation was observed upon accelerated aging for up to six months under conditions of 120 °F and 80% relative humidity for substrates cleaned with either material.

In another program, Thiokol/MSFC evaluated two cleaners, Brulin 815GD and Jettacin, in a spray process for degreasing and precision cleaning of the MNASA rocket motor case (6). The MNASA motor is a quarter scale reusable Space Shuttle booster test apparatus used for evaluation of motor materials and components. A baseline process consisting of a water blast followed by a grit blast was also assessed for comparison. Tensile adhesion and peel strength results with specimens representing the steel motor case-EPDM case insulation system indicated that all of the processes examined, including the baseline water blast/grit blast procedure, performed about the same and well above the program performance requirements defined as 100 psi tensile adhesion strength and 12 pli peel strength (Table 1).

Table 1. Steel Case-EPDM Insulation Bond Strength Results for Alternative Cleaning Processes (6)

Process	WB/SC/GB	WB/SC/GB	WB/GB
Cleaner	Brulin 815 GD	Jettacin	None
Tensile Adhesion, psi (CoV) Failure Mode (% cohesive)	387 (9.23) 93	348 (13.6) 71	399 (5.41) 99
Peel Strength, pli (CoV) Failure Mode (% cohesive)	194 (2.98) 99	196 (5.67) 99	212 (2.16) 100

Legend:
WB = Water Blast SC = Spray Clean GB = Grit Blast CoV = Coefficient of Variation

The program included a full scale spray clean/grit blast cleaning process demonstration. Surface cleanliness of cleaned motor cases was examined from non-volatile residue (NVR) analysis. In addition, tensile adhesion and peel tests were performed on witness specimens processed along with the actual hardware. NVR, tensile adhesion, and peel strength results were comparable (exceeding program requirements) to the previous coupon tests.

Based on the successes achieved in these programs, and some further development work, aqueous spray cleaning is being implemented by Thiokol and NASA to replace the current TCA vapor degreasing operation for critical bondline cleaning of Redesigned Solid Rocket Motor (RSRM) flight hardware (7).

The water blast/grit blast process is an important example of an effective solvent-free motor case cleaning method. In fact, Thiokol and NASA have obtained sufficient data to show that water blasting could also be used for precision motor case cleaning (7). According to the Phillips Lab study, the cost of implementing this type of system would be competitive to aqueous spray cleaning for large rocket motor systems (2). However, a more conservative approach has been selected for the RSRM program using water blasting for gross cleaning of boosters recovered after launch, followed by aqueous spray precision cleaning.

Aerojet has also been successful in developing an aqueous motor case cleaning/degreasing method for its tactical motor operations (8). The process system consists of agitated aqueous immersion cleaning, agitated deionized water/rust inhibitor rinse, and hot air dry unit operations. The cleaning solution used is Turco 3878 LFNC in deionized water. The system is used to remove protective grease and grit blast residue, and is capable of handling four to six cases at a time for a total of 24-36 per eight hour shift.

Conversely, Alliant Techsystems (formerly Hercules) Allegheny Ballistics Laboratory (ABL) is implementing a spray cleaning process using a specialty hydrocarbon cleaner, Exxon Actrel 1160L, for tactical motor production operations (9). A hydrocarbon solvent was selected over an aqueous cleaner mainly based on cost considerations, although it also proved to be the most effective cleaner. A pilot plant facility study was undertaken in 1994 to optimize wash/rinse conditions and processing parameters such as nozzle type/size, flow velocity, wash time, air knife solvent removal, and dry time. Successful operation of the process has been demonstrated without misting, which is important due to the flash point of the solvent (143 °F). The cleaner was also determined to be suitable for hand wipe cleaning operations (results discussed later).

Corrosion Issues With Aqueous Cleaning

Flash rusting or general surface corrosion of metal motor case materials using aqueous cleaning processes is of general concern. NASA/MSFC found that three cleaners (Turco, Remoxide, and Dextrex) were clearly incompatible with aluminum and caused visible corrosion when used in an immersion process (3). Similarly, corrosion of solid aluminum and thermal spray aluminum coatings was also observed in a study of aqueous cleaning (Turco 3878 LFNC, Daraclean 283, and Blue Gold) by Lockheed and Aerojet for the Shuttle ASRM program (8). However, in other work by Atlantic Research Corporation (ARC) using aqueous cleaners Blue Gold and Hurriclean, steel case-insulation bond strength was not degraded even when visible oxidation spots were present on the motor case specimens (8). Some corrosion of steel case substrates cleaned with various aqueous processes was also observed by Hercules ABL (9). Although some correlation between reductions in bond strength in "poker chip" tests and corrosion was observed, all samples failed in propellant indicating good bond properties. Thus, the level of corrosion permissible before degradation of bond properties in general is unclear.

Hand Wipe Operations

Hercules ABL performed a detailed study of TCA and methylene chloride replacements for precision hand wipe cleaning of metal motor case and case insulation materials representative of various production motors (9). Seven candidates from aqueous and specialty hydrocarbon solvent classes were evaluated for removal of grit blasting dust and skin oils. Cleaning effectiveness was evaluated for both case and insulation surfaces with specimens representing various rocket motor designs. These include:

1) aluminum case-EPDM insulator-liner-double base propellant

2) aluminum case-EPDM insulator-liner- hydroxy terminated polybutadiene (HTPB) based composite propellant

3) steel case-synthetic butyl rubber (SBR) insulator-liner-carboxy terminated polybutadiene (CTPB) based composite propellant.

Tensile adhesion "poker chip" and peel strength data (average of duplicate tests) from the test matrix are shown in Table 2. Many of the cleaners performed as well as the baseline solvents. Low peel strengths with some of the double base propellant samples cleaned with aqueous cleaners were attributed to insufficient drying of the cleaner off of the insulator prior to liner application. Based on a statistical analysis of the results to down-select the two best cleaners in each category, and subsequently a final assessment of safety, environmental, implementation, and cost considerations, the specialty hydrocarbon solvent Actrel 1160L was selected.

Aerojet evaluated a number of candidate MEK and TCA replacements as part of the Minuteman motor remanufacture program (8,10). MEK replacements were studied for hand wipe cleaning of titanium motor cases before application of the nitrile rubber insulation and activation of the uncured insulation during lay-up. TCA replacements for

hand wipe cleaning of the cured insulation surface prior to application of the propellant liner and cleaning of propellant areas prior to inhibitor application were also evaluated. The cleaners were evaluated for effectiveness in removing contaminants representing the effects of handling, such as skin oils and other dirt.

Table 2. Hercules ABL Bond Test Data for Candidate Cleaners (9)

	Al-EPDM-NC/NG		Al-EPDM-HTPB		Steel-SBR-CTPB	
Solvent	Tensile (psi)	Peel (pli)	Tensile (psi)	Peel (pli)	Tensile (psi)	Peel (psi)
CH_2Cl_2/TCA	75	3.6	93	3.6	91	5.2
DuBois ISW-24	73	2.7	86	3.5	82(1)	6.9
DuBois ISW-24/RI-6	73	2.6	87	4.5	90	7.6
DuBois ISW-24/Oxisolve	72	1.9	76	3.9	70(1)	6.1
Actrel 1160L	72	3.1	89	3.4	88	7.1
Oxsol 100	74	4.0	80	3.8	89	6.7
Primaclean 3600	74	3.6	62	3.0	78(1)	5.0
DuBois 422	71	1.8	84	3.3	91	9.3
No clean	66	3.5	96	4.5	88	6.1

Notes: (1) corrosion present on metal surface
(2) methylene chloride used as control for Al-EPDM-NC/NG, otherwise TCA used

ASTM lap shear test data for specimens employing titanium motor case material adherends bonded together with the adhesive-nitrile rubber insulation system used in the rocket motor is shown in Table 3. All of the MEK replacement candidates provided motor case-insulation bond strengths exceeding the design requirement of 118 psi and at least two performed as well as the MEK baseline. Two candidates, MIL-C-87936 Alkaline Cleaner and a dry abrade and wipe process, were down-selected for additional testing. The abrade and wipe method involves lightly scouring the surface with grit paper followed by wiping with clean dry cheese cloth. It may not be effective for heavily contaminated areas and may be undesirable to use with materials that have a special surface treatment; however, the method was determined to be adequate for preparation of the internal insulation.

Two candidates were down-selected for further evaluation as TCA replacements for cleaning the case insulation surface based on preliminary lap shear tests with aluminum adherends bonded with epoxy. Double plate tensile and peel tests using titanium case-nitrile rubber insulation-composite propellant samples were used to further evaluate the selected replacements. Again, a simple procedure such as wiping with cheese cloth soaked in deionized water followed by a dry cheese cloth wipe was determined to be as effective (exceeding the design requirements of 50 psi and 10 pli, respectively) as TCA. Another candidate was a 10% solution of 2-butoxyethanol, the active ingredient in many common commercial cleaners. This also performed as well as the TCA control. Cleaning operations using MIL-C-87936, 2-butoxyethanol (5% solution), and deionized water substitutes were subsequently demonstrated during the assembly of a full scale Production Quality Assurance motor.

Propellant compatibility could be a significant issue for hand wipe operations such as propellant cleaning where inhibitor is applied and situations such as field maintenance activities where accidental contact between the cleaner and propellant may occur. However, only scarce data has been reported - for the compatibility of ammonium perchlorate based composite propellant (10), and high energy RDX and HMX ingredients used in some solid propellants (8,11) - with a few select cleaners.

Table 3. Candidate Replacements Examined by Aerojet (10)

MEK Replacements	Vapor Press, mm Hg	VOC g/l	Shear Strength, psi
MEK (Control)	71	806	767
Deionized Water	15	0	623
Abrade and Dry Wipe	0	0	739
10% 2-butoxyethanol	15*	39	549
MIL-C-43616 Alkaline	Unknown	138	1126
MIL-C-87936 Alkaline	15.0	141	1239
MIAK	4.5	888	652
MIBK	15.0	798	593
Diisobutyl Ketone	1.7	805	509
Dipentene	1.0	838	610
3-methyl butanol			445

*Estimated as approximately equal to water

Cleanliness Requirements

In general, current cleaning methods have been used successfully for many years without quantitatively determining the margins associated with the cleanliness required to yield structurally sound rocket motor bondlines. With the implementation of alternate cleaning and degreasing methods in production operations, assessing cleaning requirements with respect to appropriate performance criteria may enable the use of less aggressive cleaning processes using cleaners such as distilled water or other more benign materials in some programs. Data which could support this kind of analysis has been generated in some programs (5,9,12,13). Evidence exists that some surface contamination with specific materials might not adversely affect bondline properties in some systems. If appropriate low cost process monitoring or inspection techniques could be implemented, information on cleanliness margins might even allow consideration of eliminating some precision cleaning operations. Of course, this would require a cost/benefit analysis to determine if potential savings associated with the elimination of some cleaning operations are justified.

Conclusions

The solid rocket motor industry is successfully identifying substitute cleaning methods for current operations using chlorinated and other environmentally unfavorable solvents. Success is being achieved for both large booster and small tactical motor operations. Commercial cleaning processes used in other industries appear to work reasonably well for gross cleaning and degreasing operations involving rocket motor production. NASA is implementing water jet and aqueous spray processes to replace current cleaning operations for the Space Shuttle RSRM program. Aqueous and other alternative solvent based cleaning processes are being implemented by various manufacturing facilities. Some evidence indicates that simple methods such as dry abrasion or wiping with water wet rags may be sufficient for many hand wipe precision cleaning operations. The non-solvent techniques are most desirable, eliminating potential regulatory concerns associated with occupational safety, environmental protection, and solvent waste disposal.

The major challenge in identifying alternative processes is determining the best cleaning process for a particular application with minimal resource expenditures and operational impacts. No single technology or replacement cleaning agent appears to be as universally effective, safe, and easy to handle in operations with respect to the chlorinated solvents currently in use.

A few technology issues have received little attention, or at least have not been reported on. The potential for stress corrosion cracking of metal motor cases, induced by components of alternate cleaners, has apparently not been addressed. Another concern is that limited data has been reported involving the effects of alternative cleaning methods on bondline aging characteristics.

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SOLID PROPELLANT ENVIRONMENTAL ISSUES

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ABSTRACT

The objective of the Solid Propellant Environmental Issues (SPEI) project is to demonstrate environmentally acceptable technologies that will enhance the continued production of solid rocket motors (SRMs) by complying with current and anticipated environmental regulations. Phase I of the project identifies current and anticipated environmental regulations that may affect SRMs manufacturing in the future and identify emerging process technologies which comply with these regulations. Phase II of the project established a baseline database by fabricating an 800-lbs motor using the current manufacturing process. In Phase III, environmentally acceptable process technologies were evaluated, ranked, and selected for demonstration using criteria developed by the team. The results for Phases I - III have previously been presented. This paper will present data obtained to date on Phase IV. In Phase IV, the alternate process technologies were evaluated for compatibility, cleaning effectiveness, and waste minimization/pollution prevention. The best performing candidate for each application area was selected for demonstration. The selected process technologies will be inserted into the baseline manufacturing process from Phase II. The new manufacturing process will be demonstrated and evaluated through the scale-up and fabrication of two 800-lbs solid rocket motors.

INTRODUCTION

Since the establishment of a national environmental policy in 1969, the U.S. solid rocket motor (SRM) industry has come under increased scrutiny from the federal, state, and local environmental regulatory agencies concerning the impact of SRMs manufacturing and testing on the environment. All aspect of SRMs life cycle is affected, from initial research and development, production, testing, launching, through demilitarization and disposal. The SRM industry has made significant progress in an effort to address some of these challenges; namely the reduction of HCl in motor's exhaust plume, by an order of magnitude, with a new class of "scavenger" propellant. However, these efforts do not address the major source of pollution in the industry, which is SRM manufacturing and testing.

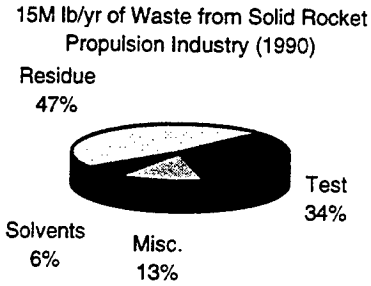

Fig. 1 Sources of waste in solid rocket propulsion industry

In 1990, the U.S. rocket industry generated 15 million pounds of solid waste[1]. These waste streams are directly related to motor manufacturing and testing (Fig. 1). At the same time, the number of hazardous disposal sites in the U.S. has decrease from over 1200 in 1980 to less than 300 by 1987. As the number of disposal sites continue to decrease and the number of environmental regulations continue to increase, as the trend would indicated, the cost associated with rocket manufacturing would continue to rise unless the issue of pollution prevention is addressed[1].

In 1993, the Air Force Phillips Laboratory (PL) initiated an effort to eliminate one source of the industry's waste streams: SRM manufacturing. The three-year effort, The Solid Propellant Environmental Issues (SPEI) project, was awarded to an industry team comprising Aerojet, CSD, and Thiokol (ACT). The objectives of the SPEI program are to: (1) review current environmental regulations to assess their effects on SRM manufacturing in the near future, and (2) demonstrate the ability to use existing environmentally acceptable (AE) process technology to fabricate SRMs which comply with current and future environmental constraints. The program focused on the manufacturing of a loaded motor from the liner fabrication to the propellant mixing and pouring. The test article selected for this demonstration is the 800-lbs SuperBATES (Ballistic Atmospheric Test Evaluation System) motor. This test configuration allows for the evaluation of technologies that can be use in the SRM manufacturing for tactical, strategic, and space launch systems.

The SPEI program is divided into five phases (Figure 2). In Phase I, Technology Assimilation, the ACT team's environmental specialists conducted a review of environmental regulations to identify their impacts on SRM design and manufacture in the year 2000 and beyond. A literature search and industry survey were conducted to identify alternative environmentally acceptable materials and processes for demonstration. Phase II, Baseline Manufacturing, was performed concurrently with Phase I at Thiokol's manufacturing facility in Utah. This Phase establishes the baseline data for SRM manufacturing using current process technology. $NaNO_3$ scavenger propellant was used to scale-up the current process and to fabricate an 800-lb SuperBATES motor and specimens for accelerated aging study.

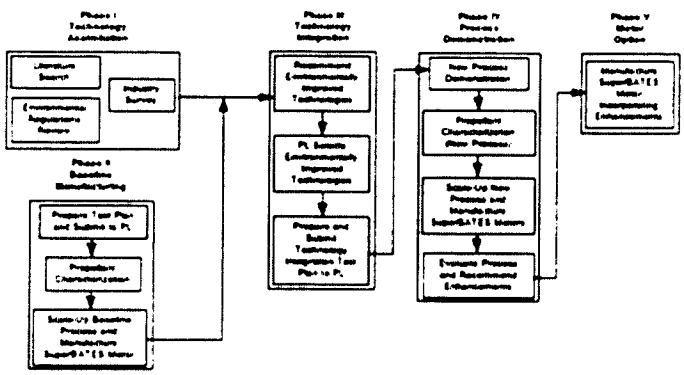

Fig.2 SPEI Program Plan

In Phase III, Technology Integration, the ACT team and PL down select those alternative technologies for demonstration in Phase IV. The criteria used in the down selection process is based on the team's forecast of environmental constrain on SRM manufacturing by the year 2000 (Phase I) and the limitations of current processes (Phase II). In Phase IV, Process Demonstration, those alternative technologies selected in Phase III will be demonstrated and evaluated through the scale-up and fabrication two 800-lb SuperBATES motors at the CSD and Aerojet facilities. These motors will be static tested at PL and enhancements to these alternative technologies will be identified. Phase V is an option for Thiokol to fabricate another large-scale motor incorporating the process enhancements (Phase IV) and those technologies that may have been developed since the end of Phase I.

PHASES I - III

Phase I, Technology Assimilation, comprise three related tasks: (1) Literature Search, (2) Environmental Regulations Review, and (3) Industry Survey. The tasks were performed concurrently by the team's environmental specialists to maximize the exchange of information in order to fully understand the complicated issues associate with environmental regulation and compliance. The first task in Phase I is the Literature Search. The team conducted a comprehensive literature search to identify those technologies that were developed as a result of current environmental regulations and those technologies that may influence future trends in environmental regulations. The search encompasses activities in the propulsion industry as well as other related industries such as aerospace and chemical. The search focused on those technologies that address the broad concerns of the SRM industry such as waste minimization, hazardous materials replacement, air emissions control, propellant waste treatment and disposal, and environmentally acceptable manufacturing methods. The literature search shows that a significant amount of work is being done by industry to overcome immediate and future environmental constraints. All of the SRM manufacturers are experiencing common problems and varied solutions to these problems exist within each company. The literature search also indicates that individual company has made significant progress in some areas of environmental compliance but much of the information has not been published outside of the companies. Proprietary information restriction plays a large part in this. There is also a significant amount of activity in related industries (i.e. chemical suppliers, etc.) concerning solvents replacement and pollution prevention. The team will continue with the literature search throughout the remainder of the program but at a reduced level to identify new technologies that may be of interest to SRM manufacturers[2].

The second task in Phase I is the Environmental Regulations Review. The purpose for this task is to allow the team to identify trends in the current and anticipated regulations. By understanding the current regulations the team will be in a better position to forecast the type of regulations in the future that may affect SRM design and manufacture. A thorough examination of the federal, state and local regulations was performed with the focus on those states where SRMs are currently being produced: Alabama, Arkansas, California, Louisiana, Maryland, Texas, and Utah. The result of this task will be a prioritized list of probable laws and regulations matl's that will drive SRM design and manufacture beyond the year 2000.

The work to date shows that federal regulations are communicated years in advance. For example, the Federal Clean Air Act Amendments of 1990 were debated in Congress for 10 years before it was passed. An exception to this is the directives from the executive branch which often has less advance notice and discussion before they go into effect such as Executive Order 12856. Typically, federal requirements drive most state and local regulations. However, the state of California has been very aggressive in the area of environmental regulation and a number of very stringent state and local regulations from California have been adopted that set precedents for their federal counterparts. The regulations' review also shows that air emissions will remain the most significant problem for the future. The trends indicate that emphasis will be placed on the areas of elimination of ozone-depleting chemicals (ODCs), reduction in volatile organic compounds (VOCs), hazardous air pollutants (HAPs), and open burn/open detonation of energetic materials. Based on the review of current and anticipated environmental regulations, the SRM industry should be prepare to deal with constraints which minimize/reduce the use of hazardous materials with a strong focus on the 189 HAPs listed under CAAA. The industry will need to reduce hazardous waste generations and discharges to the environment: land, air, and water. The installation of emission control technologies will be required in some areas and open burn/open detonation will be prohibited in the future. There is also a NESHAP for rocket engine/motor test firing which is due to be promulgated in 1998.

Phase II, Baseline Manufacturing, was performed at Thiokol's manufacturing facility in Utah. The objective of Phase II is to establish a set of baseline data to compare the alternative technologies with the current processing technologies. To achieve this objective, Thiokol's use its current manufacturing methods to scale-up and fabricate an 800-lb SuperBATES motor with $NaNO_3$ scavenger propellant. The ballistic, mechanical, and hazard properties of the propellant were evaluated along with the critical bondline properties using peel, tensile, and shear test. Propellant

samples were also subjected to accelerated aging to determine long term behaviors. The motor was successfully test fired at PL in Sep 1994.

Along with the characterization data, the team also obtained video and photo documentation of the manufacturing of the SBATES motor. This data allows the team to identify and quantify the waste streams associated with SRM manufacturing (Fig. 3 and Table 1). This data will be used to determine the waste minimization effectiveness of alternative process technologies. Since the program plan calls for CSD and Aerojet to manufacture the SBATES using the alternative technology, CSD and Aerojet engineers were invited to observe the manufacturing of the baseline motor at Thiokol's facility so as to minimize facility bias in this program. In Phase IV, Thiokol's engineers will be invited to observe the manufacturing of the motors at CSD and Aerojet to ensure commonality.

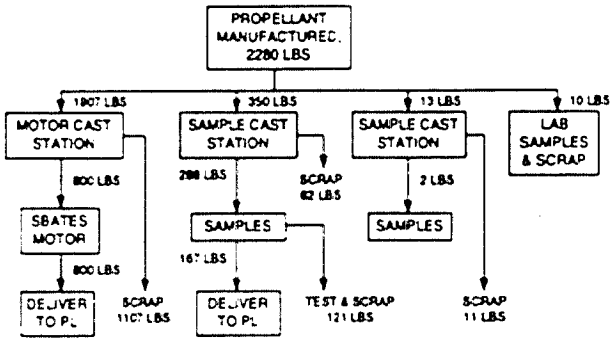

Fig. 3 Baseline SuperBATES Motor Propellant Accountability

Table 1: SuperBATES Motor Non-Propellant Waste Streams (2280 lbs of Propellant Manufactured).

	EPA Regulated	Hazardous Wastes	Non-Hazardous	Total (lbs)
Case Prep.	9.2	13.6	17.8	40.6
Prop. Manuf.	4.6	40.0	194.7	239.3
Motor Loading	13.6	6.6	7.5	27.6
Samples	14.4	38.9	1.8	55.1

In Phase III, Technology Integration, the team uses the data gathered in Phase I and II to select the alternative technologies for demonstration in Phase IV. The first task in this Phase is to identify the problem areas in the current SRM manufacturing process. The team uses its considerable experience and knowledge in SRM manufacturing procedure to identify processes which are affected by current and anticipated environmental constraints. This was done for a variety of SRM systems in the tactical, strategic, and space launch applications. Having identified those problem areas and the regulations that affected them, the team use the data obtained from the Phase I Literature Search to identify alternative environmentally acceptable process technology that can replace the current technology. The team also developed criteria to evaluate and select candidate technologies for demonstration in Phase IV.

For an alternative technology to be considered for demonstration, it must satisfied four criteria: environmental acceptability, safety, reliability, and maturity. Based on the team's environmental regulations review in Phase I, an alternative technology is environmentally acceptable if: (1) the technology will not be phased out or (2) its emission or usage will not be subjected to prohibition or severe restrictions by current or anticipated environmental regulations. The second criteria, safety, focused primarily on employee safety. A candidate technology can satisfy this criteria if it does not contain carcinogen on OSHA list or if it has a flash point above 100

deg F. The third criteria is a subjective test to determine whether a candidate technology will cause an unacceptable degradation to the SRM system' reliability. The team relied on available information from the Literature Search and its experience to address concern such as critical bondline, corrosion, substrate incompatibility, propellant materials, and variability. The final criteria which must be satisfied by candidate technology is maturity. This program seeks to demonstrate available technology for insertion into SRM manufacturing in the near future. A candidate technology 's maturity is determined by its (1) readiness for subscale motor demonstration prior to 3Q95, (2) commercial availability prior to 3Q95, and (3) readiness for insertion into SRM production in 1998. Candidate alternative technologies which satisfied these four criteria are considered for demonstration in Phase IV.

The Literature Search conducted in Phase I has yielded a wealth of information on alternative technologies currently available. The team sorted the alternative technologies into five technology areas for ease in classification. The five technology areas are: vapor degreasing, equipment and tool cleaning, hand wipe cleaning, material replacement, and propellant processing/waste minimization. The first technology area, vapor degreasing, is the largest source of ODCs emission in SRM manufacturing. Twelve candidate technologies were identified from the literature search (Table 2). The technologies were ranked against one another based on the following criteria: (1) pollution prevention, (2) waste minimization, (3) life cycle cost, (4) process impact, (5) safety, (6) commonality, and (7) long term availability [3]. The ranking allow the team to down select the top two or three candidate from each technology areas for laboratory testing and demonstration in Phase IV.

Table 2: Alternative Processes for Vapor Degreasing

Alternative Technologies	Comments
Aqueous Spray-in-Air	No ODCs or VOCs; low cost
Water Jet Blast	Good use history
CO_2 Pellet Blast	Small waste stream
Aqueous-Immersion	Non-combustible
Alternative Protection	No safety concerns
Aqueous-Ultrasonic	Prohibitive life cycle cost
Semi-Aqueous-Immersion	Deficiencies in many factors
LEVD	High life cycle costs
Semi-Aqueous-Ultrasonic	High costs for large SRM
Semi-Aqueous Spray	Form combustible vapor
Plastic Media Blast	Technology still in development
Supercritical Fluid CO_2	Technology not mature

Table 3: Equipment/Tool Cleaning Alternatives

Alternative Technologies	Comments
Hand Wipe - Aqueous	No ODCs or VOCs
Water Jet Cleaning	Versatile process
Hand Wipe-Hydrocarbon	Good use history
CO_2 Pellet Blasting	Minimum waste stream
Spray-in-Air - Aqueous	High life cycle costs
Immersion - Aqueous	High life cycle costs
Water Abrasive Cleaning	Ineffective w/ uncured
Plastic Media Blasting	Same as above
Immersion-SemiAqueous	Not adaptable to fixed equip.
Immersion - Terpene	Not adaptable to fixed equip.
Immersion-Hydrocarbon	Not adaptable to fixed equip.
Spray-in-Air - Terpene	High life cycle costs
LEVD	High costs; inc. process times

Based on the ranking criteria, the team selected aqueous spray-in-air, water jet, and CO_2 blasting from the vapor degreasing technology area for evaluation in Phase IV. Aqueous spray-in-air cleaning systems have been used successfully in cleaning large metal components. The system has been demonstrated on SRM development units but has not been used in the manufacture of production SRMs. However, extensive developmental efforts are being expended to qualify spray-in-air aqueous systems for cleaning critical bondline surfaces on large SRM motor cases because of its many advantages over other cleaning processes. These advantages include: 1) no ODC or VOC emissions, 2) competitive life cycle costs depending on component/motor size and volume, 3) non-combustible aqueous cleaners, and 4) favorable toxicological reports. The second candidate selected for evaluation, water jet cleaning, has the same advantages as spray aqueous cleaning. Water jet systems have a demonstrated capability to remove soils from contaminated surfaces and have been widely used in SRM manufacturing for gross cleaning operations. Test data exist to show that water jet cleaning could be a viable process for critical bondline surfaces. The final candidate selected for evaluation is CO_2 pellet blasting. Like the other two candidates selected in this area, CO_2 pellet blasting has been widely used in gross cleaning applications, but have not been demonstrated for critical bondline surfaces cleaning. CO_2 pellet blasting system has the same advantages as spray aqueous and water jet cleaning plus it has the smallest waste stream of the top-ranked alternative technologies for vapor degreasing.

The second technology area, which also is the second largest source of ODCs emission in SRM manufacturing, is equipment and tool cleaning. The current process uses regulated solvents such as TCA, acetone, Freon, and MEK to hand wipe the equipment and tooling contaminated with propellant, liner or adhesive. The literature search identified thirteen alternative technologies that could replace the current processes (Table 3). The three highest ranking candidates were selected for evaluation in Phase IV. Replacing the current solvents with aqueous cleaners will eliminate the ODCs, VOCs, and combustible from the process. The aqueous cleaners generate a small waste stream and have favorable toxicology. The second highest scoring alternate is water jet cleaning. This process uses mechanical energy of the water pressure to dislodge contaminants. The addition of a cleaning agent to the water may or may not be necessary depending on the contaminants. This process has been used to remove composite propellants and propellants containing energetic plasticizers. Tests have also been successfully conducted on liner contaminated equipment. The final candidate selected is CO_2 pellet blasting. This process has been extensively used for gross cleaning as discussed previously. Hydrocarbon-based cleaners were not selected for evaluation because there is a great number of efforts by the industry to identify hydrocarbon-based solvents as a short term drop-in replacement for equipment and tool cleaning.

The third technology area identified by the team is handwipe cleaning of critical surface. The applications in this area involve spot cleaning of case wall or phenolic and rubber insulators prior to bonding or lining, rubber activation during insulator fabrication, trimming and cleaning up of cured insulator, and cleaning of insulator or propellant prior to inhibitor application. The solvents used in these applications are TCA and MEK. The Literature Search from Phase I has shown that no single replacement solvent has been as universally accepted as the existing solvents. However, there are alternative solvents that can clean a surface just as good as if not better than the currently used solvent for each specific application. The candidate technologies for this area can be group into four categories. The first category is the drop in replacement solvents. These solvents can replace the currently used solvents with minimal modification to the manufacturing process (Table 4). The aqueous cleaners required an additional rinse and dry steps. However, they contain no ODCs, VOCs or HAPs and are non combustible with a good use history in other cleaning applications. The hydrocarbon cleaners do not contain ODCs but may have a high concentration of VOCs and combustible. Their capabilities and operation are similar to the current processes but they may also require additional steps.

Table 4: Alternative Replacement Solvents for Hand-Wipe Cleaning

Alternative Technologies	Comments
Aqueous Cleaners	Requires rinse and dry steps
Terpenes	High VOCs and combustible
Aromatics H/Cs	High life cycle cost
Aliphatic H/Cs	High VOC and combustible
Solvent Blends	Very labor intensive
Chlorinated Solvents	Significant life cycle costs
Glycol Ethers	High VOC and HAPs

Table 5: Alternative Mechanical Technologies for Hand-Wipe Cleaning

Alternative Technologies	Comments
Abrade and dry wipe	Very labor intensive
Dry Wipe	Very labor intensive
CO_2 Pellet Blast	High life cycle cost
Plastic Media Blast	High life cycle cost
Sponge Jet	High life cycle cost
Water Jet Blast	Significant life cycle costs
Wheat Starch Blast	High life cycle cost
Supercritical CO_2	Not mature

The second category is mechanical cleaning. The technologies in this group rely on mechanical energy to enhance the cleaning capability of the process (Table 5). Of these technologies, dry wipe with and without abrading and CO_2 pellet blast were selected for Phase IV evaluation. Abrading and dry wiping the insulator eliminates the need of a cleaning solvent but is labor intensive and there is a risk that the contaminants on the surface will be displaced to another spot rather than removed. The final candidate selected for evaluation is CO_2 pellet blasting. The mechanical cleaning action of this process may be too aggressive for some insulators. The third category of hand wipe cleaning is rubber activation. For the rubber activation during insulator fabrication application, there were four alternative technologies identified from the literature search: (1) no activation/wipe; (2) hydrocarbon cleaners; (3) rubber reformulation; and (4) bond promoter. The candidates selected for evaluation are no activation/wipe and hydrocarbon-based cleaners. No activation/wipe is the best environmental alternative for this application because it

generates no waste. The disadvantages associated with this process are: (1) shorter shelf life of rubber, (2) may only be applicable to compression molded insulators, (3) poor interlaminar adhesion, and (4) difficulties during lay up. Because of these risks, hydrocarbon-based solvent cleaning was also selected for evaluation. These cleaners do not contain ODCs but may have a high concentration of VOCs and combustible. Their capabilities and operation are similar to the current processes but they may also require additional steps.

The final category of hand wipe alternative technology includes the peel ply technique and no clean. The peel ply (or release fabric) is applied to the uncured insulator during the vacuum bagging process and is typically removed immediately after autoclave curing of the insulator. The peel ply technique involves leaving the plastic cover on the surface of the insulator and removing it only at the last minute prior to bonding or lining. When the peel ply is removed, a very thin layer of rubber which has impregnated the cloth is also removed. If the appropriate peel ply is selected, the surface can be acceptable for bonding without further preparation. This process does not added any additional waste while eliminating a processing step. The associated risks are possible increase in handling requirements and contamination of surface during handling and storage. The peel ply will act as a barrier to many types of contamination, but may not be impervious to all. From a pollution prevention and waste minimization stand point, the elimination of current hand-wipe cleaning processes is obviously the best choice. However, for critical surfaces the feasibility of this approach is limited due to the requirement to maintain surface cleanliness throughout multiple processing, handling and storage operations. The cost of training personnel to handle the hardware differently, protective equipment and facilities for the hardware and additional protections of the surface to verify cleanliness may be prohibitive. For most critical applications, the no clean technique is not a mature or reliable technology. However, hand wipe cleaning of cases prior to bonding or lining may be feasible. After grit blasting, the case can be used immediately in the next processing step or it can be sealed, purge with nitrogen gas, and then put in storage until needed. This is the best environmental option since it does not generate any waste or pollution. The risk involved with this process includes leaving grit residue in the case or contamination of surface while in storage.

The fourth technology area in SRM manufacturing is material replacement. This area involves replacing the VOCs and HAPs containing primers and adhesives currently used in SRM manufacturing. There were four alternative technologies identified from the literature search (Table 9). The two highest scoring candidates, waterborne primers and adhesives and epoxy paste adhesive, were selected for evaluation. The use of waterborne primers and adhesives for installation of rubber components in SRM cases have been tested extensively. These systems contain no ODCs or VOCs and can be clean up with water rather than chlorinated solvents. The epoxy paste adhesive also does not contain ODCs or VOCs but the process is labor intensive.

The final technology area is waste minimization/ propellant processing. This technology area focus on using alternative technology to minimize or reduce waste generate during propellant mixing and loading. Depending on the motor size, the amount of propellant and non-propellant wastes can be substantial relative. For the Phase II Baseline SuperBATES motor, 2280 lbs of propellant were manufactured to scale up and cast an 800 lbs SuperBATES motor. This procedure generated 363 lbs of non-propellant waste, 1311 lbs of propellant scrap and test samples (Fig. 3), and 400 gal of wash water contaminated primarily with AP. Of the 363 lbs of non-propellant waste, 99 lbs (27%) are hazardous waste (solvents contaminated rags, containers, etc.) and 42 lbs (12%) are regulated materials such as TCA, MEK, and other environmentally restricted materials (Table 1). These wastes can be eliminated or reduced by using alternative processing technologies.

Since the amount and source of propellant and non-propellant wastes are related to the quantity of propellant being mixed, not all alternative technologies can be demonstrated on an 800 lbs SuperBATES motor manufacturing. The first processing step in SRM manufacturing is receiving/inspecting chemicals. To minimized waste associated with the QA procedure, testing could be eliminated by relying on vendor certification. This will also reduce the cost of testing and employee exposure to hazardous materials. There is a potential for facility bias between vendor and user. The second alternative is to procure chemicals in bulk quantity. This will reduce the number of lot testing but shelf life will be a concern and not all chemicals can be procure in this manner. These two alternative processes will not be evaluated in Phase IV be cause of the small size of the propellant being mixed. An

alternative process that will be evaluated is to use reusable containers. This will reduces residual wastes but exposes the chemicals to cross-contamination if the containers are not properly handled.

The second processing step in SRM manufacturing is liner mixing. The waste from this process comes from scrap materials and cleaning the mixer. These wastes can be reduced by (1) reducing the mix/kit size, (2) eliminate cleaning between mix, (3) reduce kit components, and (4) use alternate mixers. The last candidate will not be evaluated in Phase IV because of the capital expense required. This alternative process is appropriate for a high-volume program because it significantly reduces the number of processing steps and associated waste streams. The first candidate will significantly reduce the amount of scrap materials but raise the concern for adequate material for the motor. Eliminating the cleaning process will significantly reduce the associated waste streams but is appropriate for high-volume mixing. The third candidate that will be evaluated in Phase IV is to reduce the components of the mix. This will reduce the quantity of containers and process steps but is formulation dependent and storage life will be a concern.

After mixing the liner, the next step in motor manufacturing is liner application. The waste associated with this process come from containers and rags used in tool cleaning. The alternative processes that will be evaluated in Phase IV are recycle containers and hand application. Recycling the containers will moderately reduce the waste streams and number of process steps but could result in cross contamination. Using brush or trowel to hand apply the liner will reduces cleanup wastes and process steps compared to applying liner with tools. However, the disadvantages are increase employee exposure and potential for uneven coverage or insufficient thickness. Hand application will also depend on motor configuration and production volume.

The next series of steps in motor manufacturing deal with propellant processing. The first of these steps is propellant submix preparation. This procedure involves mixing several ingredients together before adding them to the mix bowl. The associated waste comes from sampling and testing and contaminated containers. Three alternative processes were identified for this process but only one will be evaluated in Phase IV because of the small volume of propellant being mixed. Eliminating the submix testing will be evaluated in Phase IV. This will reduce the number of process steps, employee exposure to hazardous materials, and eliminate all waste associated with sampling and testing. There is a potential for use of discrepant submix. The other alternative processes are to procure submix in 55 gal drums or tank car and to purchase chemical in large containers. These alternative processes reduce the waste stream by reducing mixing steps and sampling frequency. Employee exposure will also be reduced. The disadvantages are shelf life limitation and chemical and formulation dependencies. These two processes are more appropriate for high volume mixing and will not be evaluated in Phase IV.

Before the propellant is actually mixed in a mixer, the main ingredients will usually be put in the same containers and QA sampling will be performed. The waste in this process step will come from containers' cleanup and sampling and testing. These wastes can be minimized by eliminating the premix testing. Sampling and scrap waste can be reduced by reducing sample quantity required for test or by on-site testing. The waste stream will be reduced moderately but the potential for test bias between sites and uniformity of test sample will be a concern. All three of these alternative processes will be evaluated in Phase IV. Dedicated containers can also be used for each ingredient to eliminate residual wastes. The containers can be recycle to the vendor to eliminate cleanup at the manufacturing site. This will require vendors' cooperation and increase material tracking. This process is will not be evaluated because of the small quantity of propellant being mixed for this project. After the ingredients are premixed, the premix is transfer to the main mixing bowl. The waste associated with the cleanup and transfer of materials can be significantly reduced by using one-bowl processing. This will also significantly reduce the process steps and employee exposure. The risk associated with this process is a potential increase in batch-to-batch variability and requires accurate weighing capability. Thiokol is currently using this process at its facility for the shuttle solid booster. This process will be evaluated by CSD and Aerojet in Phase IV.

For final fuel preparation, the associated waste can be reduced by reducing or combining mixing steps, reducing cleaning frequency, and direct mixing in pot. All three of these alternative processes will be evaluated in Phase IV. Moderate reduction in waste associated with cleanup, material transfer can be achieved. Also, the number of processing steps and employee exposure to hazardous materials will be reduced. The potential for increase in batch-to-batch variability and cross-contamination will increase with the alternative processes.

The final step before propellant mixing and casting is to prepare cast/core tooling. The waste streams in this process come from tooling fabrication and cleanup. Using multiple use release will reduces the frequency of cleaning and associated waste as well as process steps and employee exposure. Compatibility between propellant and release agents will be a major concern for this alternative process which will be evaluated in Phase IV. Waste from tooling fabrication and cleanup can also be reduced by using alternative core material. This requires eliminating the use of unacceptable foams and molding operations. Compatibility between propellant and adequate release agents is also a concern for this alternative process. The tooling cost may also increase. This alternative process will not be evaluated in Phase IV.

Depending on the motor size and configuration, the amount of propellant waste associated with propellant mixing/casting can be a significant problem for SRM manufacturer in light of a prohibition on open burn/open detonation. OB/OD has always been the most cost effective method of disposing of propellant and propellant contaminated wastes. As indicated in Fig. 3 and Table 1, the amount of scrap propellant in a single motor manufacturing operation could be as much as 60 percent of the amount of propellant being mixed. There are many alternative processes that will significantly reduce the amount of propellant waste. One of the alternative process is to reduce the batch size of the mix. By using only enough ingredients to make the necessary amount of propellant for motor loading and sampling and testing, a significant quantity of propellant waste can be reduced. The risk of not having sufficient quantity of material to support motor casting and testing will be minimized with experience and thorough planning. Using a follower plug to burp the cast pipes will significantly reduce the quantity of propellant trapped in cast lines and ensure the maximum use of all propellant in a mix. This process requires a sufficient pressure differential to clean the cast pipes. The same waste reduction can also be achieved by reducing the cast pipe size. This process required significant capital cost to replace the current pipes. There is a potential for the smaller size pipe to change the propellant flow rate and rheological behavior.

A significant source of propellant waste is sampling and testing of propellant during scale-up and mixing. Moderate reduction in propellant waste can be achieved by reducing the sample size and sampling plan. This may result in insufficient material for retest/motor acceptance. Moderate reduction in waste can also be achieved by conducting on-site testing. The final alternative process that will be evaluated in Phase IV under the propellant mixing/cast process is the segregation and combining of like waste streams. This process will minimized the quantity of waste that requires specialized treatment or disposal which reduces the disposal cost associated with SRM manufacturing. A significant reduction in propellant waste associated with cleanup and testing can be achieved with the use of continuous mixing operation. This process is appropriate only for very high volume operations and required a high capital expense. This alternative process will not be evaluated in Phase IV.

CONCLUSIONS

The alternative technologies selected in Phase III will undergo laboratory testing to determine their compatibility with propellants, liners, insulations, and case materials. The effects these technologies have on critical bondline strength will also be determined. The laboratory testing will act as a preliminary screening of the alternative technologies to help the team select the technologies for demonstration. The most successful technologies from the laboratory testing will be incorporated into the current manufacturing process and two 800 pounds SuperBATES motors will be manufactured. The manufacturing data from these motors will be compared to the data obtained in the manufacturing of the baseline motor in Phase II. The alternative technologies' impacts on SRM manufacturing will

then be evaluated. The motor will also be test fired to determine if their ballistic characteristics have also been affected. The results will be published in the Final Report in 4Q97.

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THE GREEN MISSILE PROGRAM

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Abstract

The Green Missile Program is a Tri-Service/DOE/EPA pollution prevention research effort to eliminate major sources of toxic/hazardous materials used in solid rocket propulsion systems. Based on regulatory impact, an interagency team prioritized environmental research needs for solid propulsion systems. Three high priority research tasks were submitted and approved for FY 97 funding under the Strategic Environmental Research and Development Program (SERDP). These tasks are: 1) elimination of lead in minimum smoke propellants; 2) elimination of HCl as a combustion product; and 3) minimization of solvents used in energetic oxidizer processing.

Introduction

Many missile system materials are now regulated, restricted or banned by federal regulations such as the Resource, Conservation, and Recovery Act (RCRA) and the Clean Air Act (CAA). Executive Order 12856 mandates a 50% reduction in quantities of hazardous waste by 1999. This was reemphasized by Secretary of Defense William Perry's Strategy for Compliance which directs all DoD agencies to reduce quantities of hazardous materials and waste. On September 1, 1995, the "National Emission Standards for Hazardous Air Pollutants for Source Categories: Aerospace Manufacturing and Rework Facilities" became effective. This regulation specifically targets missiles, rockets and space vehicles and further restricts materials used in missile/rocket systems.

Pollution prevention research is imperative for compliance with regulations such as the above since missiles/rockets are complex systems with many components and processes utilizing millions of pounds of hazardous and/or toxic materials which usually generate large quantities of hazardous emissions and/or waste. Examples of these hazardous/toxic materials are: heavy metals (e.g. lead, mercury); Ozone Depleting Chemicals (ODCs) e.g. CFC-113, carbon tetrachloride; Volatile Organic Compounds (VOCs), e.g. 1,1,1-trichloroethane, benzene; Hazardous Air Pollutants (HAPs), e.g. toluene, xylene, cadmium, chromium; and toxic substances, e.g. isocyanates, methylene dianiline. Regulatory restrictions on these materials could detrimentally affect production schedules of missile systems and/or use of systems in training. The net result would be a negative impact on defense readiness. In response to this need for pollution prevention research for solid rocket propulsion systems, SERDP issued a statement of need requesting proposals for elimination/minimization of hazardous materials in missile propulsion systems.

Project Description

An interagency team (Army, Navy, Air Force, NASA, DOE, and EPA), which was interfaced with JANNAF, coordinated in developing a research proposal in response to the SERDP statement of need. The team assessed solid rocket propulsion system pollution prevention needs, with emphasis on those that were common to several agencies. These needs were then prioritized based on regulatory impact (Figure 1).

The resulting proposal, which was approved for FY 97 funding, has three research objectives, or tasks: 1) to develop and characterize high performance minimum signature propellants which do not contain lead for both extrudable and castable propellant processes; 2) to develop and demonstrate the complete and clean (HCl-free) combustion of UFAL with non-halogen containing oxidizers; and 3) to develop and demonstrate use of liquefied gases and supercritical fluids for environmentally friendly processing of energetic oxidizers and components. The proposed research also includes further development and adaptation of basic pollution prevention materials and/or technologies developed by other programs, such as the Clean Agile Manufacturing of Energetics (CAME), for utilization with missile systems.

AVERAGE PRIORITY RANKINGS

Greatest regulatory importance
High regulatory importance
Moderate regulatory mportance
Low regulatory importance

Materials addressed in proposal

Missile System Components

Hazardous/Toxic Materials	Propellant	Propellant Manufacture/ Processing	Propellant System Components	Cleaning	Testing/Analysis of Materials	Annual Quantity (LB)
Methyl Chloroform/ 1,1,1-Trichloroethane						!
Lead/Cmpds/Emissions						161,000
Trichloroethylene						!
Tetrachloroethylene						!
Toluene diisocyanate						
Isocyanates						
Freons						
Ammonium Perchlorate						24M
Monomethyl Hydrazine						
IRFNA						
NOx Emissions						
HCl Emissions						7.4M
Methylene Chloride*						!
Methyl Isobutyl Ketone						!
Methyl Ethyl Ketone*						!
Nickel & Compounds						
Chromium & Compounds*						
Benzene						!
Mercury & Compounds*						
Toluene*						!
MDA						
Cadmium & Compounds*						
Carbon Tetrachloride						
Cyanide Compounds						
Xylene*						!

* Regulated by 1 Sep 95 NESHAP

! = Total for these solvents is 7M lbs.

Figure 1. Priority matrix for pollution prevention research needed for solid propulsion systems.

Background

Large quantities of toxic and hazardous materials are used/generated in the production/use of solid rocket motor systems. A majority are associated with propellant, the primary ingredient by weight in a missile system. Three materials of concern are lead, HCl and VOCs. All current minimum signature solid propellants use lead to obtain the necessary ballistic properties. These include systems such as the Army's HELLFIRE and TOW and the Tri-Service 2.75 rockets. The overall annual production of minimum signature propellant involves 161,000 pounds of lead compounds. Tactical and strategic booster propellants must burn aluminum (Al) to achieve required performance. In the past it has been necessary to use oxidizers such as ammonium perchlorate (AP) to efficiently combust the Al fuel, but AP yields HCl in the exhaust plume. Attempts to efficiently burn Al with non-halogenated oxidizers have been unsuccessful due to the inert nature of the aluminum oxide coating on the Al particles. Estimates based on current annual production of AP, 24,000,000 pounds, indicate there are potential emissions of 7,440,000 pounds of HCl per year. Furthermore, approximately 4,000,000 pounds of solvents such as MEK or toluene are used annually to process oxidizers for these propellants.

Technical Approach

Extrudable and castable formulations of ADN, CL-20, AN, or KDN rocket motor propellants will be developed. The associated energetic polymeric binders, including thermoplastic elastomers (TPE) developed by the CAME program, will also be evaluated and selected for development with the candidate formulations. Data from the characterization of the final formulations shall be compared to baseline data to determine the amount of pollution prevention obtained using the new formulation and that the user requirements are still being met. Technology demonstrations will be done for the Tri-Service 2.75 and Army's HELLFIRE systems.

Propellant formulations containing ultra-fine aluminum (UFAL) and non-halogenated oxidizers will be developed and characterized. Formulation studies shall be conducted to determine the optimum processing procedures. The combustion efficiency shall be determined as well as the identity of the combustion products to demonstrate clean burning.

A method to produce comminuted ADN, CL-20, and AN oxidizers in a size, shape, and purity suitable for propellant manufacture will be developed. Process parameters that influence the behavior of these solvated oxidizers, when crystallized in a liquefied gas antisolvent, will be evaluated and optimized. Included in these evaluations will be the effects of atomization droplet size, nozzle configuration, oxidizer concentration, solution viscosity, and liquid surface tension on particle size and structure. Process scale-up will be demonstrated with materials to be used for the 2.75 and HELLFIRE systems. Supercritical fluid processing of energetic components will be achieved through supercritical chemistry, supercritical processing and energetic material processing. Technology demonstrations will be done with RDX/HMX.

Expected Payoffs

Total DOD cost savings resulting from this project are estimated at $4.5M annually. Costs such as higher material prices and equipment/process changes are offset by cost savings from hazardous waste elimination, reduced environmental management costs, and decreased quantities of raw materials

Development of extrudable and castable lead-free propellants would significantly reduce quantities of toxic materials currently generated from production and use of Army and Navy minimum smoke systems. Approximately 60,000 pounds of lead compounds are used annually for Tri-Service 2.75 rocket propellant production. Disposal costs for lead contaminated waste would be eliminated at DOD propellant manufacturing sites. Also, lead contamination and clean-up costs would be avoided. Elimination of lead from minimum smoke propellants would result in annual DOD cost savings of $1.5M. There will be no or minimal capital costs as current equipment would be used. Technology demonstration will be done with the Army's HELLFIRE and Tri-Service 2.75 rockets. These systems account for 95% of the current pollution problems with lead containing propellants.

In addition to eliminating staff and military personnel exposure to hazards of lead and HCl emissions, significant reductions in the required personal safety equipment and EPA-mandated exposure and health monitoring will result from development of green energetic materials. At present, personal protection accounts for up to 30% of a facility's environmental management budget.

The HCl elimination research will apply to all AP containing propellants. Current annual production of these propellants is estimated at 22,000,000 pounds per year. This represents 50% of the total annual potential HCl emissions. Testing will be done on TITAN type booster propellant which has potential annual HCl emissions of 2,000,000 pounds.

Preliminary results indicate solventless oxidizers and clean energetic processing may result in up to ten fold reductions in organic solvent processing requirements. Manufacturing facilities typically purchase commodity solvents, such as hexane, acetone, toluene, isopropanol, etc. in bulk quantities. Prices typically average $1-$3 per gallon for these solvents when purchased in tank car quantities (i.e., 5,000 gallons). Fifty gallon drum quantities are considerably more costly. The vast majority (90%) of these solvents are ultimately repackaged for commercial disposal. These spent solvent wastes, which usually contain residual energetic materials, return no net value to the manufacturer. The spent solvents are mixed with diesel fuel and burned for energy conversion. The process destroys non-renewable resources and emits toxic contaminants. The remaining 10% of the solvents are either consumed in the product stream, released into the waste process stream, or reclaimed for reuse by distillation. These consumption quantities will vary according to the specific manufacturing processes. The alternative processes proposed should significantly reduce the total quantities of VOC solvents that are currently being consumed for these missile energetic components. Based on current production rates, annual DOD cost savings would be $3M from reduced solvent procurement and hazardous waste disposal costs. These savings more than offset capital investment costs which are estimated at $100K/facility.

Clean energetic processing technology will be demonstrated with oxidizers used in the lead-free minimum smoke propellants. This will account for 60% of the solvents in missile systems which could use ADN/CL-20 as oxidizers. The technology can also be adapted for use in missile systems which have other oxidizers such as RDX and HMX.

Conclusions

The reseach described in this paper will demonstrate that solid rocket motor propulsion systems, existing and new, can be made in an environmentally friendly fashion. Further, new 'green" materials and technology can reduce costs through elimination/minimization of hazardous wastes. Finally, this research should provide the groundwork for additional "green missile" developments.

Acknowledgments

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ENVIRONMENTAL POLICY

HALON AS HAZARDOUS WASTES: POLICY IMPLICATIONS OF MONTREAL PROTOCOL DECISION VII/12

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ABSTRACT

At their recent meeting, the Parties to the Montreal Protocol adopted a significant change to its provisions. The aim of the Protocol is the reduction of damage to the stratospheric ozone layer by manmade chemicals, in particular CFCs, HCFCs, and halons. To date, this aim has been addressed entirely by means of controls imposed on the production of these chemicals (1). In Vienna Decision VII/12, however, the Parties have moved markedly towards controls on use, by recommending "limiting the use of halons in new installations to critical applications" and "promoting the environmentally safe destruction of halons, when they are not needed in halon banks (existing or to be created)." Another aspect of this potentially landmark decision is the incorporation of environmental considerations other than ozone depletion: the Parties recommend "evaluating and taking into account only those substitutes and replacements of halon for which no other more environmentally suitable ones are available."

Reaction to this decision by the largest and most important users of recycled halons, including the aerospace industry, may set the tone and future direction of the Montreal Protocol. Despite extensive and energetic research, feasible alternatives to halons have yet to be found for retrofit in most aerospace applications, and the likelihood is that current build and in-service aircraft will continue to rely on (recycled) agent for their lifetimes. It will be a serious challenge to frame and administer regulations that do not cause the halon bank, on which (at least) existing aircraft are likely to depend for a number of years, to become valueless. Worse, halon may effectively be categorized as a hazardous waste and thus become a liability, greatly increasing the likelihood of widespread venting with the associated environmental damage and depletion of the potential bank. The aerospace community needs to consider urgently how it can respond to Decision VII/12 - or the likely consequences in years to come of inaction now.

1 INTRODUCTION

During their November 1995 meeting in Vienna, a decision was reached by the Parties to the Montreal Protocol which represents a significant change in its political complexion. It is known as Decision VII/12. To understand how it was arrived at, it is important to appreciate the history of the Montreal Protocol, the regulations and methods it has so far used to control stratospheric ozone depletion, and their effect to date. This leads to a comprehension of the options that were available at the Vienna meeting and shows why Decision VII/12 was adopted by the policy makers. An assessment of its impact will be presented, together with recommended actions that the aerospace community should consider taking to minimize any potential adverse consequences.

2 THE MONTREAL PROTOCOL

2.1 History and Status

The Montreal Protocol derives from the Vienna Convention for the Protection of the Ozone Layer. Signed in Vienna in 1985, the Vienna Convention requires signatories to take appropriate measures to comply with its provisions including all protocols in force to protect against human activities that modify the stratospheric ozone layer. The major protocol under the Vienna Convention is the Montreal Protocol on Substances that Deplete the Ozone Layer, signed in 1987 (2). At present, there are 156 Parties to the Protocol. The first major Amendments to the Protocol were enacted in 1990 during a meeting in London and are hence termed the London Amendments, to which 109 Parties are signatory. In 1992, further Amendments were made in Copenhagen, and 54 Parties have currently ratified the Copenhagen Amendments.

In the USA, the Protocol was ratified by the Senate in 1988. In the European Union, the Protocol and its Amendments have been adopted as European Union Regulations. In the UK, as a member of the EU, the Protocol is ratified by Parliament (in the form of the European Regulation rather than of the Protocol itself), and subsequent Amendments have been adopted by Order in Council. An interesting consequence of this is that in most territories, the status of the Protocol as an International Treaty means that it takes precedence over national law. For example, in the USA, Title VI of the Clean Air Act Amendments of 1990 (CAAA) requires that the more stringent control measures listed within the CAAA or the Protocol must be followed; the US Environmental Protection Agency has the responsibility to administer the regulations to adjust the control measures to ensure, as a minimum, compliance with the Protocol. As long as a Party remains a signatory to the Protocol, the Amendments, once ratified by at least the minimum number of Parties, are legally binding, regardless of whether or not the Party in question agreed with the change.

2.2 Organization

The Montreal Protocol is "owned" by the Parties, who have of late met annually. They are supported by the Open-Ended Working Group (OEWG), which is obliged to meet at least once a year to make preparation and to draft Decisions which are finalized, approved, and enacted by the Parties. Except during meetings of the Parties, the custodian and day-to-day administrator of the Protocol is the United Nations Environment Programme Ozone Secretariat, a permanent UN office based in Nairobi. Also reporting to the Parties are a number of Assessment Panels of international experts on topics including Science, Effects, and Technology and Economics. Reporting in turn to the Technology and Economic Assessment Panel (TEAP) are a number of Technical Options Committees, which include the Halon Technical Options Committee (HTOC) (2,3). Their purpose is to provide technical advice to the TEAP and the Parties, especially on Essential Use nominations (see 2.6 below) and to answer specific technical queries raised by the Parties. Currently, HTOC meets two to four times per year.

2.3 Policy

Prior to the meeting in Vienna, the two most significant Decisions relating to halons are the ones that introduced and accelerated the production phase-out, Decisions II/1 (the London Amendments) and IV/2 (the Copenhagen Amendments)*. However, these are only two of at least fourteen Decisions that have had, or continue to have, an effect on halons. Throughout the Amendments and the other Decisions, four factors have been constant: (1) all were deemed appropriate based on the latest scientific assessment provided by the Science and Effects Panels, (2) all were based solely on ozone depletion, (3) all applied only to production, and (4) all have been successively more restrictive.

2.4 Effect of the Montreal Protocol

To assess how the Protocol has contributed to the resolution of the stratospheric ozone problem, Figure 1 shows a series of projections of stratospheric chlorine loading taken from the 1994 Scientific Assessment Panel report (4). The vertical axis shows chlorine loading equivalent in parts per trillion; this takes into account the other halogens, in particular bromine, at an equivalent loading. Chlorine loading in the stratosphere is directly related to stratospheric ozone depletion.

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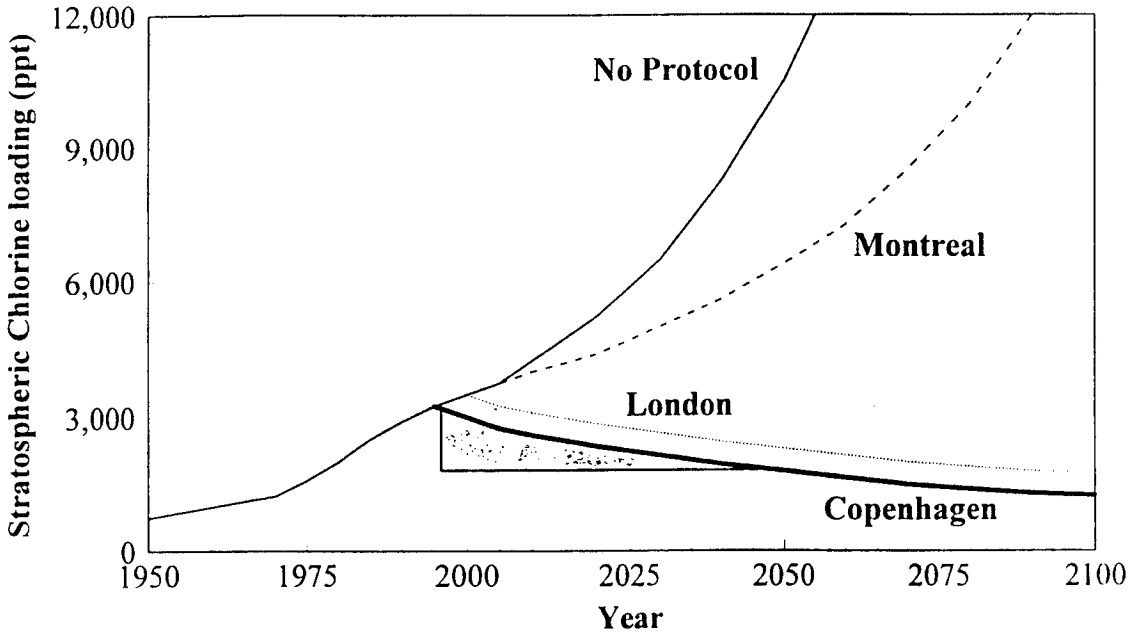
* The first part of a Montreal Protocol Decision number is a roman numeral indicating the meeting of the Parties at which the Decision was agreed upon (2,3) — Decisions reached at the first meeting of the Parties in 1989 begin with I, those from the second meeting of the Parties in London in 1990 with II/, those from the fourth meeting of the Parties in Copenhagen in 1992 begin with IV, and so on up to VII/ in Vienna in 1995; the second part of the Decision number is an arabic numeral indicating the serial order of Decisions for that particular meeting.

Figure 1



The solid curve depicts the estimated level of chlorine loading and hence ozone depletion without the Montreal Protocol; as can be seen, chlorine loading would have continued to rise at an increasing rate with no foreseeable limit.

The dashed curve shows the projected loading with the Montreal Protocol. Its provisions on halons were, in retrospect, rather mild, providing only that, from 1992, production would be capped at 1986 levels, the latest year for which data were available. As can be seen, chlorine loading is reduced, but very high levels are still reached albeit at a later date — ozone depleting substances are still being produced at a rate faster than natural atmospheric processes can destroy them.

In London in 1990, Decision II/1 required that, from 1995, production be halved compared to the 1986 baseline and that, from 2000, production cease in developed countries. Less developed countries, operating under Article 5 of the Protocol, were given a 10-year grace period before the ban on production would be applied (2,3). Recognizing that there were possible instances, particularly with respect to halons, where there would be no practical alternative to using ozone depleting substances, another Decision, II/3, allowed for continued production to support so-called "Essential Uses," though the meaning of the term was not yet precisely defined. Additionally, though not an official Decision, a number of the Parties agreed to the London Resolution which stated that, if the Ozone Depletion Potential (ODP) of an agent not explicitly covered by the Protocol was greater than zero, its use would be permitted for a transitional period only and that these "transitional substances" would have a phase-out date between 2020 and 2040 (2,3). The dotted curve shows that the London Amendments, in particular the production ban, resulted in a significant reduction in projected chlorine loading.

In Copenhagen in 1992, Decision IV/2 brought forward the production ban for halons to 1994. In addition, the transitional substances first mentioned in the London Resolution were defined, and in Decision IV/3, the Parties gave them a specific date of 2015 for a 90% reduction (2,3). The thick-line curve shows that the effect of the Copenhagen Amendments was to reduce the peak level of chlorine loading and to advance it in time. Nevertheless, the maximum depletion of the ozone layer is still to come, and its greatest vulnerability will occur over the next ten years: if, for instance, there is a major volcanic eruption during that period, there could be significant increases in the level of ultraviolet radiation reaching the earth's surface, with the associated environmental implications.

Corroboration of the projections is provided by recently published findings by Montzka et al. (5), which record the first observed decrease in tropospheric chlorine loading. Tropospheric chlorine loading leads stratospheric loading by the period of some 4 to 5 years required for gases to diffuse through the tropopause, which divides the two atmospheric layers. These results are consistent with the Science Panel's model and with the predicted peak in stratospheric chlorine loading in 1999 or 2000.

2.5 The Halon Bank

Cessation of halon production, but not of its use, naturally lends great significance to the supplies already in existence — the so-called "halon bank." Use of this term appears to have encouraged the misconception that the bank exists as a physical place or places where all available halon is stored, ready to be issued. This is not the case. The halon bank (just like a financial bank) is made up of both liquid and invested assets. The liquid portion of a financial bank may be viewed as that portion available in the vault, available to be withdrawn at any time, but probably the bulk of the assets are tied up in mortgages, loans, and other investments. Similarly, the halon bank is made up of halon not currently in use, ready to be issued within the organization which owns it or purchased by others, but the vast majority of the bank exists in current fire protection systems that, unless discharged, will be decommissioned at some future date when the halon will become available to be stored or to meet current needs.

2.6 Essential Uses

During the Copenhagen meeting, the Parties also defined the criteria for Essential Use approval. Decision IV/25 established that a use should qualify as Essential "only if

1. it is necessary for the health, safety or critical for the functioning of society, (encompassing cultural and intellectual aspects); and

2. there are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environmental and health (6)."

This definition is relatively simple, but the process for obtaining an Essential Use approval is complex. The first requirement is to convince the Environmental Ministry or Department in the applicant's country of the soundness of the case. Once persuaded, the country will submit the nomination to the Parties, who delegate its consideration via the TEAP to HTOC. HTOC's recommendation is passed back via the TEAP (which, in principle, could amend or even reverse it) to the OEWG, who will formulate it for the Parties. Finally, the Parties are required to achieve consensus before an Essential Use approval is given. None has so far been obtained for halon 1301 or 1211.

Such approval does not in itself allow for production. It is additionally necessary to show that "all economically feasible steps have been taken to minimize the use and any associated emission" and that halon "is not available in sufficient quantity and quality from existing stocks (2,3)."

In addition, it is worth noting that there are doubts that the chemical manufacturers, previously the suppliers of halon, would be willing or able to resume producing the material at an economic price; their halon plants have been disassembled or reconfigured, and it would be a costly process to re-convert them.

3 VIENNA MEETING OF THE PARTIES AND DECISION VII/12

3.1 Options at Vienna

Thus, the position facing the Parties in Vienna was that, with the implementation of the Copenhagen Amendments, chlorine loading was already projected to return to its pre-ozone hole levels over the next 50 to 75 years. Little could be done to affect the height of the peak or its timing — the gases which will cause it are already released, present in the troposphere, and cannot be recaptured. What could be addressed was the integrated chlorine loading over the decades subsequent to the peak value, shown as the hatched area in the Figure.

It is important to recognize that the precise forms of the projections in the Figure are determined by assumptions made in the model, notably as to the release date of the chemicals into the troposphere. If they are released sooner that predicted, the peak of the curve may be higher or broader than shown; if later, then the initial rate of reduction after the peak will be faster, but the curve will have a longer tail. Regardless of the date on which it occurs, release of a given quantity of a chemical will have the same impact on total ozone depletion integrated over time. Similarly, reductions in releases, irrespective of when they occur, will result in the same reduction in integrated ozone depletion. However, in view of the peak susceptibility of the ozone layer over the next few years, earlier releases are of particular concern.

It is the authors' understanding that the model used in generating the projections used in the figure assumes that all halons (along with all other ozone depleters) will be released by 2010. At least in the case of halons, this assumption is not entirely valid: several users,,representing an important minority of applications, have identified needs which could last for thirty years or more. Among them are the aerospace industry, particularly for newer, existing airframes. For such long-term uses, the belief that options must be considered immediately is misplaced; their delayed release dates mean that there is still time available to make an informed decision on further controls without jeopardizing the ultimate reduction in integrated ozone depletion achieved. It seems that the special circumstances of this minority were not appreciated at the Vienna meeting (nor is it well understood by environmental advocates today).

Thus, the small number of possible measures which were put forth before the Parties took no account of the needs of these long-term uses. Production of halons having already ceased in the developed world, all that remains as a further measure is to prevent release of already existing halons, in other words to destroy stored agent; destroying it all would yield a reduction of 10 percent. Other options that were considered but not accepted were eliminating the use of methyl bromide by the year 2001 which would achieve a 13 percent reduction and advancing the phase-out of hydrochlorofluorocarbons (HCFCs) to 2004, offering a reduction of 5 percent.

3.2 Decision VII/12

Based on the foregoing considerations, Decision VII/12 recommends that all non-Article 5 (developed) Parties should endeavor, on a voluntarily basis, to limit emissions of halon to a minimum by taking a number of prescribed steps. As a voluntary measure, its implementation is not mandatory, but it might be noted that the Montreal Protocol has never yet been amended to be any less stringent, instead having always increased in severity.

The full text of Decision VII/12 is shown as an Appendix, but it contains four key points which together represent a significant change in the political complexion of the Montreal Protocol. Each of these areas warrants additional discussion.

1. It seeks to limit halon use to "Critical Uses" (which would meet the Essential Use criteria previously defined but which do not necessarily need new production) (1). The introduction of the concept of Critical Use as a justification for the continued use of existing halon sets the scene for use controls; all previous measures of the Protocol have applied strictly and solely to production of halon, never to its use.

2. It recommends decommissioning non-Critical installations as quickly as possible (1). This is the first appearance of a resolution on active decommissioning.

3. It advocates taking into account only replacements for which no other more environmentally suitable ones are available (1). The explicit aim of the Protocol, and of the Vienna Convention from which it derives, is to protect the ozone layer; now, for the first time, formal recognition of other environmental issues is built into the Protocol.

4. It promotes the environmentally safe destruction of halons which are not required immediately or in banks (1).

3.3 Critical Use

Previously, a free market driven by supply and demand has been seen as sufficient to limit use of halon (all supplied from the "bank" now that production has ceased) to the most important applications. Decision VII/12 appears to advocate the need for outside intervention and determination through a Critical Use approval process.

It is possible that in the future only Critical Uses of halons will be allowed to continue. For such a policy to take effect, uses would have to be "certified" as Critical. A first real problem is the process for determining Criticality. It could work in the same way as the current Essential Use approval process described in 2.6 above, which takes more that a year at best. However, the volume of nominations is likely to be much greater than for Essential Uses, possibly rendering such a process unworkable. Alternatively, such a decision could be reached locally, regionally, or nationally. Also in question is for how long an approval will be valid. Another area of concern arises from the definition of Critical Uses, which includes the concept of economic feasibility; very different views on this might well be held by the owners of an installation, their insurer, an environmentalist, and a regulator. Almost certainly, evidence of an active search for alternatives will be one of the preconditions for obtaining and retaining a Critical Use approval. Finally, it must be borne in mind that the international movement of halon was one of the tenets on which the Protocol and the rapid and early phase-out of halon were originally based; if decisions on Critical Uses are reached on anything other than an international basis, different territories are certain to reach different decisions in equivalent cases, raising major implications for trade between those two countries.

3.4 Decommissioning, Destruction and Halon Supplies

Another major change in Decision VII/12 is the introduction of explicit provisions on decommissioning and destruction. If Critical Uses cannot be demonstrated to need all of the halon which is in existence at present, either now or in the future through banking, the "surplus" agent is liable for destruction. Halon 1211 is widely perceived as being in surplus (although no quantified basis for this perception has been published) (7). When the international community makes it known that halon 1211 is in excess and should be destroyed, those who currently own halon and who had believed it to be an asset will be suddenly faced with the cost of its destruction, thus making that agent a financial liability to the owner. In the case of less diligent owners, that is likely to lead to deliberate venting of the agent to avoid the liability. With this potential loss through venting, added to the potential losses by destruction, there is a likely reduction in the availability of a commodity which is currently critical for safety in the aviation industry and for which no alternative has yet been proven.

The pressure represented by Decision VII/12 to decommission non-Critical systems will mean that the present decommissioning process will accelerate and that the majority of systems will, in a relatively short period of time, complete the process. As a result, the availability of agent — both 1301 and 1211 — in the long term, is likely to be reduced compared with previous assumptions. This halon represents the majority of the potential halon "bank." If industries, specifically the aviation industry, require halon to protect their future needs, then halon reserves ("vaults") need to be built very soon, or the contents of the bank will either be unavailable or will be extortionately expensive. The decision to construct a bank is difficult because if, in due course, use of halon becomes completely impossible, the bank owners are likely to incur its destruction cost. Against this must be set the risk that halon becomes unavailable and it becomes necessary to retrofit the aircraft fleet with alternative agents, an extremely expensive process.

3.5 Other Environmental Requirements

The third major change in the direction of the Protocol is the introduction of environmental issues unrelated to ozone. The search for alternatives, which are already actively pursued, needs to make allowance for such issues as global warming, atmospheric lifetime, and perhaps for ground-water pollution and others. If agents with environmental impact are unavoidable, then the same battle is likely to have to be fought as has already occurred for ozone depleting substances. In addition, the aviation industry is not presently perceived as being an active participant in the search for alternatives although, in fact, a significant amount of work is being undertaken; it is important that the industry publicizes the fact that these alternatives are being sought and just how technically challenging a problem it is facing in achieving equivalent safety in an acceptable manner. Even where alternatives

have been identified which are widely regarded as being effective, there is still delay in implementing those alternatives. Such delays need to be minimized and implementation, once achieved, publicized.

4 RECOMMENDATIONS FOR THE AEROSPACE COMMUNITY

Firstly, banking mechanisms and halon reserves, if they are needed, must be built now. A cost benefit analysis may be needed to confirm that the risk and potential cost of destruction is justified by the savings in projected retrofit costs, and then a process should be implemented of listing inventories of existing halon stocks in non-Critical Uses (simulators, computer installations, etc.) and assessing the needs of the fleet, including future acquisitions. If a deficiency is identified, the halon to fulfil the needs of the fleet must be found, purchased, recycled, and stored.

Secondly, the aerospace community needs to continue to pursue the search for acceptable alternatives, perhaps at a faster pace than at present. The existence of this search, its extent, and the technical difficulty which it poses, need to be publicized. Alternatives need to be implemented when they are available, if necessary expediting the removal of any regulatory barriers.

Thirdly and finally, the industry needs to be involved in the political process. It will soon be one of the very few remaining users of halon. Representatives from the aerospace industry need to be involved in this process and make their needs and legitimate concerns known: for example, on the HTOC, the Halon Alternatives Research Corporation, Halon Recycling Corporation in the U.S., and the Halon Alternatives Group and Halon User National Consortium in the U.K.

5 CONCLUSION

The changes of the Montreal Protocol have occurred in only one direction: toward tighter controls. There was no restriction on the use of halon until 1986; in 1987, its production was capped; in 1990, it was banned from 2000, and in 1992 banned from 1994; now use controls are being considered. The provisions of the Protocol may progress no further, but it would be prudent to anticipate the continued tightening of international and national regulations. Unless the aerospace industry — which will be one of the sufferers if that occurs — is involved in the process, the damage which it will sustain could be very significant.

6 APPENDIX: DECISION VII/12

1. To recommend that all non-Article 5 Parties should endeavor, on a voluntary basis, to limit the emissions of halon to a minimum by

   (a) Accepting as Critical those applications meeting the Essential Use criteria as defined in Decision IV/25, paragraph I (a);

   (b) Limiting the use of halons in new installations to Critical Applications;

   (c) Accepting that existing installations for Critical Applications may continue to use halon in the future;

   (d) Considering the decommissioning of halon systems in existing installations, which are not Critical Applications, as quickly as technically and economically feasible;

   (e) Ensuring that halons are effectively recovered;

   (f) Preventing, whenever feasible, the use of halon in equipment testing and for training of personnel;

   (g) Evaluating and taking into account only those substitutes and replacements of halon, for which no other more environmentally suitable ones are available; and

(h) Promoting the environmentally safe destruction of halons, when they are not needed in halon banks (existing or to be created).

2. To request the Technology and Economics Assessment Panel and its Halon Technical Options Committee to prepare a report to the Eighth Meeting of the Parties to provide guidance on the above.

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NATIONAL AEROSPACE STANDARD 411
DOES IT FIT INTO DoD ACQUISITION REFORM?

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ABSTRACT

This paper discusses the history of NAS 411, its early implementation and the question of whether it conforms to the tenets of recent Department of Defense (DoD) Acquisition Reform measures and policies.

NAS 411 was first issued in July 1993. Acceptance and success of its implementation have varied greatly. Not by coincidence, NAS 411 implementation success is directly attributable to both the government and industry understanding of the standard, its intent and limitations. This paper provides insight into NAS 411, for achieving consistent implementation success. The paper also includes the latest information regarding DoD's implementation of Acquisition Reform and how NAS 411 does and doesn't fit the current DoD initiatives. The status of successful NAS 411 implementation within current DoD weapon system programs are included. Specific obstacles to NAS 411 implementation are discussed with recommendations for overcoming them.

INTRODUCTION

In the decades before the 1990's, the federal government reacted to the environmental problem at hand - cleaning up the millions of acres of polluted federal land and installations. In the early 1990's superfund cites seemed to be everywhere and the job was to cleanup. Unfortunately, not many folks stopped to asked how the federal government had landed itself in this situation. Within DoD, weapon systems were suspected as primary contributors, but no one could quantify with certainty the actual percentage of hazardous wastes they generated.

At the beginning of the 1990's, environmental stewardship gained increasing attention within the federal government. The relative solace of many federal employees loyally working in their oftentimes maligned jobs was rudely awakened when Congress passed the Federal Facilities Compliance Act (FFCA) in 1992. This law waived sovereign immunity for all environmental infractions where federal employees were involved. From Old English Law, sovereign immunity stems from the concept that neither the sovereign nor subjects of the Crown could be persecuted by the general populace. The FFCA seemed to sweep away this age-old protection enjoyed for so long by all federal employees. This was the beginning of the end of the "*Hey, that law doesn't apply to us - does it?*" mentality. Seeming to compound the situation was the fact that federal employees were not even assured their legal fees would be reimbursed, *even if found innocent of the charges!*

Interestingly, preventing pollution as an integral part of DoD's acquisition policy had been around since the 1980's (1). Integrating Environment, Safety and Health (ESH) considerations into the systems engineering process had been DoD policy since 1991 (2). Management attention was missing to ensure the policies were being implemented within the acquisition community.

The traditional end-of-the-pipe mentality began to shift in President Clinton's administration (3). Within DoD, leaders began to understand that Acquisition Managers, not the Facility Managers, held the key to preventing the problem (4). DoD recognized that Facility Managers have limited authority over pollution prevention implementation. Their authority domain ends with the support infrastructure at the installation. This includes: supplying power, water, heat and air conditioning; physical plant maintenance; and waste stream controls (such as, paint scrubbers, incinerators, waste water treatment, and solid waste disposal). Facility Managers implement limited pollution prevention when they replace Ozone Depleting Substances (ODS) from plant air conditioners with more environmentally friendly chemicals. They cannot change the primary cause of hazardous waste generation at their facility - the production, operation, and maintenance of weapon systems. The DoD Inspector General (DoDIG) found that these three weapon system actions account for more than eighty percent of all DoD-generated hazardous wastes (5). Among other reasons, this lack of authority to change the weapon system operational or maintenance processes is the systemic reason why DoD's environmental focus has been on pollution control (paint scrubbers, incineration, waste water treatment etc.) instead of pollution prevention (changing the weapon system specifications that control the painting, plating and cleaning requirements of a weapon system). Facility Managers have traditionally been aligned with civil engineering which typically includes environmental managers. Unfortunately, the expertise and authority to fix the problem (i.e., changing the cadmium plating process to Ionized Vapor Deposition (IVD) or replacing CFC-113 with aqueous concepts in cleaning Liquid Oxygen (LOX) Systems) resides in the acquisition community. It should be noted that in most cases within DoD, only the PM has the authority to change weapon system operational and maintenance specifications that control materials and processes. This is critical to ensure the performance characteristics of the weapon meet the operational requirements safely and consistently. In 1992, the DoDIG concluded "*...although the Department is committed to reducing the use of hazardous materials, it has not ensured that the mechanisms needed to accomplish this goal are an integral part of day-to-day operations...*" (6). At the same time DoD was struggling with how to best influence the acquisition community to address the beginning-of-the-pipe issues of pollution prevention, it faced an even broader challenge - Acquisition Reform.

Anyone who has been associated with federal acquisition over the past decade has most likely heard the incessant industry chant that the federal government over-specifies. Industry complaints usually surface at three levels: the products, the shop floor industrial processes associated with the product (such as soldering), and the management processes supporting the corporate infrastructure (such as cost accounting). A common theme from most industry sectors focuses on government specification and standards and includes such comments as: they are inflexible; they do not account for proven industry best practices; they conflict with each other; they are blindly added to contract requirements; and they are not tailored to the specific program. That the federal government tends to be non-responsive to industry's suggestions is probably the most often heard and perhaps most important industry criticism.

Convinced that a change was required in how the federal government conducts its acquisition business, Congress passed two landmark laws in the mid-1990's: the Federal Acquisition Reform Act and the Federal Acquisition Streamlining Act. Both laws have caused significant changes in how the federal government conducts acquisition. DoD implementation of Acquisition Reform concentrated on six major themes: Teamwork, Tailoring, Empowerment, Cost as an Independent Variable, Commercial Products, and Best Practices (7). The new policy that implements Acquisition Reform and authorizes mandatory procedures that apply to all programs was issued in March 1996 (8). For the first time, DoD requires all programs, regardless of acquisition category, to integrate five key ESH issues into the systems engineering process. These are: the National Environmental Policy Act (NEPA), Environmental Compliance, System Safety & Health, Hazardous Materials, and Pollution Prevention. It is this mandatory requirement that forms the thrust of DoD's landmark move toward serious implementation of ESH considerations within the acquisition of weapon systems.

Based on the most recent GAO report, the federal cleanup bill facing taxpayers is now estimated at over $400 Billion (9). On the same order of magnitude as the Savings & Loan bail-out, the federal government must be ready for the onslaught of public criticism over this situation. The timing could not be better for a fully integrated, industry proven, cost saving approach to reducing the use of hazardous materials in the design of DoD's weapon systems.

NATIONAL AEROSPACE STANDARD (NAS) 411

In the midst of the acquisition and environmental policy turmoil in the early 1990's, the Aerospace Industries Association (AIA) and a few DoD leaders worked quietly to leverage a great idea initiated in the Air Force F-22 Program. The concept was simple yet revolutionary. If industry's claim was accurate that it was ahead of the federal government in reducing its reliance on hazardous materials, why not permit them to show the federal government how to do it in acquisition programs. NAS 411 was the result of this challenge (10). First issued in July 1993, NAS 411 has undergone two revisions in 1994. Dr. Paul Kaminski, the Under Secretary of Defense for Acquisition and Technology has required NAS 411 "...be utilized by all system acquisition program managers in all phases of all systems, life cycle..." (11). This endorsement from DoD's highest acquisition executive came after the Military Specifications and Standards Process Action Team determined NAS 411 "...should be adopted for mandatory DoD use." (12)

As a non-government standard to be tailored, NAS 411 meets two of the primary themes of Acquisition Reform within DoD - the use of industry Best Practices and tailoring to meet program objectives. The standard is well written, easy to follow and establishes the tenets for a contractor's Hazardous Materials Management Program (HMMP). The first of two key documents identified is the HMMP Plan. The HMMP Plan describes the how, what, and when of the contractor's plan to eliminate, reduce, or minimize the use of hazardous materials. Recognizing the realities of an imperfect world, the standard also requires that when the contractor needs to use a hazardous material, plans for the control of that material must be addressed across the life cycle. The second key document is the HMMP Report. The HMMP Report tracks how well the contractor is doing against the HMMP Plan. The goal of implementing NAS 411 is to protect human health and the environment while minimizing system cost and risk to performance. The term "system cost" used in the standard has resulted in some criticism that the standard does not meet the new requirement to address life cycle costs (cost of ownership) versus the more traditional acquisition costs (system cost). To those who have not read through the entire standard, this unfortunate use of "system cost" can be a reason to prohibit its use. Clearly, NAS 411 requires a life cycle approach to eliminating the use of hazardous materials. The use of the term "system cost" should be changed to "life cycle cost" in the next revision.

The authors of the standard intended its application across the broadest spectrum of materials and processes. To this end, the definition of Hazardous Materials used in the standard includes; "*Any material that due to its chemical, physical, or biological nature that causes safety, public health, or environmental concerns.*" The term "public health" has been used by some to indicate the standard does not focus on occupation health issues as required by current policies. Again the use of this term should be revised at the next opportunity to simply include the broader term "health".

NAS 411 supports each of the five mandatory issues that must be integrated into the systems engineering process of every program. These are NEPA, Environmental Compliance, System Safety & Health, Hazardous Materials, and Pollution Prevention.

NEPA. By identifying the hazardous materials that may be used, NAS 411 supports the NEPA analysis that identifies potential environmental impact. The standard can also support the mitigation of these impacts be identifying alternatives or control measures planned across the life cycle

Environmental Compliance. The HMMP Plan and Report data can provide useful information in the PM contractor evaluation of how environmental regulations will impact life cycle costs, schedule and performance

System Safety & Health. NAS 411 can provide input for the analysis that will address system safety and health issues. In an unusual move, the Electronic Industries Association has recommended that DoD "...consider not canceling and continuing to maintain MIL-STD-882C" (13). The input from NAS 411 can ensure system safety and health analyses required by specific MIL-STD-882C tasks take into account the hazardous materials that will be used throughout the life cycle of the system.

Hazardous Materials. Obviously, NAS 411 can provide the primary information for the PM to meet this mandatory requirement.

Pollution Prevention. Perhaps one of the most often misunderstood issues is the difference between the HMMP and the requirement for the PM to establish a Pollution Prevention Program (PPP). The PPP is typically broader in scope and may include government initiatives such as developing new technologies or testing new environmentally acceptable alternatives where there is little incentive for industry. One recent example is the Joint DoD Federal Aviation Administration Halon Alternatives Steering Committee (HASC). This effort includes fire protection research and development associated with threat-induced fires and explosions. If a PM had work under the HASC, it would be included in the PPP but not necessarily in the HMMP. If however, a technology matured sufficiently to transition to the contractor for integration into the systems engineering process, the HMMP would then include the new material or process.

As shown, NAS 411 can be used as common tool across all of the mandatory issues now required in every DoD weapon system program. To date, the primary limiting factor in full NAS 411 implementation has been a lack of understanding on the part of both government and industry. This may be a systemic issue because there has been no concerted, well publicized effort to provide accurate and consistent training. The Defense Acquisition University (DAU) has begun to include some limited discussion on NAS 411 in the courses now being developed. Industry should consider expanded instructional forums specifically for NAS 411 implementation.

A number of programs throughout DoD have used NAS 411 in their contracts. There are at least four ways that NAS 411 can be used. While some are better than others, each tailored application is acceptable. The first way NAS 411 can be used is as a part of the Statement Of Work (SOW). In this case, the HMMP Plan and Report are post-award contract deliverables. This example fails to determine how well the winning contractor understands the concept of the HMMP and may result in several iterations of the Plan before it is accepted. This method has the potential to require more time and money than the others. The second example seems to be most preferred. It consists of using NAS 411 as a direct part of the overall source selection contract award process. In this case, the standard is cited in the Request For Proposals (RFP) and the offeror is required to submit a draft HMMP Plan for evaluation by the government. After the selection has been made, government comments are provided to the winning offeror and a revised HMMP Plan is provided in the initial stage of the period of performance. The third way to

use the standard is as a portion of the RFP's Section L, "Instruction to Offerors". While not contractually binding on the winning offeror, this section typically contains important guidance. The last, and often most overlooked, use of the standard is in RFPs for Commercial Off The Shelf (COTS) and Non-Development Items (NDI). In these situations, the government can use NAS 411 as a portion of the Market Survey/Investigation, during which time the government ascertains if commercial items can be acquired directly or if some modification to an existing product may meet operational requirements. In this case, the government must not imply it wishes a potential offeror to implement NAS 411 but rather asks the potential offerors if they have such a program in place for their commercial product line. The government can also ask if the commercial item contains hazardous materials embedded in the product or required as a portion of maintenance or operation. The information received can then be used by the government to make more informed management decisions on COTS and NDI acquisitions.

One final criticism recently aimed at NAS 411 is the contention that it is no longer needed after the International Organization for Standardization (ISO) 14000. While some of the details of ISO 14000 are still being debated in this country and abroad, the general premise of the standard will most likely prevail. NAS 411 is completely compatible with the planning and implementation aspects of ISO 14000. Unless some radical changes take place in ISO 14000 (which seems unlikely), NAS 411 and ISO 14000 are mutually supportive not mutually exclusive. When NAS 411 is revised, it should clearly demonstrate its compatibility with the ISO 14000.

CONCLUSIONS.

As can be seen from this paper, NAS 411 complies with the spirit of Acquisition Reform. It has been endorsed by the most senior acquisition executive within DoD and it supports the five mandatory issues required for integration into the systems engineering process of all DoD acquisition programs. It can be tailored to meet the needs of various types of programs to include the traditional developmental as well as COTS and NDI types of acquisition.

AIA needs to revise the standard to clarify three issues: the aspects of life cycle cost instead of system cost, the more generic issue of health instead of public health, and its compatibility with other new initiatives such as ISO 14000 and Acquisition Reform.

To date, the primary limiting factor in full NAS 411 implementation has been a lack of understanding on the part of both government and industry. This may be a systemic issue because there has been no concerted, well publicized effort to provide accurate and consistent training. AIA should consider expanded instructional forums specifically for NAS 411 implementation.

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CLEANING: OXYGEN SYSTEMS ISSUES AND APPROACHES

George C. Marshall Space Flight Center

Oxygen Systems Cleaners for Aerospace Applications

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Abstract:

New environmental regulations have forced extensive evaluations of many different cleaning agents for use in oxygen systems. This is no simple process because pure oxygen is a very strong oxidizer, and when placed in contact with a foreign substance, the combination may be explosive. This foreign substance can easily be a cleaning agent residue left over in the oxygen system after cleaning.

This paper focuses on the factors that must be considered when selecting a cleaning agent for oxygen systems, as well as the approval processes which are currently being utilized by NASA for oxygen compatibility of materials. This paper will provide a working description of how to begin selecting a cleaning agent for oxygen systems. The paper will present the following: Background information on the necessity of a stringent selection process for oxygen system cleaners; Specifications and regulations concerning cleaning for oxygen service; Changing oxygen cleaning specifications given current environmental concerns; Testing for cleanliness in oxygen systems; Cleaning agents that have been tested for oxygen systems, including an extensive list of some of the newer "environmentally friendly" cleaning agents; Test results and conclusions from the testing. The paper will also provide instructions on the proper procedures for obtaining NASA approval on a candidate oxygen systems cleaning agent.

Introduction:

The aerospace industry has always faced the need to clean its oxygen systems, both in the propellant systems and in the breathing oxygen systems. Oxygen systems have proven to be difficult and dangerous systems to clean because of the combustion characteristics of a strong oxidizer in contact with many other substances.

The aerospace industry has been fortunate in previous years to have the closest thing to universal cleaning agents as can be imagined. These cleaning agents, or solvents, as classified by their chemical formulations, are known as Chlorofluorocarbons (CFCs). These will clean away both the non-volatile residues and the particulate contamination, and will also evaporate quickly in air. CFCs, to the benefit of

oxygen systems cleaning, also prove to be compatible with liquid and gaseous oxygen. CFC's have been the answer to oxygen system cleaning needs for many years.

Chlorofluorocarbons, however, have recently faced serious allegations about their effects on the Earth's Ozone Layer. The U. S. Environmental Protection Agency has classified CFC's as Ozone Depleting Compounds (ODC's), and the Congress of the United States has outlawed the production and restricted the use of all ozone depleters. CFC's are no longer usable as cleaning agents and the aerospace industry must, therefore, find new chemicals and processes to perform the cleaning needed for oxygen systems.

Background:

Since the introduction of the liquid oxygen engine, the aerospace industry has faced the dangers of using pure oxygen. The combustion process used in propulsion makes use of the strong tendency of materials to burn when exposed to an oxygen environment. This, however, presents a grave problem in that contaminants can act as fuel when exposed to oxygen. This problem, unfortunately, can be demonstrated with the large number of oxygen systems that have been destroyed by fires resulting from contamination within the systems. Oxygen systems must therefore be cleaned "well enough" so that they do not burn up from contamination.

The question of "how clean is clean enough" led Marshall Space Flight Center to develop MSFC-SPEC-164. This document defines how clean an item must be in order to be exposed to 100% oxygen when used within NASA. The cleanliness levels in the first writing of MSFC-SPEC-164 were dictated mainly by the ability of the cleaning procedures of the day. MSFC has recently revised this document to more closely reflect the true cleanliness needs within oxygen systems.

NASA has decreed that the revised MSFC document will dictate all oxygen cleaning within NASA, so MSFC-SPEC-164B has become the governing cleanliness document for oxygen systems used on NASA programs.

The cleanliness levels specified in MSFC-SPEC-164B are only goals and the document does not indicate how these goals are to be achieved. This leaves the selection of both the cleaning agents and cleaning processes open to anyone trying to clean an oxygen system. This selection process is a key to proper cleaning.

Many characteristics of a cleaning process are involved in the selection of the best one for oxygen systems. These include, as well as many others: (1) The compatibility of the cleaning agent with liquid oxygen. This is most important when cleaning solvents are left inside oxygen systems after cleaning. (2). The type of possible contaminants and the ability of the cleaning agent to remove these contaminants. Some cleaners are good for removing one type of contaminant, but not for others. (3) How easy the cleaning agent is to use for the areas needing cleaning. Cross-country pipes require totally different cleaning processes than small parts, etc. (4) The initial investment price of the cleaning process. (5). The cost of the cleaning agent and supporting processes. (6). Compatibility of the cleaning agent with the items to be cleaned.

Due to the magnitude of this problem, this paper covers only the subject of the compatibility of cleaning agents with liquid oxygen.

Specifications, Regulations and Significant Events:

Several United States Laws, Regulations and NASA Specifications govern the selection of cleaning agents for oxygen systems in NASA programs. These include MSFC-SPEC-164B, "Specification for Cleanliness of Components for Use in Oxygen, Fuel, and Pneumatic Systems," the Clean Air Act, the Montreal Protocol, Presidential Decrees, and many others.

The following listing highlights the most significant events that have affected the cleaning of oxygen systems for NASA programs:

Nature Magazine: 1974	First published theory of compounds destroying the Earth's Ozone Layer.
Montreal Protocol: 1987	This agreement between nations dictated that the production and use of Ozone Depleting Compounds will be greatly reduced.
NASA Report: 1988	NASA report concluded that the ozone layer had been depleted more than previously estimated, and CFCs were the primary cause.
Clean Air Act (Amend.): 1990	This United States Law dictated that the United States will comply with the London Amendments to the Montreal Protocol and discontinue production of CFCs by the year 2000, and place severe restrictions on the use of CFCs.
Presidential Decree: 1992	President George Bush decreed that the United States will discontinue the production of Ozone Depleting Compounds by the year 1995.

MSFC-SPEC-164B/Summary LOX/GOX Cleanliness

Item to be Cleaned	Cleanliness Level	Maximum Allowed Particle Count and mg NVR/0.1 sq.m.
LOX/GOX Systems:		
Metallic & Fluorocarbon Components:	I-A	6 particles and 1 mg NVR
Metallic Vessels:	I-B	6 particles and 5 mg NVR
Nonmetallic (Except Fluorocarbon):	V	Visually Clean/No Silting
Space Shuttle Main Engine:		
GSE and Engine Systems LOX/GOX:	III-A	0 particles > 800 microns, and 1 mg NVR
Propellants and Pressure Vessels:	III-B	0 particles > 800 microns, and 5 mg NVR
Test Facilities:	IV-A	0 particles > 400 microns, and 1 mg NVR
External Tank:		
Tanks and Vessels:	II-B	0 particles > 1000 microns, and 5 mg NVR
System Equipment:	III-A	0 particles > 800 microns, and 1 mg NVR

Test Procedures:

Introduction to the Ambient Pressure Liquid Oxygen Mechanical Impact Tester:

Since its development by MSFC more than thirty years ago, the Ambient Pressure Liquid Oxygen Mechanical Impact Test has been the baseline standard in defining the acceptability of materials for exposure to a liquid oxygen environment. For this reason, the Ambient Pressure LOX Mechanical Impact Test is the method employed in the study of the compatibility of cleaning agents with oxygen systems.

The tester uses a 20-pound plummet that drops from a height of 43.3 inches onto a metallic striker pin in contact with a sample of the candidate material. This produces an Impact Energy of 72 ft-lbs, or equivalently, 10 Kg-m, or 98 Joules. The candidate material is submerged in liquid oxygen that has been placed in a test cup. The test cup has been placed in the tester base where the impacting will occur. The base is cooled with liquid nitrogen to keep the liquid oxygen from boiling off too quickly. The candidate material is contacted by a striker pin, for cleanliness and plummet safety, that transfers the energy of the falling plummet to the sample.

The standard test procedure for the Ambient Pressure LOX Mechanical Impact Tester is contained in NHB 8060.1C, "Flammability, Odor, Offgassing, and Compatibility Requirements for Materials in Environments that Support Combustion," and described by Test 13A, "Mechanical Impact for Materials in Ambient Pressure LOX." This test dictates that for any candidate material, a total of 20 impacts, or 20 drops, must be conducted on that material. A "Reaction" is defined as a visible flash or audible report upon impact, and determined by the test conductor. Test 13A defines the following rating criteria:

(a) 0 reactions out of 20 impacts at 72 ft-lbs - material "passes."
(b) 2 or more reactions out of 20 impacts at 72 ft-lbs - material "fails."
(c) 1 reaction out of 20 impacts at 72 ft-lbs - "inconclusive." Forty additional impacts are conducted, and one or more additional reactions indicates the material "fails."

Test Procedure for Cleaning Agents:

Two disclaimers must be addressed before any data is presented. First, as stated before, there are entirely too many topics regarding oxygen system cleaning to be addressed within one paper, so only the first, the compatibility of the cleaning agent with liquid oxygen, will be covered. Second, the best method for testing these cleaning agents is still in debate. There is no clear answer to some important questions, such as: How much cleaning agent should be tested? What is the best method of sample preparation, sample dilution, and worst-case applications? What substrate is the best to use for testing? Is Test 13A (ASTM D-2512) the best method by which to test? Should testing be conducted at higher pressures?

The test procedure employed in this study, which also corresponds to ASTM D-2512, is as follows:

(1) Liquid samples are to be tested, as necessary, in any or all of three forms, full-strength, diluted per manufacturer's specifications, and as the residue left upon evaporation.
(2) Solid samples are diluted to the maximum concentration achievable, following manufacturer's recommendations, and tested as in step (1) above.
(3) Test substrates will include any of the following, as necessary: Stainless Steel disks, unsealed Sulfuric Acid anodized Aluminum disks, 0.050 inch deep Aluminum cups, and 0.050 inch deep Stainless Steel cups.
(4) Samples and substrates are placed into tester cups and the cups placed into the base of the Ambient Pressure LOX Mechanical Impact Tester.
(5) Tester is configured per usual setup, i.e., as defined by the specifications of NHB 8060.1C, Test 13A (ASTM D-2512).
(6) Testing is conducted at an impact energy of 72 ft-lbs, and energy thresholds are determined as necessary.
(7) Reactions are noted.

Test Results:

The following tables provide a detailed summary of the results obtained, to date, for the cleaning agents tested at MSFC. This data is presented without ratings, and its applicability to any specific cleaning process is at the discretion of the user. **Presentation of this data is not an endorsement of any product, or recommendation of one product over another.**

The attached tables represent a simplified summary of the test data available as of July 31, 1996, for those cleaning agents tested at MSFC. More detailed information, and up-to-date test data, can be found on the Materials and Processes Technical Information System (MAPTIS) part of the Materials, Processes and Environmental Engineering Network (MPEEN) database. Any interested individual can establish an account on MAPTIS, and have easy access to much needed materials information.

Test Number	Trade Name	Manufacturer	Sample Preparation Method	Sample Preparation Method	Sample Preparation Method	Sample Preparation Method	Sample Prep. Method	Sample Preparation Method	Sample Prep. Method
			Diluted on H_2SO_4 anodized Al disks	Full-strength on H_2SO_4 anodized Al disks	Full-strength, 0.050" in Al grease cups	Full-strength, 0.050" in SS grease cups	Residue	Diluted, 0.050" in Al grease cups	Diluted, 0.050" in SS grease cups
101382	Oakite STC	Oakite Products Inc.				5K			
101681	Blue Gold	Carroll Co.			amb	1K, 6K			
101722	Blue Gold	Carroll Co.			amb	*6K			
102364	Turco 4215-NC-LT	Elf Aquitaine Inc.	10K				10K		
102470	Oakite 31	Oakite Products Inc.		10K		5K			
102471	VAC-1	Pacific Anchor Chemical		10K		10K	10K		
102577	Turco 5578-L	Elf Aquitaine Inc.		*10K, *5K			10K, 5K		
102655	Neugenic 4175	Rochester Midland	1,050 L,G						
102911	Oakite 31	Oakite Products Inc.				5K			
102912	Micropure CDF	Sentry Chemical Co.			(*amb)		*amb		
102913	Partsprep Degreaser	Sentry Chemical Co.			(*amb)		**amb		
103096	LCS-1000	LOXClean Systems Inc.		amb	amb				
103106	CCS-4000	LOXClean Systems Inc.		amb	amb				
103171	99% TCE	PPG Industries Inc.		amb			amb		

* Failure at this condition

** More than one preparation method at this condition

() Tested at other than 0.050" thickness at this condition

Test Number	Trade Name	Manufacturer	Sample Preparation Method	Sample Preparation Method	Sample Preparation Method	Sample Preparation Method	Sample Prep Method	Sample Preparation Method	Sample Prep Method
			Diluted on H_2SO_4 anodized Al disks	Full-strength on H_2SO_4 anodized Al disks	Full-strength, 0.050" in Al grease cups	Full-strength, 0.050" in SS grease cups	Residue	Diluted, 0.050" in Al grease cups	Diluted, 0.050" in SS grease cups
103198	Hi-Tri (99.9% TCE)	Dow Chemical Co.			amb		amb		
103228	Amberclean L21	Innovative Organics Inc.		*amb	amb			amb	
103229	Amberclean L12	Innovative Organics Inc.		*amb	amb			amb	
103315	Asahi Klin AK-225	Asahi Glass Co Limited				(amb)	amb		
103383	DOT 111/113	Delta-Omega Technologies Limited	amb	*amb	amb			amb	
103419	Sprayeze LT	Elf Aquitaine Inc				10K			**10K
103504	Genesolv D	Allied Signal		amb					
103513	IPA	Fisher Chemical		amb	*amb				
103566	ATTAR-C	Delta-Omega Technologies Limited	amb	amb	*amb	(*amb)		amb	(amb)
103631	PF-5050	3M Co		amb					
103632	PF-5052	3M Co.		amb					
103633	PF-5060	3M Co.		amb					
103732	Asahiklin 225	Asahi Glass Co Limited		amb					
103944	Detergent 8	Alconox Inc.		*amb					
103945	Citranox	Alconox Inc		amb					
103946	Liqui-nox	Alconox Inc.		amb					
103947	Alcojet	Alconox Inc.		amb					
103948	Alconox	Alconox Inc.		amb					
103949	Terg-a-zyme	Alconox Inc		amb					
104896	Cascade Dishwashing Liquid	Proctor and Gamble		amb					

* Failure at this condition

** More than one preparation method at this condition

() Tested at other than 0.050" thickness at this condition

Chart Notes:

All chart data is from standard 72 ft-lbf (10 kg-m) energy level tests. Additional test information is provided below.

101722 at 6000 psia, full-strength, 0.050" thick in aluminum grease cups, produced reactions at 72, 55, and 40 ft-lbf. 0/20 reactions at 25 ft-lbf.

102577 at 10,000 psia, full-strength, on H2SO4 anodized disks, 3/6 reactions. Reactions were severe enough to cause damage to test equipment.

102577 at 5,000 psia, full-strength, on H2SO4 anodized disks, 1/7 reactions. Reaction was severe enough to cause damage to test equipment.

102655 at 1,050 psia, diluted (1 part cleaner to 4 parts DI water), on H2SO4 anodized disks, was tested in both liquid and gaseous oxygen.

102912 at ambient pressure, was tested at varying thicknesses: 0/20 reactions at 0.023" thickness; 2/20 reactions at 0.018" thickness; and 5/5 reactions at 0.005" thickness.

102913 at ambient pressure, was tested at varying thicknesses: 2/22 reactions at 0.023" thickness; 6/20 reactions at 0.018" thickness; and 5/20 reactions at 0.005" thickness.

103228 at ambient pressure, full-strength, on H2SO4 anodized aluminum disks, 19/20 reactions.

103229 at ambient pressure, full-strength, on H2SO4 anodized aluminum disks, 7/20 reactions.

103315 at ambient pressure, full-strength, in SS grease cups, unmeasurable thickness.

103383 at ambient pressure, full-strength, on H2SO4 anodized aluminum disks, 6/20 reactions.

103419 at 10,000 psia, diluted (5 oz in 1 gal DI water, and 1.5 oz in 1 gal DI water), 0.050" thick in SS grease cups.

103513 at ambient pressure, full-strength, 0.050" thick in aluminum grease cups, produced reactions at 72, 55, 40 and 25 ft-lbf. 0/20 reactions at 10 ft-lbf.

103566 at ambient pressure, full-strength, 0.050" thick in aluminum grease cups, produced reactions at 72 ft-lbf. 0/20 reactions at 55 ft-lbf.

103944 at ambient pressure, full-strength, on H2SO4 anodized aluminum disks, produced reactions at 72 and 55 ft-lbf. 0/20 reactions at 40 ft-lbf.

Future Testing and Test Sample Submission:

The task of finding more "environmentally friendly" cleaning agents to fit the different applications involving oxygen systems is still ongoing. Only a small fraction of the different cleaning agents that currently exist have been tested, and even more cleaning agents are being marketed. MSFC obtains its test samples from a variety of sources. Many of these are manufacturers or vendors seeking approval of their products, or users seeking oxygen compatible replacements for CFCs in their applications. For this reason, the procedure for sending a test sample to MSFC for verification of its oxygen compatibility is included below.

Test Sample Submission Procedure

1. At least 8 fluid ounces, (250 ml) of liquid sample must be submitted

2. MSDS and Products Data Sheets must be included for all materials submitted

3. A completed "NASA MSFC Test Request Form" must be included for each item to be tested (The authors may be contacted for a copy of this form.)

4. Address sample and all information to

NASA-Marshall Space Flight Center
ATTN: Eddie Davis or Freida Lowery
Mail Code EH42
Building 4623
Huntsville, Alabama 35812

After a test sample is received, all information supplied with the sample is verified with the supplier or manufacturer, and any questions are answered before testing begins. Samples are tested using strict cleanliness and quality control techniques to ensure the accuracy of results. Upon completion of testing, all information is subjected to an engineering review, in which test data is scrutinized for consistency with past test results on similar materials, accuracy of testing and test methodology is verified, and problem areas have been resolved. Samples are retested if any question remains. After all checks are complete and the data is shown accurate, the information is put into the MAPTIS database. This process takes approximately four weeks, from sample arrival to MAPTIS availability.

Conclusions:

The tables in this report provide information on getting started in selecting the cleaning agents that are the most compatible with liquid oxygen. This is the first place to start when selecting a cleaning agent. All of the other related factors, however, must be considered before the best cleaning agent and cleaning process selection can be made.

The cleaning of oxygen systems can be a tricky and dangerous task unless the right cleaning agent for the job is selected. Employing a "bad" cleaning agent can have catastrophic effects on the flight system, if not on the people doing the cleaning. As can be determined from the test data, not all cleaning agents are acceptable and great care must be taken in this first step of cleaning oxygen systems.

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ELIMINATION OF CHLORINATED SOLVENTS AND OTHER HAZARDOUS MATERIALS IN THE MANUFACTURE OF HIGH PRESSURE LIQUID OXYGEN SSME TURBOPUMPS

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Abstract

Pratt & Whitney is developing alternatives to trichloroethylene in precision cleaning and verification operations for the manufacture of high pressure Turbopumps for the SSME program. Although the elimination of ODC materials has been accomplished with the elimination of 1,1,1-Trichloroethane and Freon 113, there is significant additional pressure to eliminate the trichloroethylene due to regulatory reporting and costs as well as corporate environmental goals. Pratt & Whitney (P&W) is pursuing both an aqueous precision cleaning operation and a high pressure liquid carbon dioxide precision cleaning method to totally replace the degreasing operation presently used. The liquid CO_2 unit is being evaluated to permit an integral non volatile residue (NVR) analyzer with the unit. Alternative verification methods to the present chlorinated solvents are being investigated. In addition, P&W is eliminating all hexavalent chromium materials used on the pumps in applications such as sealing of anodized surfaces. P&W is also working to implement a low VOC, water based maskant for plating and chemical milling operations.

Precision Cleaning

Presently, Pratt & Whitney employs the use of vapor degreasing with trichloroethylene (TCE) solvent as the primary mechanism for precision cleaning of rocket hardware. The requirement to change the P&W precision cleaning operation comes from two primary drivers. The first is the impending Clean Air Act (CAA) National Emission Standards for Hazardous Air Pollutants (NESHAP) for degreasers due to impact P&W in December of 1997. The second is an internal company/corporate policy which requires elimination of most halogenated solvents for use in both handwiping and degreasing applications beginning in 1997. P&W has already eliminated all ozone depleting chemicals from its rocket manufacturing, cleaning, and assembly operations.

Numerous methods for precision cleaning of hardware have been developed, many of which are more environmentally acceptable than chlorinated solvent degreasing. Many of these processes were considered for development testing; each underwent preliminary evaluation for anticipated cost, technical risk, historical success for precision cleaning, and probability of successful implementation at P&W. From this evaluation two technical approaches were selected for further investigation for replacement of the TCE degreaser. The first was a liquid CO_2 cleaning method. Much work has been reported in regard to CO_2 cleaning, however most of the effort has been in the area of solid cleaning such as CO_2 snow, and also with supercritical CO_2 cleaning, which is typically limited by the size of the cleaning chamber. With liquid CO_2 the chamber size is increased significantly over the supercritical chamber, permitting a much larger range of part sizes to be cleaned. In addition the liquid CO_2 is apparently more effective in removing particles due to greater momentum of the cleaning media. P&W is performing studies in conjunction with Batelle Pacific Northwest Labs. The second approach for precision cleaning replacement is an aqueous process. P&W is presently performing preliminary qualification of its aqueous cleaning operations at the National Defense Center for Environmental Excellence (NDCEE) in Johnstown, OH. The NDCEE is operated by Concurrent Technologies Corporation (CTC). Several

approaches to development of the aqueous process have been pursued. One process involves a single precision cleaning step with ultrasonic assistance followed by multiple rinsing steps. The second aqueous method involves a dual cleaning step followed by multiple rinsing steps.

Subsequent tests will be conducted with the following selected substrates employing the optimal cleaning cycle to substantiate the cleaning effectiveness with unique materials such as: thin dense chromium electroplate applied to AISI 9310 bearing material, IVD copper applied to thin dense chromium electroplate, P-5N carbon interpropellant seal material, Berylco 25 precipitation hardenable copper alloy, silicon nitride bearing ball material, and Armalon teflon coated glass fabric bearing cage material.

Aqueous

The first approach for precision cleaning replacement is an aqueous process. P&W is presently performing preliminary qualification of its aqueous cleaning operations with the National Defense Center for Environmental Excellence (NDCEE) in Johnstown, OH. The NDCEE is operated by Concurrent Technologies Corporation (CTC). Several approaches to development of the aqueous process have been pursued.

The first aqueous process under investigation involves a single precision cleaning step with ultrasonic assistance (up to 60 watts per gallon) followed by an ultrasonic rinse and a agitated rinse, both flowing countercurrently. Both rinse tanks have spray nozzles with fresh deionized water to flush the parts upon removal from the solution. In addition, the automated line is able to use robotic control for pneumatic oscillation of the parts to facilitate cleaning effectiveness. Preliminary evaluation indicates this to be a viable method. The second aqueous method involves dual cleaning steps. The first cleaning solution has ultrasonic capabilities (up to 30 watts per gallon). This is followed by a single rinse. Then the parts are immersed in the second cleaner, which is then followed by multiple rinsing steps. In both the single and dual process lines fresh deionized water is available to spray the components after each tank to aid in removal of residual particles, cleaning solution, and other contamination. Optimum filtration pore size and flow rates for the cleaning tanks are being determined. Other factors being optimized are immersion times, mechanical agitation in ultrasonic tanks (typically mechanical agitation is turned off during ultrasonic agitation), cleaner concentration and temperature, ultrasonic power settings, rinse water temperature, and rinse water purity.

The cleaners chosen for final evaluation were Brulin 815 GD, Turco 3878 LF-NC, and Turco 4215 NC-LT. Tested along with the Turco 4215 NC-LT is a surfactant additive which improves both particle and soil removal effectiveness. The criteria for selection of the cleaners was based on composition (e.g. little or no silicates are desired), and historical experience as precision cleaning materials. The cleaners selected for evaluation are presently being used for precision cleaning of rocket components or support equipment at other aerospace facilities.

NVR evaluation with TCE will be performed to both validate the new cleaning process and provide a comparison to historical experience with TCE degreasing.

Liquid CO_2

A series of assumptions were made to yield a test matrix that comprised a rationale for determining the feasibility of liquid CO_2 cleaning of SSME hardware. The parameters selected form a subset of a much larger matrix of conditions that may be evaluated later to better define the CO_2 fluid cleaning process.

Soiling compositions were initially chosen to represent what has historically been the most stubborn deposits with TCE degreasing. A synthetic soiling mixture was derived from various contaminants

commonly encountered in SSME component processing. A357 aluminum specimens were electrical discharge machined (EDM) into coupons measuring approximately 1" x 1" x 0.1" to provide a consistently rough finish to represent one of the most difficult surfaces likely to be encountered for cleaning. Fluid test parameters were selected that represent the extreme capabilities of the equipment to yield a better understanding of the cleaning process and increase the likelihood of successfully demonstrating feasibility. Two temperatures, pressures, and agitation's that bracket the equipment capability were selected. Furthermore, in the interest of simplicity, only two cleaning cycle duration's were selected.

Cleaning evaluations will be conducted in four phases. In phase one cast A357 aluminum alloy coupons modified by wire EDM, soiled with the synthetic soiling mixture, were exposed to liquid and supercritical CO_2 at two different pressures per phase (60 bar / 100 bar and 75 bar / 100 bar, respectively), two different temperatures per phase (20° / 30° C. and 40° / 80° C., respectively), two different agitation parameters (150 rpm and 400 rpm), and two duration periods (10 minutes and 20 minutes). Cleaning effectiveness was determined gravimetrically.

The effect of component geometry will be evaluated by soiling or attaching soiled witness coupons to 5 - 10 SSME components in difficult to clean locations and exposing the hardware to the optimal cleaning cycle(s). Non-volatile residue (NVR) and particle size/distribution will be assessed relative to the standard TCE NVR process to confirm conformance to specification (MSFC-SPEC-164B) criteria. Weight change, volume change, hardness, and metallographic analyses will be performed to assess any deleterious effects to various substrate materials.

Preliminary feasibility testing of wire EDM, A357 aluminum coupons uniformly soiled by solvent evaporation of a soil mixture (12 grams Silicone Stopcock Grease, 11 grams Braycote Grease, 11 grams Safe Tap Lubricant, 11 grams DuoSeal Oil, 2.5 grams Silica Flour in 500 ml of CFC 113) indicated the dense phase carbon dioxide to be as effective a cleaning agent as TCE.

Table 1. Preliminary Results of CO_2 Cleaning

Solvent	Process	Soil Wt. (g)	Bake (°F)	Time (min.)	Removal (%)
TCE	*Vapor*	*0.062*	---	*20*	*92.9*
TCE	*Vapor*	*0.072*	*140 F*	*20*	*95.6*
TCE	*Vapor*	*0.065*	*180 F*	*20*	*90.2*
CO_2	*Liquid*	*0.096*	---	*10*	*96.3*
CO_2	*Liquid*	*0.099*	*180 F*	*10*	*98.4*

More rigorous screening tests were begun to determine the optimal cleaning parameters. These tests incorporated a more tenacious 25 milligram deposit of 70% Braycote 640 AC-MS grease and 30% Conoco HD grease that was dabbed on the coupons rather than uniformly dispersed. Braycote is a fluorocarbon grease with molybdenum disulfide. Conoco HD is a calcium grease.

Table 2. Cleaning Results of Grease Mixture

Cleaner	Temperature (°C)	Pressure (bar)	Time (min)	Agitation (rpm)	Removal (%)
CO_2	20	59	10	150	50.0
CO_2	20	59	10	400	55.6
CO_2	28	73	10	150	46.4
CO_2	28	73	10	400	47.6
CO_2	29	98	10	150	52.2
CO_2	28	99	10	400	56.4
CO_2	20	59	20	150	51.4
CO_2	20	58	20	400	56.2
CO_2	28	98	20	150	53.4
CO_2	28	98	20	400	57.0
Trichloroethylene	ambient	ambient	10	150*	99.6*
Trichloroethylene	ambient	ambient	20	150*	99.6*

* = Deposit dislodged, not dissolved

The maximum contaminant removal obtained in the liquid CO_2 phase evaluations was less than 60% irrespective of increased cycle duration's. The CO_2 solvent is apparently selectively extracting the more soluble Conoco grease, leaving the Braycote component on the surface. Cleaning efforts in the supercritical range have not yielded improved results.

Despite the fractionation problem, some useful data can be gleaned from the evaluations. Increased agitation, higher pressures, and lower temperatures seem to benefit contaminant removal for the Braycote/Conoco grease mixture. Future testing to remove the contaminant mixture will explore these regimes more thoroughly. The use of surfactants, co-solvents, and/or hot oil pretreatment is being investigated. Also, the precision cleaning evaluations will continue with other representative soils.

Precision Cleaning Verification

In accordance with MSFC-SPEC-164 P&W is presently using TCE as a rinsing solvent for performance of the cleanliness verification operation. To evaluate cleanliness 500 ml of TCE is rinsed over a component surface area of 0.1 square meters. The fluid is filtered through a 0.45 micron PTFE media and the surface is examined for particles. The maximum particle size permitted is 800 microns for liquid oxygen components and 400 microns for liquid hydrogen components. The filtered solvent is then evaporated and the non volatile residue (NVR) is quantified by gravimetric means. A maximum of 1 milligram is permitted. If the NVR is determined to be greater than 1 mg then the part(s) must be re-cleaned. Although most of the solvent can be recovered by distillation, company goals have necessitated the replacement of the TCE in the process. Alternate methods to validate the cleaning process are under investigation at this time. Potential techniques include verification with alternate solvents, with a water process, or if a CO_2 cleaning system is implemented, an integral cleaning/NVR method will be pursued. This last methodology would permit the verification to be performed in the cleaning system rather than subsequent to the cleaning process. Examples of analytical techniques that may be mated with the dense phase CO_2 cleaning system include: Supercritical fluid chromatography, total organic carbon by pyrolysis, mass detection by attenuation of a tapered element oscillating microbalance, and laser light-scattering particle counter.

Chromate Replacement

Several forms of hexavalent chromium are used in the manufacture of various turbopump components. Hard chromium plating, chromic acid anodizing, chromate sealing after sulfuric acid anodizing, and chromate wash primers are typical examples. The anodizing is used to prevent corrosion and to provide increased surface wear and abrasion resistance of aluminum alloys. Efforts have focused primarily on the chromic acid anodizing and the chromate seal after anodize. Design changes are underway which will replace the chromic acid anodize with sulfuric acid anodize.

Presently, a chromate seal has been specified to ensure sufficient corrosion resistance. To replace the chromate seal a nickel acetate seal has been evaluated. The seal was applied at 180°F for 10 minutes at a concentration of approximately 5%. Initial testing was on A357.0 aluminum alloy which was sulfuric acid anodized per AMS 2471. Three sealing mechanisms were evaluated: the standard chromate seal, a hot water seal, and the 5% nickel acetate seal. Table 3 summarizes the applications parameters for the three seal processes.

Table 3. Application Parameters for Anodizing Seals

SEALING MECHANISM	TEMPERATURE (°F)	TIME (min.)
Hot Water	190	15
Dichromate	195	20
Nickel Acetate	180	10

The sealing mechanisms were initially tested per ASTM B117 for 336 hours. All of the samples passed the salt spray test; however it was found that the dichromate seal was superior to both the nickel acetate and hot water seal, and that the nickel acetate seal was slightly superior to the hot water seal. A second alternative to replace the chromic acid anodize is a Teflon impregnated anodizing process, NITUFF.

High VOC Maskants

Conformal masking materials are used during chemical operations to protect surfaces from damage or alteration. Examples of the uses of maskants are to protect areas from being plated during electroplating (silver, nickel, chromium, and gold), to protect selected areas from chemical milling, and to protect identification marking and precision machined surfaces during acid etch inspection procedures.

Most masking materials have a very high solvent content, and the solvents typically used are toluene, xylenes, and perchloroethylene. These solvents are classified as hazardous air pollutants, are EPA 17 priority toxic materials, and will be subject to the upcoming Aerospace NESHAP. The NESHAP will significantly restrict solvent emissions for certain operations, one of which is chemical milling maskants. The solvent based maskants are typically applied by dipping or brushing and are cured by air drying (solvent evaporation).

Pratt & Whitney has qualified alternative masking materials which are effective in protecting metallic surfaces during plating, chemical milling, and etch inspection procedures, but contain very low amounts of VOC. The most widely used material, CAX-100-LA from Malek, has only 80 grams/liter of VOC content. This maskant, which is a water based compound, contains a small amount of toluene (approximately 4%), but conforms to NESHAP regulations for maskant composition. Parts to be coated with the water based maskants can be dipped, but are typically spray coated for better uniformity. Unlike the solvent based maskants the Malek material must be baked to correctly cure the material. The coating is dried at 120°F then cured in an oven following application for 120 minutes at 200°F. In addition to its

use in chemical immersion operations the maskant is an effective barrier for thermal spray coatings and is used widely for this purpose.

A second maskant approved for use on hardware is also manufactured by Malek. MBP-100, contains no hazardous solvents and has a VOC content of 20 grams/liter. P&W is now seeking to implement these materials at its supplier base for production of certain SSME HPOTP components. These maskants will yield both environmental and occupational health and safety improvements for the supplier base.

SUPERCRITICAL FLUID CLEANING OF OXYGEN SERVICE INSTRUMENTATION

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ABSTRACT

The Montreal Protocol incorporates a ban on the production of a number of chemicals that have historically been used for cleaning and degreasing operations. Bourdon tube pressure gauges for oxygen service are an example of a component that requires a high degree of cleanliness but is not adequately cleaned by conventional alternative solvents such as water-based formulations. Supercritical fluid cleaning appears to offer a solution to this problem. Simulated bourdon tubes were filled with 2190 TEP lubricant in order to represent a worst-case contamination scenario. Supercritical carbon dioxide ($SCCO_2$) was used to remove 97% of this material in a five minute cleaning cycle. Preliminary results are promising and further tests are underway to qualify this process for cleaning actual oxygen service gauges.

INTRODUCTION

Precision parts cleaning and degreasing are vital steps in many manufacturing and maintenance operations. For example, high levels of cleanliness are needed to prepare surfaces for subsequent operations such as coating, plating or final assembly. In addition, removal of residues from fluid systems is essential when these contaminants are incompatible with process fluids. Important examples that will be discussed in detail, below, are components of oxygen systems.

Currently, many crucial cleaning/degreasing operations require the use of chlorofluorocarbon solvents, most notably CFC 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and methyl chloroform (1,1,1- Trichloroethane). The EPA estimates that in 1993 approximately 170 million pounds of CFCs were used in the US for industrial cleaning operations (Seinfeld). Unfortunately, these chemicals are believed to participate in the catalytic destruction of stratospheric ozone. Under the Montreal convention, these and other Ozone Depleting Substances (ODSs) have been banned from production since December 31, 1995.

In many cases, aqueous (water based) cleaners have been substituted for ODS solvents. While this approach has met with considerable success, the physical and chemical properties of aqueous cleaners make them poor choices for certain parts cleaning problems. For example, the surface tension and wetting properties of water make it difficult for aqueous solutions to adequately penetrate small interstices, blind holes, or crevices. In addition, water can cause corrosion of many materials, resulting in the need for stringent rinsing and drying procedures to ensure the complete removal of residual moisture from sensitive components.

Although other solvents (such as TCE, terpenes, alcohols, ketones, HCFCs, and PFCs) have been used to replace CFCs, many of these substances are regulated as Hazardous Air Pollutants (HAPs) or Volatile Organic Compounds (VOCs). In addition, these chemicals often present health or flammability problems and may be targeted for phaseout.

There remains a need for an environmentally benign cleaning technology that is very effective at removing contaminants from parts, including those with complex geometries (e.g. blind holes, porous surfaces or small voids). Supercritical fluid cleaning has been proposed as a solution to this problem. The remainder of this report is a discussion of supercritical fluids and their applications as solvents, particularly for cleaning oxygen service pressure gauges.

SUPERCRITICAL FLUIDS

Many materials can exist in several different physical forms, including the solid, liquid, and vapor phases. The state of a pure material is governed solely by its temperature and pressure. A phase diagram is a graphical representation showing the interrelationships between these properties and the equilibrium state of a chemical species. Figure 1 is a phase diagram for carbon dioxide. At normal ambient temperatures, the stable form of CO_2 is either a liquid or a gas, depending on where the pressure lies relative to the vapor pressure curve, which separates the liquid and gaseous regions. Changes in temperature and/or pressure that take the species from one side of the line to the other result in a transformation from liquid to vapor or vice-versa. This causes sudden and discontinuous changes in the physical properties (e.g. density) of the fluid.

The vapor pressure curve ends at the critical point. When heated and compressed to temperatures and pressures above its critical point values (88 °F and 1070 psia, respectively), CO_2 forms a new phase, called a supercritical fluid. Changes in temperature and pressure within this region result in dramatic but continuous changes in fluid properties (Van Wylen and Sonntag). Supercritical fluids possess some of the properties of both gases and liquids. Like gases, supercritical fluids have very low viscosities and high diffusivities (LaGrega et. al.) and no surface tension. These factors endow supercritical fluids with exceptional penetrating power; Hoyer states that "Because of their favorable mass transport properties, supercritical solvents allow a more rapid approach to equilibrium, and they penetrate substrates more readily and deeper than do liquid solvents." Supercritical fluids have relatively high densities. The resulting concentration of intermolecular forces causes them to behave like liquids in terms of solvating power.

An important property of supercritical fluids is that at conditions near the critical point the density and viscosity change dramatically with only minor changes in temperature or pressure. Figure 2 shows the density of CO_2 as a function of reduced pressure and temperature. At the critical point temperature ($T_R = 1.0$) changing the reduced pressure by 10% (i.e. increasing P_R from 1.0 to 1.1) results in a 60% increase in density (ρ_R increases from 1.0 to 1.6). Since the solvent power of a supercritical fluid is related to its density, increasing operating pressures make supercritical fluids behave like more powerful solvents. This effect is illustrated by Figure 3, which shows the solubility of palmitic acid (a fatty acid) in supercritical CO_2 as a function of temperature and pressure. A sixfold increase in pressure results in a two order of magnitude increase in solubility.

The supercritical solvent phenomenon was first described in 1879 by Hannay and Hogarth, who determined the solubility of cobalt chloride in supercritical ethanol. Industrial use of supercritical fluids began in the 1950s (McHardy et. al.). Today, supercritical fluids are used in a number of analytical, production, environmental remediation, and cleaning processes.

Supercritical Fluid Chromatography (SFC) is a column chromatographic technique in which the mobile phase is a supercritical fluid instead of a gas or liquid. SFC can achieve higher efficiencies in shorter analysis times than liquid chromatography and can perform the separation of thermally labile molecules that cannot typically be studied using gas chromatography (Lee and Markides).

Supercritical Fluid Extraction (SFE) is a process in which a supercritical fluid is used to selectively remove specific chemicals from complex matrices. SFE is used as an analytical technique, for example in extracting hydrocarbons from a soil sample in order to perform total petroleum hydrocarbon tests. On a larger scale, supercritical fluids are used to recover essential oils from spices, to decaffeinate coffee, and to extract beer flavoring agents from hops (McHugh and Krukonis). As an indication of the growing importance of SFC and SFE processes, a 1992 review of this technology cites more than 400 journal articles published in the preceding two years (Chester, et. al).

SUPERCRITICAL CARBON DIOXIDE CLEANING

The use of supercritical fluids for parts cleaning has received considerable attention in the last several years. This technology is a natural outgrowth of SFE. The chief distinction between the two processes is the fact that the solute is removed from a surface rather than from within a three-dimensional substrate matrix.

Although a number of chemical species, including ethylene, ethane, propane and butane, have been successfully used in supercritical fluid processing applications (Gallagher-Wetmore, et. al.) carbon dioxide has emerged as the solvent of choice for cleaning processes. Factors which make CO_2 attractive for use in cleaning systems include:

CO_2 is nontoxic
Does not support combustion
Exhibits readily attainable critical parameters
Is commercially available in highly pure form
Is environmentally friendly

In addition, carbon dioxide has acceptable solvent properties. McHardy et. al. state that "At temperatures and pressures close to or above the critical point ... CO_2 possesses solvent characteristics equal to or better than CFCs. It is also inert, ozone-friendly, non-combustible, naturally occurring, inexpensive, and does not contribute to smog." A number of studies have investigated the solubilities of various materials in supercritical carbon dioxide. Francis tabulated the solubilities of 261 species, and presented triangular phase diagrams for 464 ternary systems. Although his data applies to liquid CO_2, they can probably be extended, at least in a qualitative sense, into the supercritical regime. More recently, Bartle et. al. presented solubility as a function of pressure and temperature for every low volatility compound studied as of 1989.

Since CO_2 is essentially nonpolar, it is relatively ineffective at dissolving polar contaminants, including fingerprints, rosin flux, particulates or metal salts (Farncomb and Nauflett; Messer and Rancourt). In spite of its lack of affinity for polar molecules, Taylor indicates that "In the area of cleaning and degreasing materials, pure CO_2 may suffice for many applications since the components to be removed are not highly polar" and that high solubility is not necessarily required for supercritical fluid cleaning to be effective. In addition, removal of surface oils and greases can help loosen and dislodge trapped particulates, even though these materials are not directly affected by supercritical CO_2. A means of enhancing the solvating power of $SCCO_2$ is the addition of a miscible polar solvent to the carbon dioxide. These additives are referred to as modifiers, cosolvents or entrainers. Alcohols are the most commonly used cosolvents.

Although carbon dioxide is considered to be a "greenhouse gas" and a contributor to global warming, the use of $SCCO_2$ for cleaning adds no net CO_2 to the global environment. The CO_2 sold for commercial uses is recovered from production processes (i.e. fermentation broths). This carbon dioxide is therefore already "part of the ecological envelope" and that supercritical CO_2 processes "are just borrowing (CO_2), not creating it" (Gallagher-Wetmore, et. al.).

Figure 4 is a simplified schematic that shows the major features of a typical $SCCO_2$ cleaning system. In this apparatus, room temperature liquid CO_2 is pumped into a heated extractor vessel containing the items to be cleaned. The temperature and pressure in this vessel are above the critical point; the resulting supercritical fluid dissolves surface contamination. In some cases, an impeller is used to agitate the fluid, increasing its cleaning effectiveness.

The supercritical fluid, carrying dissolved contaminants, flows out of the extractor vessel and through a pressure reducing valve or restrictor. As the pressure drops, the CO_2 flashes into a gas, causing the contaminants to fall out of solution and collect in a concentrated form in the bottom of the separator vessel. The gaseous CO_2 can then be cooled, condensed to a liquid, and recycled.

A number of laboratory, pilot scale, and low-rate production tests of the supercritical CO_2 cleaning process have been reported in the literature. In addition to cleaning coupon type samples (Williams and Bongianni; Phelps, et. al.; Gallagher-Wetmore, et. al.), a number of investigators have reported on the cleaning of actual parts. Components cleaned in these studies include disk drive parts (Purtell and Rothman), motor components (McHardy et. al.), slip ring assemblies (Reed), ball

bearings (Farncomb and Nauflett), navigation instruments (McHardy et. al.; Gallagher-Wetmore; McGovern et. al.), various electronic components and assemblies (Farncomb and Nauflett; McHardy et. al.), stainless steel bottles (Bagaasen) and oily solid waste (Adkins, et. al.).

Some of the factors that must be considered in order to determine if $SCCO_2$ cleaning is suitable for a particular part are discussed below.

Current Cleaning Practices. $SCCO_2$ cleaning is indicated for parts that are currently cleaned with solvents that are in limited supply, such as Freon-113, or with hazardous solvents, or for which no acceptable cleaning processes exist. Components that require a great deal of time and effort to clean may also be strong candidates for this process.

Part Size. Because the process occurs at elevated pressures (1100 psi or greater), parts that can fit within a moderately sized pressure vessel are the best candidates for $SCCO_2$ cleaning. This technology may also be suited for larger parts that are designed to withstand high pressures (such as gas cylinders). This type of part can be cleaned simply by connecting it to an external manifold on a $SCCO_2$ system as shown in Figure 4.

Part Geometry. Components that incorporate blind holes or other surface features that can prevent aqueous cleaning solutions from effective contact with contaminants may be strong candidates for $SCCO_2$ cleaning.

Type(s) of Contaminant(s). Although $SCCO_2$ is most effective at removing nonpolar contaminants such as greases or oils, polar soils such as fingerprints or soldering flux can be dissolved by introducing a small quantity of a cosolvent such as methanol. In some cases, $SCCO_2$ is effective as one component of a multistage cleaning process.

Materials of Construction. $SCCO_2$ cleaning is well suited to parts that are sensitive to corrosion, since carbon dioxide is compatible with most common metals and evaporates completely, leaving no residue. As with many traditional solvents, $SCCO_2$ can swell certain elastomers and damage some polymeric materials. Cosolvents may interact with metals under some conditions (Russick et. al.).

Because contaminants are collected in an essentially pure form, it may be beneficial to use the $SCCO_2$ process if a particular contaminant has a high intrinsic value and can be recycled.

Degree of Cleanliness Required. Although $SCCO_2$ can clean components to very exacting standards (such as the oxygen pressure gauges discussed below) it may be a cost-effective solution even for routine cleaning problems. In some cases, lower pressure and temperature processes using liquid, rather than supercritical, carbon dioxide may be more efficient.

Techniques developed for analytical processes, such as $SCCO_2$ chromatography, can be adapted to measure contaminant levels in the process fluid. This makes $SCCO_2$ useful for applications that require monitoring and documentation of cleanliness.

OXYGEN INSTRUMENTATION

Components of oxygen systems must be cleaned to very stringent standards in order to ensure safe operation. Even traces of oils, greases, or particulates can react with high pressure oxygen gas or liquid oxygen and lead to catastrophic fires or explosions. Aqueous cleaners such as Tribasic Sodium Phosphate (TSP) or the new Naval Oxygen Cleaner (NOC) formulation have been used as an alternative to Freon-113 in oxygen piping systems. Unfortunately, these water-based solutions are not acceptable for cleaning instrumentation such as pressure transducers or gauges (NAVSEA 1994, 1995).

Figure 5 shows a typical pressure gauge, which incorporates a curved bourdon tube. This tube deflects under internal pressure, driving an indicator needle through a mechanical linkage. Because the bourdon tube is flattened and sealed at one end, it is difficult for an aqueous cleaner, with its relatively high viscosity and surface tension, to penetrate into the recesses of the tube to remove contaminants. In addition, it is impossible to ensure that all of the water and cleaner residues are removed subsequent to cleaning operations. For these reasons, shipyard and depot level oxygen gauge cleaning operations

still utilize Freon-113, which is in increasingly short supply because of the production ban implemented as part of the Montreal Protocol.

Supercritical carbon dioxide cleaning appears to be a viable solution to these problems. Because of its exceptional penetrating power, $SCCO_2$ should be able to reach contaminants throughout the bourdon tube, even in "direct drive" gauges, which have bourdon tubes as small as 1/8" in diameter. Since residual CO_2 evaporates completely to form an inert gas which can easily be flushed from the gauge, there is no concern about cleaner residue remaining behind to contaminate or react with the oxygen gas.

A survey was conducted to determine the distribution of gauge types cleaned during routine maintenance procedures at Naval Shipyards. It was discovered that approximately 40% of these gauges were rated for pressures below 1500 psi. While high pressure gauges can be cleaned in a manifold configuration (see Figure 4) those with lower pressure ratings would have to be immersed completely in the supercritical medium. Fortunately, the results of the survey indicated that essentially all of the gauges to be cleaned in an immersion configuration were relatively small units (dial sizes of 4.5" or less). This would allow a moderately sized extractor vessel to be used.

Because cleaning is the last step in gauge maintenance (following inspection and calibration), it is necessary that the gauge mechanism be fully assembled during the cleaning process. This requires that the gauge face be immersed in the supercritical medium. A series of material compatibility tests were performed in order to ensure that gauge face paint and markings were compatible with supercritical carbon dioxide. Test coupons were cut from six gauge faces and installed in a 256-ml Berty autoclave at Pacific Northwest National Laboratory (PNNL). The coupons were exposed for two hours to a 50 ml/minute flow of $SCCO_2$ at 200 bar (2900 psia) and 100 °C (212 °F). No deleterious effects were noted.

Based on information from shipyard personnel, a common lubricant, 2190 TEP oil, was selected as a test contaminant. A high pressure cell with sapphire view ports was used to evaluate the solubility of this material. It was determined that 2190 TEP is only slightly soluble in $SCCO_2$, and then only at pressures greater than 2600 psi.

For the first series of feasibility tests, simulated bourdon tubes were constructed from a 15 cm (5.9") lengths of 1/16" OD x 1/64" nominal wall thickness (.031" ID) stainless steel tubing. These tubes were completely filled with the test contaminant using a syringe, then capped on one end with a compression fitting. These test items were mounted on the PNNL bench scale $SCCO_2$ system as shown in Figure 6. Note that although the carbon dioxide in the manifold line was heated, the tubes were not.

The simulated gauges were treated with $SCCO_2$ at a variety of pressure/ temperature/ flowrate conditions. The most effective combination proved to be a 230 °C (450 °F) manifold temperature, with pressure cycled repeatedly between 2000 and 3000 psi. Approximately 97% of the test contaminant was removed in a five minute cleaning cycle (cleanliness levels were determined gravimetrically). When the tubes were detached from the system, it was found that the bulk of the remaining contaminant was concentrated near the open end of the tube.

As anticipated, the pressure cycle and temperature differential along the length of the simulated bourdon tube resulted in a significant density gradient. The solubility of the test contaminant was higher at the blind end, resulting in a net flux of contaminant out of the tube. Thus, $SCCO_2$ cleaning was effective at removing this relatively insoluble material.

The next phase of this investigation will follow a test protocol developed by the NASA White Sands Test Facility (Biesinger and Beeson) that has been accepted by the Naval Sea Systems Command. This procedure uses a standard mixture of five contaminants, including synthetic and petroleum based hydraulic fluids, a lubricating oil, a gauge calibration fluid, and a perfluoralkylether grease. To date, solubility tests have been performed on each individual contaminant and indicate that all five are quite soluble in $SCCO_2$, with the exception of the Teflon fraction of the PFPE grease.

CONCLUSIONS AND FUTURE WORK

The results of these preliminary tests indicate that $SCCO_2$ cleaning promises to be an effective method for cleaning bourdon tube pressure gauges for oxygen service. The conditions of this test (an extremely narrow bore tubing completely filled with a marginally soluble contaminant) represent a worst case scenario. Actual conditions should be less severe, since bourdon tubes usually have a much larger inside diameter and are contaminated to a lesser extent.

In the near future, a representative series of bourdon tubes will be doped with contaminants and cleaned, following the NASA protocol discussed above. Gauges will be treated in both the manifold and immersion cleaning processes. Because it will not be possible to impart a strong density gradient across a gauge immersed in the $SCCO_2$ cleaning medium, the cleaning power of the supercritical solvent will be enhanced by fluid dynamic effects.

Cleaning of additional types of oxygen system instrumentation, including bellows-type differential pressure gauges and electronic pressure transducers, will be demonstrated at a later date. Techniques for quantifying cleaning results for quality control and validation purposes are being developed.

$SCCO_2$ cleaning appears to offer a valid long term solution to a number of otherwise intractable parts cleaning problems. The Applied Research Laboratory has initiated a search for additional aviation system components that may benefit from the application of this technology.

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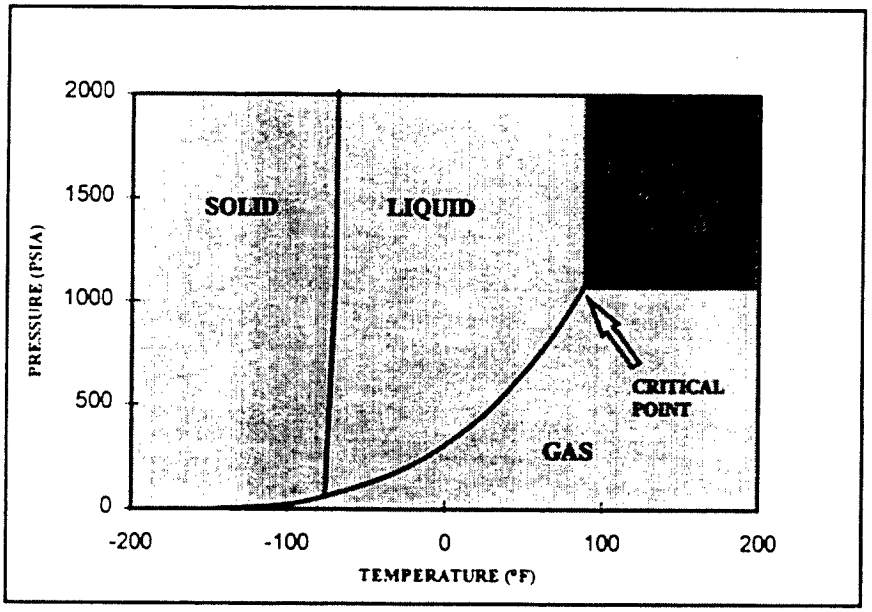

Figure 1: Carbon Dioxide Phase Diagram

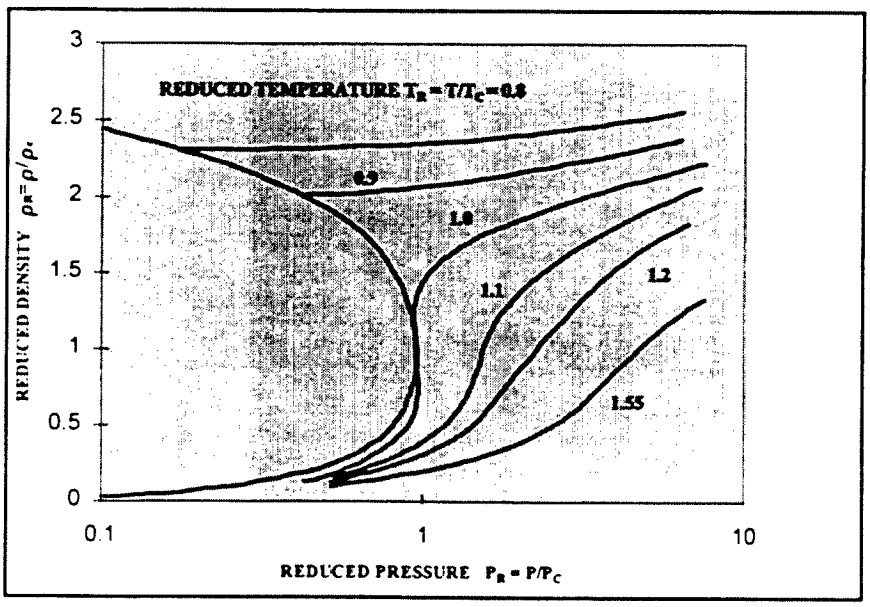

Figure 2: Generalized Density Chart (McHugh and Krukonis)

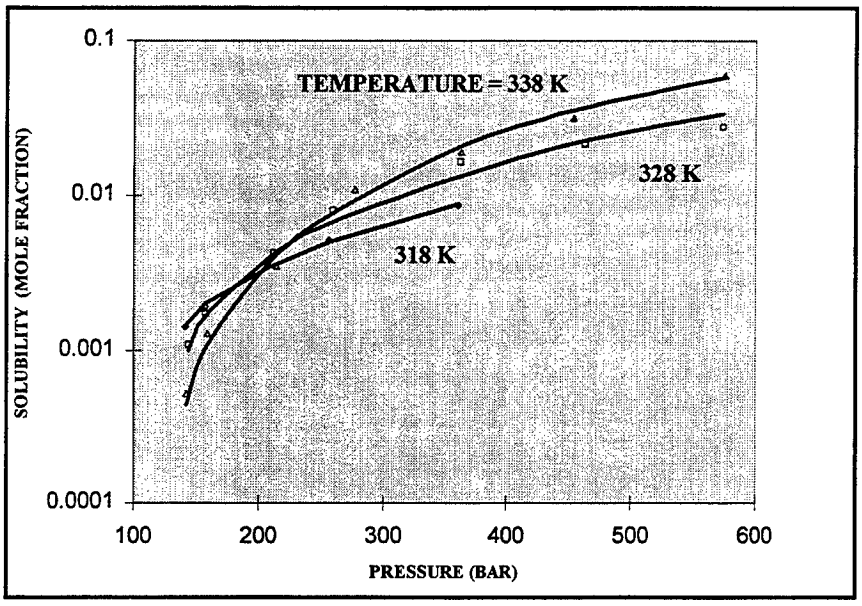

Figure 3: Solubility of Palmitic Acid in $SCCO_2$ (Kramer and Thodos)

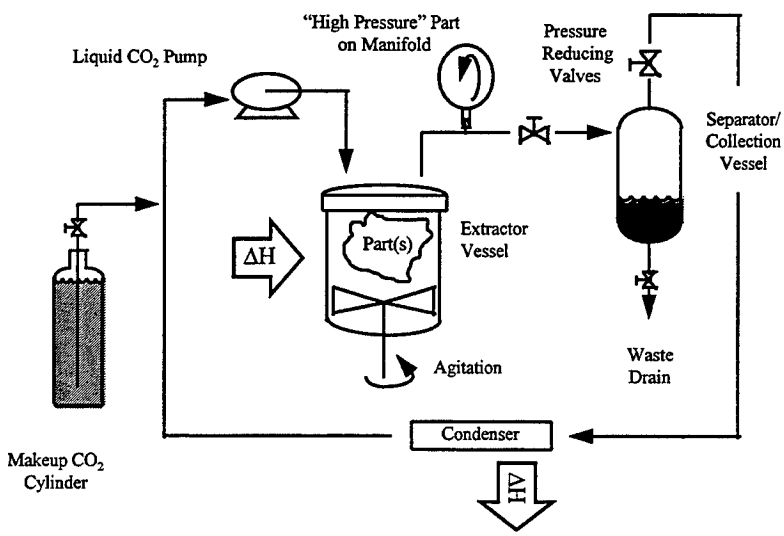

Figure 4: Simplified Schematic of $SCCO_2$ Cleaning System

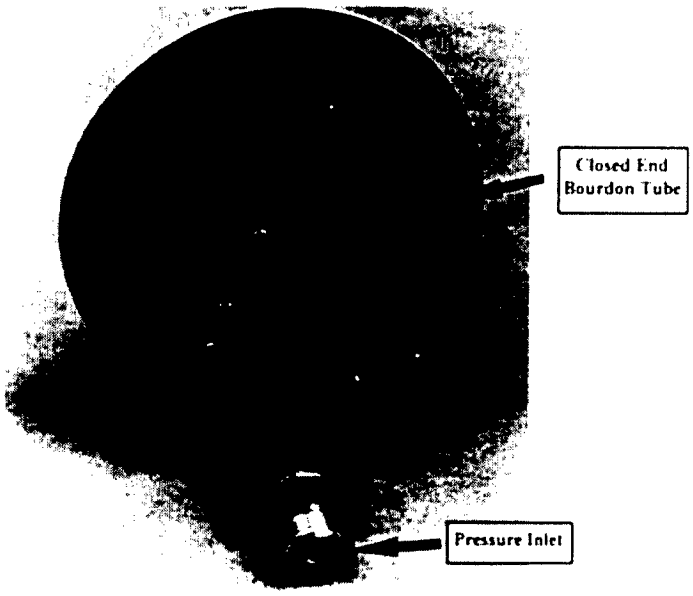

Figure 5: Typical Bourdon Tube Pressure Gauge

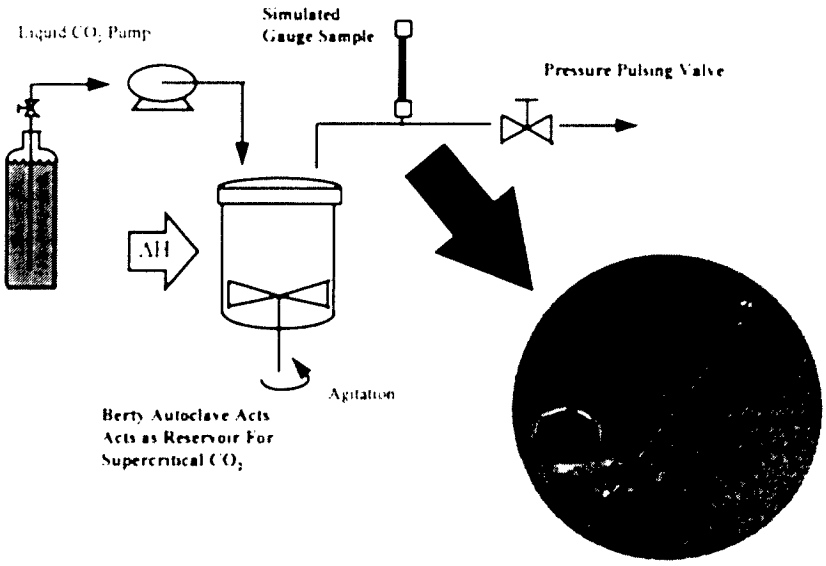

Figure 6: Schematic for Gauge Cleaning Feasibility Studies

REPLACEMENT MATERIALS AND PROCESSES—I

NEW TECHNOLOGIES AND CLEANING PERFORMANCE BASED ON VOLATILE METHYL SILOXANES.

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ABSTRACT

Linear volatile Methyl siloxanes (VMS) are a new class of solvents that are VOC exempt, non ozone depleting, SNAP approved, are not hazardous air pollutants, and have negligible global warming potential due to their less than 30 day atmospheric lifetimes. Based on their favorable environmental qualities, linear VMS are the #1 preferred cleaning materials for substrate cleaning, precision cleaning, and electronics cleaning by the California South Coast Air Quality Management District. They have negligible odor, very low viscosity, low surface tension, good toxicology properties, and 100 % evaporation for effective cleaning, drying, and rinsing. Ultra high purity versions of these products have been commercialized that have very low nonvolatile residue, making them suitable for operations involving secondary bonding and painting. Straight VMS will clean non polar contaminates including silicone residue, greases, and oils. These materials will also soften, greatly swell and lift many cured silicones, allowing easy removal, as well as removing any remaining residue. This allows bonding of organic adhesives and paints to surfaces previously covered by silicone. New azeotrope formulations have been developed which enable the cleaning of rosin flux from circuit boards, and liquid crystal display residue, and optics cleaning.

1. INTRODUCTION

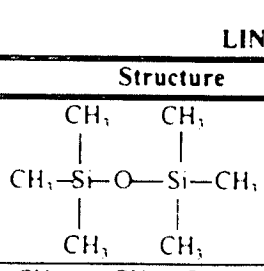
Many materials and process engineers are scurrying to find alternatives to replace the solvents and cleaners being banned by changing government regulations. No direct drop in alternatives have been found for previous industry-standard chlorinated and fluorinated solvents. CFCs, which are being phased out in accordance with the Montreal Protocol, were as close to ideal solvents as possible. They were inexpensive, non flammable, non toxic, and effective cleaners. There are no replacements that offer all these advantages. Even more frustrating, some of the initial cleaners that the industry turned to, such as HCFCs, were also banned from cleaning operations after a very short time of usage.

Since all of the solvent alternatives have drawbacks or limitations, it is important for those looking for new cleaning procedures and materials to be familiar with many of the alternatives, so they can pick the best for their application. This paper will highlight the pros and cons of a new class of solvents that can be used as cleaners and carriers based on ultra pure low molecular weight linear volatile methyl siloxanes (VMS). Table 1 shows some of the pros and cons of linear VMS. Table 2 shows the structure and nomenclature for commercial linear VMS products.

Table 1
PROS AND CONS OF LINEAR VMS

Pros	Cons
non ozone depleting	Low-moderate flashpoint
non VOC, not a HAP	moderate cost
negligible global warmer	mild solvency
good toxicological profile	
very low odor	
readily available at moderate cost	
fast evaporation without residue	
tailored evaporation rate	
compatible with most materials	
mild solvency which can be enhanced with azeotropes	
#1 preferred cleaner by the California South Coast Air Quality Management District	

Table 2
LINEAR VMS STRUCTURES AND NOMENCLATURE

Structure	Chemical Name	Dow Corning Trade Name
	disiloxane, hexamethyl	OS-10
	trisiloxane, octamethyl	OS-20
	tetrasiloxane, decamethyl	OS-30

2.0 WHAT ABOUT SILICONE CONTAMINATION?

Silicones have very low surface tension, so silicone contamination can greatly affect secondary bonding and painting operations. The idea of using a silicone based cleaner may seem "counter intuitive" at best, but in actuality this low surface tension can be used to the benefit of the cleaning performance of VMS, enabling it to thoroughly wet out surfaces, displacing particles, contaminates, and water for drying applications. The secret is to make the linear VMS at such a high purity that it will evaporate completely, without leaving any residue behind that could affect adhesion. It is imperative that special test procedures, and handling precautions be established to assure the silicones remain pure during distillation, storage, and packaging. If these precautions are not taken, then a residue ranging from several hundreds to thousands of parts per million can be detected, which can cause painting and adhesion problems.

To eliminate some of the confusion, here are some key definitions for terms used in this paper:

Silicone polymers: high molecular weight polydimethyl siloxane (PDMS) polymers used as mold release agents, lubricants, greases, and sealants. These materials can leave a slippery residue that is difficult to remove, affecting painting and adhesion.

Volatile methyl siloxane (VMS) - a general class of materials based on very volatile, low molecular weight polydimethyl siloxane. Approved by the United States of America Environmental Protection Agency (EPA) as substitute for ozone depleting substances under a program known as SNAP (Significant New Alternative Policy), also granted VOC exception status from the EPA.

OS Fluids: Product name for a highly distilled, ultra pure form of linear VMS and azeotropes manufactured by Dow Corning. These represent the simplest linear permethylated siloxane molecules, including the disiloxane, trisiloxane, tetrasiloxane, and an azeotrope of disiloxane and glycol ether. Dow Corning is marketing these materials as OS-10, OS-20, OS-30, and OS-120 respectively. Each of these products is distilled to 99.9% minimum of a single component. Products are tested and certified to <1 ppm silicone residue for every lot. OS-10, OS-120, and OS-20 are flammable. OS-30 has a flash point in the combustible range.

Various surface analysis and performance tests have been conducted to assure the OS fluids do not affect adhesion or leave a residue. Sensitive surface analysis techniques, including ESCA and contact angle, were used to examine metal surfaces after the OS Fluids had been allowed to evaporate from them. No evidence of silicone residue was found in either experiment, as compared to untreated controls. In a second study, paintability was checked after steel and aluminum panels had been cleaned with OS fluids. Standard coating rating tests, including appearance and cross-hatch adhesion (ASTM D 3359 - 78 B), were made and found to be at least as good as panels cleaned with toluene.

A quantifiable test was done to assure that the Dow Corning OS fluids do not leave any residue that may affect adhesive bonding operations. Clean metal panels were dipped in OS fluids and allowed to air dry. Lap shear specimens were then made from the OS exposed panels with 3-M 2216 gray epoxy, 3 M 8101 Urethane, and Bondini "Super Glue" adhesives. As demonstrated in Table 3, in all cases the panels exposed to OS fluids had as good or better adhesion than the clean control panels, which were wiped with isopropyl alcohol. This shows that not only do ultra pure versions of linear VMS not hurt adhesion, but they actual prepare the surface for improved adhesion.

Table 3

LAP SHEAR ADHESION TESTING WITH OS FLUIDS

Sample	3-M 2216 Epoxy	3-M 8101 Urethane	Bondini2 Super Glue
Control	1213 PSI	344 PSI	475 PSI ± 50
OS-10	1233 PSI ± 20	494 PSI ± 20	581 PSI
OS-20	1440 PSI ± 50	383 PSI	640 PSI
OS-30	1478 PSI ± 100	395 PSI +	507 PSI

Lap shears are based upon soaking the substrate in the OS Fluids, then allowing them to air dry

The control samples were cleaned with IPA and wiped

3. CLEANING CAPABILITIES

With the exception of their flash points, the physical properties of VMS are very favorable for precision cleaning. Like CFCs, surface tensions and viscosity's are very low, providing rapid wetting, even into tiny crevices and complex geometry. These properties also lead to rapid draining and drying, especially for disiloxane.

VMS solvents are not aggressive, with low Kauri-Butanol and solubility parameter values. Their solubility characteristics match non-polar materials best, such as mineral and silicone oils. Their relative mildness results in very few materials compatibility issues, as is discussed in more detail elsewhere in this paper. Table 4 shows a comparison of linear VMS and a VMS azeotrope with CFC 113 on key properties required in precision cleaning.

Table 4

PHYSICAL PROPERTIES (25C) FAVORABLE FOR PRECISION CLEANING

	Disiloxane (OS-10)	(OS-120)	Trisiloxane (OS-20)	Tetrasiloxane (OS-30)	CFC-113
Viscosity (cp)	0.49	0.49	0.82	1.3	0.68
Surface Tension (dyne/cm)	15.2	16.3	16.5	17.3	17.3
Density (g/ml)	0.76	0.77	0.82	0.85	1.57
Solubility Parameter $(MPa)^{1/2}$	12.7	13.2	12.1	12.1	14.7
Kauri-Butanol Value	16.6	--	15.1	13.4	31

Given the mild nature of VMS in terms of compatibility, we find that they are not aggressive solvents. However, for non-polar soils such as light oils, and of course silicones, VMS are very effective. Simple coupon studies, analyzed gravimetrically, show complete removal of light oils. These trials were done by gently shaking at room temperature for three minutes. For more viscous soils, such as thick fluids and greases, linear VMS are still a good match in terms of solubility, but either more vigorous agitation, increased temperature, or longer cleaning times would be needed over the conditions used here to completely remove the soils. Table 5 shows the cleaning performance of linear VMS for various contaminants.

Table 5

CLEANING PERFORMANCE			
Percent Soil Removed from Steel Coupons			
	OS-10	OS-20	OS-30
Motor Oil	99	100	99
Quenching Oil	100	100	100
Cutting Oil	100	100	100
Gyroscope Fill Fluids*	100	100	100
200® Fluid, 350 cst	100	100	100
200® Fluid, 100,000 cst	94	88	89
Grease HD #2	84	75	76
DC 550 Fluid	99	99	99
DC 710 Fluid	97	96	100
Uncured Silicone Conformal Coating	100	99	99

*Results from 4 fluids used at Newark AFB

Under funding from the US Air Force Defense Construction Supply Center, Bob Kaiser from Entropic Systems has evaluated the performance of VMS as particle removers, in his Entroclean™ ultrasonic cleaning system in which parts are cleaned and the fluid is monitored continuously for particle concentration. These studies showed that trisiloxane and tetrasiloxane were more effective than disiloxane for displacing particles, and were better than all other candidates he tried (including CFC-113, HFC-43-10, PF5070 and IPA), with the exception of a mixture of fluorocarbon surfactant in PFC, which removed the most particles (Reference 1). See Table 6 for the summary of the particle removal data.

Table 6
DOW CORNING® OS FLUIDS
PARTICLE REMOVAL DATA

Summary of Data for Stainless Steel Nuts & Bolts Cleaning Tests
(Particles greater than 2um removed in first 15 minutes ultrasonic cleaning)

Cleaning Solution	Ultrasonic Power (watts)	Liquid Flow Rate (ml/min)	Particles Removed
CFC-113	15	300	160,000
IPA	15	300	140,000
HPC-43-10 mee	15	300	180,000
PF 5070	240	300	300,000
PF 5070 + surf.	60	300	335,000
		900	435,000
OS-10	60	30	250,000
	240	30	350,000
OS-20	60	30	360,000
OS-30	60	30	400,000

Test pieces: 2 each 1/4 x 20 x 1/2 inch long nut & bolt

An azeotrope of OS-10 and glycol ether (OS-120) has been patented and commercialized because polar contaminates, such as rosin flux are not effectively cleaned with pure VMS. An azeotrope based on OS-20 and glycol ether has also been developed and patented. Work is underway to develop additional azeotropic blends of OS fluids with organic cosolvents for use in cleaning polar contaminates.

OS-120 has been shown to effectively remove rosin flux and some cured silicone conformal coatings from circuit boards without harming the board or its components. By immersing a circuit board coated with Dow Corning(R) 3-1753 Conformal Coating into OS-120, the coating will begin to lift from the board in less than a minute. After 10 minutes to one hour, the coating will be loose enough over the entire board to be blown clean with an air hose.

MACHINE CLEANING:

Processes using volatile methyl siloxanes require designs which are safe for flammable solvents. One approach is pneumatically controlled machines, which require no electrical components. Air driven pumps are used to circulate the cleaning fluid, and the compressed gas supply also can be directed to the final stage to speed the drying step. Depending on the parts and soils involved, separate cleaning and rinsing chambers, plus a drying section can be used. When using OS-10 or OS-20, no cosolvents or additional rinsing or drying agents is necessary, since these dry completely, spot free at room temperature. One example of this equipment is the Jet-Clean machines from Martin Marietta, which are being marketed and are available for demonstration through Micro Care. Micro Care also has OS-120 under the name Vericlean in pressurized cans equipped with trigger grips and brushes.

A second process which has been demonstrated for OS-30 is to convert a vapor degreaser to a vat cleaner. By allowing heating to no more than 45°C, the vapor pressure is maintained below 25% of the LEL for this product. There are vapor phase degreasers which are engineered for safe operation with flammable chemistries, most notably the S&K IG-200. S&K has successfully demonstrated the use of OS-10 in this machine in the vapor phase degreasing mode.

Similarly, a multi-tank machine designed for flammables is a good choice for the OS Fluids. One demonstration in the Forward Technologies A series machine, using three tanks plus a drying region, resulted in cleaning silicone oils from metal parts to a degree of cleanliness ten times better than the customer's spec. The process consisted of a 70°C wash in a tank with ultrasonics, a rinse by immersion in 40°C fluid, and a final rinse in the condensing vapor region of a boil sump. FTI designs the machine so that the dirtiest fluid moves to the boil sump, which produces pure OS-10 vapor that cascades into the rinse tank after condensing. The rinse in turn overflows to the wash tank, thus maintaining a process in which the parts see increasingly clean solvent as they are moved from tank to tank.

The initial cost of VMS Fluids is higher than for some alternative chemistries. However, the total operating cost for our customers is very competitive, since they are able to reuse these fluids due to their ease of distillation, whether operated as part of the cleaning process, or off-line in a distillation central unit. The use of adsorbent beds, desiccants, and filters also are effective in returning spent OS fluids to fresh cleaning quality.

4.0 MATERIALS COMPATIBILITY

As stated previously, VMS solvents are relatively mild, and thus are safe for use with most common materials of construction. We have conducted compatibility testing using an approach similar to the protocol described by the National Center of Manufacturing Sciences, who have created a computerized data base of compatibility data after testing of seven ozone-depleting chemical alternatives. Incidentally, this group plans testing of six additional solvents, including Dow Corning's OS-30.

The Dow Corning program looked at 16 plastics and 10 elastomers. The procedure is to suspend 1" x 2" specimens in the solvent for three hours at 50°C. For disiloxane, exposures were also done at reflux (100°C). Weight, volume, and appearance changes were negligible for each of the plastics listed in Table 7. In the case of acrylic and polycarbonate, which are susceptible to crazing, no change in optical properties was observed after immersion in linear VMS, using a colorimeter. The compatibility with acrylic and polycarbonate, even at 100°C, is especially noteworthy, since these materials are quite susceptible to this problem with many solvents.

Table 8 shows the elastomers tested where durometer hardness plus weight and volume changes were measured after exposure, and the OS fluids totally evaporated. The Vitons and Hypalon are essentially unaffected, even after refluxing disiloxane. Those listed in the second category are not swelled after exposure by VMS solvents, but we find these solvents are effective in removing extractables, such as plasticizers and other additives. Hardness values are typically changed a few percent in these cases.

VMS solvents will swell some low consistency silicone sealants, neoprene rubber and natural rubber. Once the solvent has been dried from the elastomer, its properties return to normal except that some non-crosslinked species are apparently extracted. Due to the large degree of swell, these two materials should not be exposed to linear VMS unless such swelling is shown to be of no consequence in the application.

Table 7

MATERIALS COMPATIBILITY		
• Plastics linear VMS are compatible with:		
ABS	Nylon	Polyethylene
Acetal	Polytetrafluoroethylene	Polyethylene Terephthalate
Acrylic	Polyvinylidenefluoride	Polypropylene
Chlorinated PVC	Polycarbonate	Polystyrene
Epoxy	Polyetherimide	Polysulphone
Ionomer	Polyvinylchloride	

Table 8

MATERIALS COMPATIBILITY (continued)	
• Elastomers - Immersion on linear VMS at 50°C produced following:	
Little or No (<2%)	Fluoroelastomers (Viton A & Chlorosulfonated Polyethylene)
Slight Change: (2-5%)	high consistency polydimethylsiloxane rubber Fluorosilicone Ethylene-Propylene Terpolymer Isobutylene-Isoprene Acrylonitrile-Butadiene (Buna)
Not (>5%)	low consistency silicones, Natural rubber Polychloroprene

A compatibility study funded by the US Air Force, conducted at Battelle Institute, was recently completed. It was designed to study the effects of linear VMS on metals and adhesive bond integrity. 1,1,1 trichloroethane was used as the control, and linear VMS were concluded to result in no effects greater than those of the control for eight different adhesives and five metals commonly used in aerospace inertial guidance assemblies. (Reference 2)

5. ENVIRONMENTAL AND TOXICITY PROPERTIES

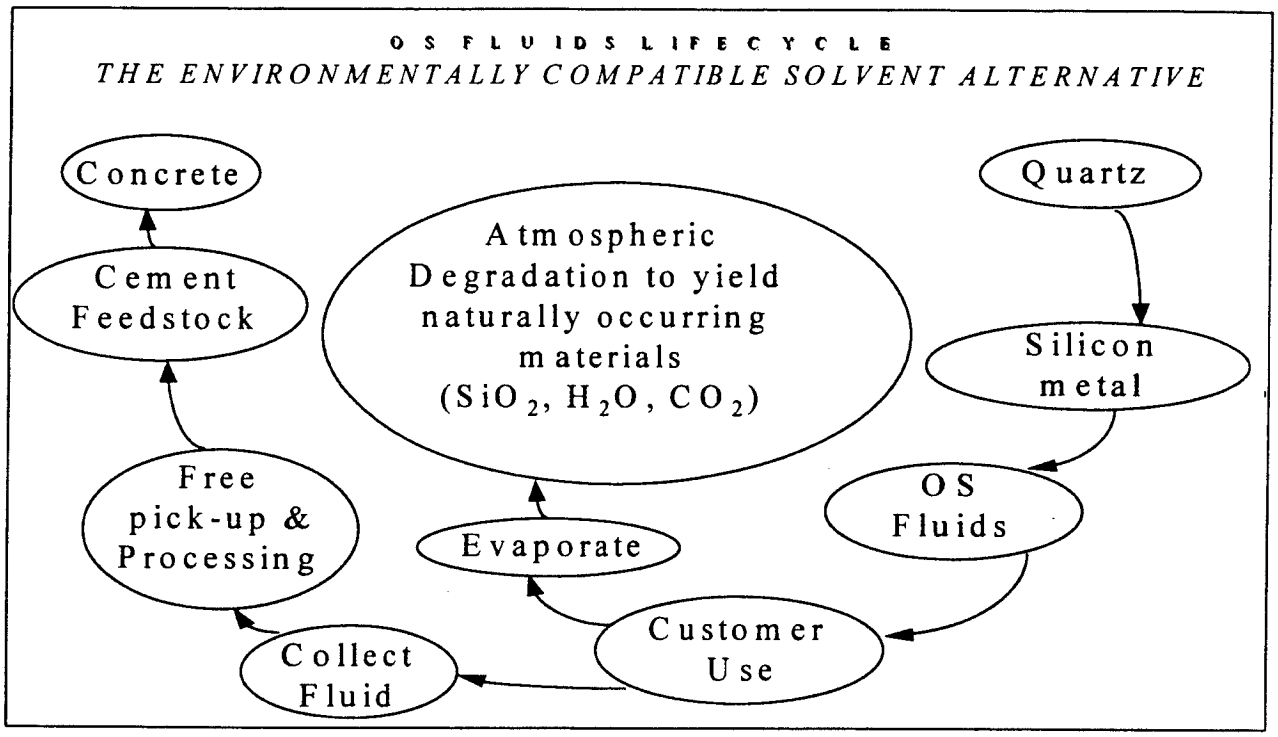
In early 1994 the EPA granted the volatile methyl siloxanes approval under the SNAP program as alternatives to ozone depleting solvents for precision cleaning (Reference 4). Additionally, VMS are not regulated as Hazardous Air Pollutants (HAPs) nor controlled under NESHAP requirements. In addition, they are not controlled by the Clean Air Act National Ambient Air Quality Standards.

Studies carried out for Dow Corning by the Statewide Air Pollution Research Center at the State University of California at Riverside were cited in a petition to EPA to exempt VMS materials from being regulated as VOCs. This exemption was granted in late 1994. Since VOCs are regulated at the state and regional levels, we are now working with these agencies to implement the federal exemption. As of June 1, 1996, 40 states have implemented the VOC exemption, including California, and none have turned it down.

VMS chemicals exhibit unique behavior in the atmosphere. It is rare that a chemical breaks down rapidly in the atmosphere, but does not participate in the free radical chemistry leading to ozone formation, which is the main cause of lower atmosphere smog. The siloxane molecule has a lifetime of from 10 to 30 days in the atmosphere. A series of chemical reactions occur in which methyl groups are replaced by hydroxyls, with the ultimate degradation products being CO_2, water, and water dissolved silica, which of course are abundant, naturally occurring compounds. The environmental lifecycle of OS fluids is shown in Figure 1. Notice that Dow Corning offers a free recycling program for the OS fluids, where drum quantities of material will be picked up free of charge and used as feedstock for cement kilns.

To summarize the environmental aspects, VMS are not ozone depleters, are not VOCs, and by virtue of their conversion to CO_2, water and silica, have negligible contribution to global warming (CO_2 <2). They are truly environmentally friendly, and can be selected for cleaning processes with the assurance that they will be environmentally and regulatory acceptable for years to come. In fact, the California South Coast Air Quality Management District has selected linear VMS as their #1 preferred cleaner for precision cleaning and substrate cleaning, second only to no-clean solder flux for electronics cleaning in their January 11, 1996 report for Ozone Depleting Compounds Replacement Guidelines (Reference 5).

Figure 1



VMS materials are low in toxicity as evidenced by results of acute oral, inhalation and dermal exposures; subchronic oral and inhalation studies including a recently completed 90 day study on OS-10; and tissue culture biocompatibility and genotoxicity evaluations. In the acute studies, no adverse effects were observed even at the maximum achievable doses in laboratory animals. Contact of the fluid with eyes may result in temporary eye discomfort. Subchronic oral and inhalation studies did not reveal any toxicological responses significant to human health.

Based on the recently completed 90 day study, Dow Corning's toxicologists and industrial hygienists have set an internal Industrial Hygiene Guideline (IHG) at 200 ppm for OS-10, OS-20, and OS-30. This is defined as the maximum average exposure level to which workers may be exposed over an eight hour work day. Additional testing is being done on OS-120, the azeotrope of 91% OS-10 and 9% glycol ether. The glycol ether has an IHG of 100 ppm. Field testing with 14 users at two different sites using pressurized dispensing cans of OS-120 as a bench top cleaner showed 8 hour time weighted average exposures to range from less than one ppm to 16 ppm.

6. THERMAL AND FIRE PROPERTIES

The vapor pressure of disiloxane at 20°C is 33 mm, and at 25°C is 42 mm. It would therefore not be restricted by the proposed 45 mm (20°C) ceiling in the new NESHAP standard for volatile solvents used in the aerospace industry, but it is sufficiently high to provide rapid drying. Table 9 shows the thermal properties of linear VMS compared to CFC-113.

Table 9

THERMAL PROPERTIES

	Disiloxane (OS-10)	(OS-120)	Trisiloxane (OS-20)	Tetrasiloxane (OS-30)	CFC-113
Vapor Pressure @ 25°C (mm Hg)	42.2	44.6	3.9	0.43	331
Boiling Point (°C)	100	98	152	194	47.5
Heat of Vaporization at the b.p. (BPU/gal)	528	705	450	398	819
Drying Rate (n-butyl acetate =1)	3.8	3.5	0.7	0.15	14.7

Drying rates, based on ASTM 1901, have been measured in which solvent is allowed to drain and evaporate from an aluminum panel. With the rate for butyl acetate defined as 1, we find OS-10 to be 3.8 times faster, and OS-20 to be slightly slower. This test provides more realistic drying data than a simple evaporation from the bulk, and would be expected to be dependent on not only the vapor pressure, but the viscosity, surface tension, and relative humidity. For example, we have observed a tendency for hydrophilic solvents such as acetone and alcohol to attract condensed moisture as they evaporate, thus slowing the drying process compared to what would be expected strictly based on their respective vapor pressures.

Volatile methyl siloxanes are able to readily support combustion, and can burn more intensely than hydrocarbon fires. The disiloxane and trisiloxane flash points put them in the DOT flammable classification, while with a closed cup flash of 57°C, the tetramer is rated combustible. Data for two other commonly used flammable solvents is included in Table 10 for comparison. With lower flammable limits of about 1%, it only takes a vapor pressure of around 7 mm for VMS to reach the explosive limit. Thus, disiloxane reaches the LEL without heating, and trisiloxane only needs to reach 7°C above room temperature. The autoignition temperatures of the linear VMS are well over 300°C.

Table 10

FLAMMABILITY PROPERTIES

	Disiloxane (OS-10)	(OS-120)	Trisiloxane (OS-20)	Tetrasiloxane (OS-30)	IPA	Cyclohexane
Flash Point °C (°F)	-3 (27)	-4 (24)	34 (94)	57 (135)	12 (53)	-20 (-4)
Lower Flammable Limit (%)	1.25	1.25	0.9	0.9	2	1.3
Upper Flammable Limit (%)	18.6	--	13.8	>3.6	12	8
Autoignition Temperature (°C)	341	365	350	350	399	260

7. SUMMARY

Linear volatile methyl siloxanes (VMS) are a new class of solvents comprised of permethylated linear siloxanes. VMS's low surface tension and viscosity make them ideal for precision cleaning operations

especially for non-polar soils such as light oils and silicone residue. Azeotropes are now available which enable cleaning of more polar soils such as rosin flux. VMS are mild cleaners and thus compatible with most materials including plastics and elastomers. Cleaning processes can range from hand wiping and cold bath soaking to ultrasonics and vapor degreasers specially rated for flammable chemistries. VMS are not regulated as Hazardous Air Pollutants (HAP) nor do they fall under NESHAP requirements. They are not ozone depleting compounds and are rated VOC exempt by the EPA and most states. VMS have low toxicity and negligible odor. These materials are available at very low non-volatile residue levels as Dow Corning ® OS-Fluids which will not adversely affect painting and bonding operations. In fact, the OS fluids are especially effective at cleaning silicone contaminated surfaces. The key limitation of these products is their flammability, with flashpoints that range from 28 F to 135 F. They are particularly well suited for hand and benchtop cleaning applications, where their VOC exemption, low odor, and tailorable drying rates are useful.

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Experimental Strategies in the Development of a Polyisocyanurate Foam Insulation with HCFC 141b Blowing Agent

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Abstract

The MSFC TPS Materials Research Laboratory has utilized statistical techniques in the design of experiments to develop an insulation that meets the requirements for usage on the External Tank of the Space Shuttle. This insulation, with an average density of 2.15 lb/ft^3, is foamed with the environmentally friendly blowing agent HCFC 141b. HCFC 141b has an ozone depletion potential that is approximately one tenth that of the previous blowing agent CFC 11, but the thermodynamic properties of HCFC 141b affect the reaction kinetics and material properties. Statistically based experiments were designed to optimize the formulation for maximum mechanical strength at cryogenic temperatures with a minimum foam density. The experimental approach, chemistry, processing, and foam properties are described.

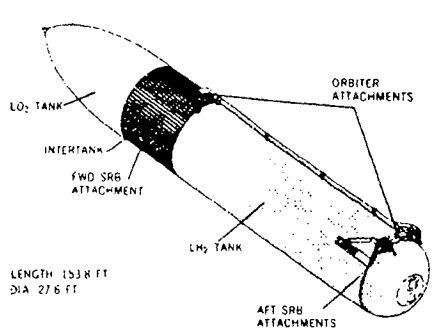
Introduction

The purpose of this study was to develop a low density polyisocyanurate insulation with mechanical properties meeting the requirements for use on the External Tank. Initial studies with a low density foam produced an insulation with a poor cell structure and a broad standard deviation in mechanical properties. The objective was to use the current system as a foundation, and with minimal changes to the formulation, increase the mechanical strength by improving the foam homogeneity. Emphasis was placed on tensile strength and substrate adhesion, with the possible sacrifice of the margin in thermal stability.

External Tank Insulations

The External Tank serves as a cryogenic propellant tank and also as a structural backbone for the Space Shuttle system. Figure 1 shows the main components of the External Tank: they are a forward liquid oxygen tank, an intertank, and the aft liquid hydrogen tank. Thermal Protection Systems (TPS) of NASA's Space Shuttle External Tank include polyurethane and polyisocyanurate modified polyurethane foam insulations. These insulations, previously foamed with CFC 11 blowing agent, serve to maintain cryogenic propellant quality, maintain the external tank structural temperature limits, and minimize the formation of ice and frost that could potentially damage the ceramic insulation on the space shuttle orbiter. During flight the external tank insulations are exposed to mechanical, thermal and acoustical stresses. TPS must pass cryogenic flexure and substrate adhesion tests at -253°C, aerothermal and radiant heating tests at fluxes up to approximately 14 kilowatts per square meter, and thermal conductivity tests at cryogenic and elevated temperatures.

Figure 1. External Tank Structure



Blowing Agents

Due to environmental concerns, the polyurethane insulation industry and the External Tank Project were tasked with replacing CFC 11. The flight qualification of foam insulations employing HCFC 141b as a foaming agent was recently completed. HCFC 141b blown insulations were implemented into the production process in 1995. NASA's TPS Materials Research Laboratory has evaluated second and third generation blowing agents with reduced and zero ozone depletion potential. Data presented in this paper is with foam insulations blown with HCFC 141b, some foams, where indicated, were co-blown with carbon dioxide.

Chemistry

The urethane based insulations are produced from the reaction of multifunctional isocyanates (RNCO) with multifunctional polyols (ROH). The urethane reaction is presented in equation 1. Excess stoichiometric levels of isocyanate are used to produce isocyanurate foams with greater thermal stability. Equation 2 presents the trimerization of isocyanate to produce the isocyanurate ring structure. Both of these reactions are exothermic and serve to vaporize the volatile liquid blowing agent, HCFC 141b. Additionally isocyanate can react with water to produce a carbamic acid which spontaneously decomposes to produce a catalytic amine and gaseous carbon dioxide with serves as a co-blowing agent. This reaction is presented in Equation 3.

Equation 1 Urethane	RNCO + R'OH	RNHCOOR'	
Equation 2 Isocyanurate	3 RNCO	RNCORNCORNCO	
Equation 3 Carbamic Acid	RNCO + HOH	RNHCOOH	$RNH_2 + CO_2$

Typical formulation ingredients other than isocyanates and polyols include: blowing agent, surfactant, catalysts, and flame retardants. Surfactants and catalysts are typically considered minor ingredients as they represent less than 5% of the formulation weight. The isocyanate to polyol component ratio in this case is 2:1, for an isocyanate index of 378. Typically, foams with higher isocyanate indices are more thermally stable, but also more difficult to process. Pure urethanes, with no isocyanurate trimer, have an isocyanate index around 100, with a 1:1 isocyanate: polyol ratio. Urethanes are more easily processed and are less brittle with improved substrate adhesion.

Experimental

Density

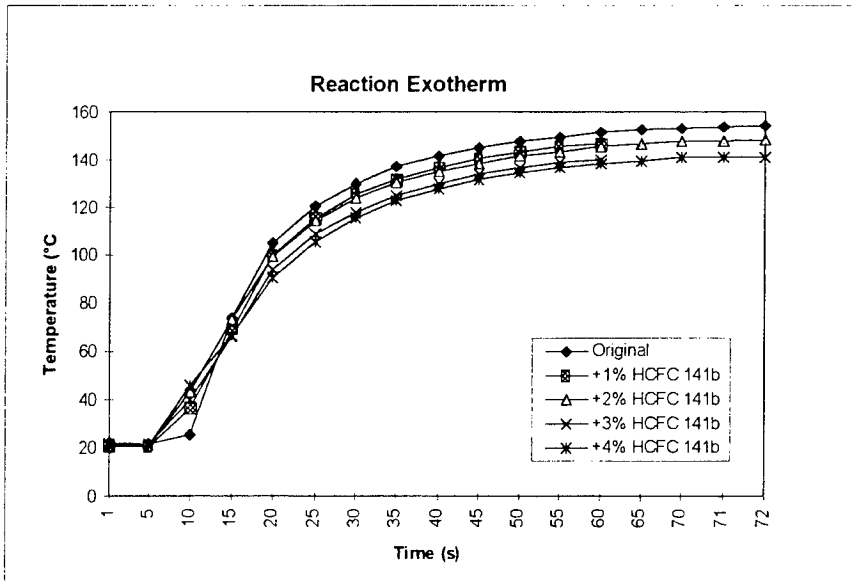
The foam density was adjusted by adding HCFC 141b blowing agent to the chemical formulation. Table 1 shows the effect of added blowing agent on foam density and reactivity.

Table 1. Reactivity and Density with Addition of HCFC 141b

HCFC 141b (% Added)	Cream (s)	Gel (s)	Tackfree (s)	Rise (s)	Cup Core Density (lb/ft³)
0	6	13	17	34	2.16
1	6	12	18	37	2.09
2	7	13	20	42	1.89
3	7	14	20	44	1.81
4	7	14	23	44	1.72

HCFC 141b has a higher heat capacity, boiling point, and heat of vaporization than CFC 11. foam exotherm data seen in Figure 2 illustrates a stepped exotherm profile with a delayed initiation of the isocyanurate reaction.

Figure 2. Exotherm Measurements of Hand Mixed Foam



The exotherm graph illustrates the delayed isocyanurate reaction with additional blowing agent. This agrees with previous exotherm data from other systems. The initial reactivity, measured as cream and gel times, is not significantly affected by the added blowing agent, but the latter portion of the reaction measured as tackfree and rise times is significantly effected. The following table lists the maximum exotherm temperature and maximum rate of temperature rise with additional blowing agent.

Table 2. Exotherm Temperature and Rates

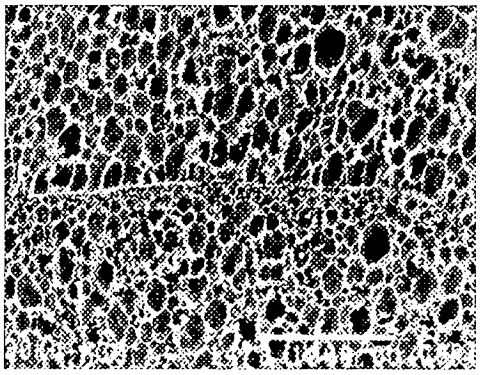
	Maximum Temperature (°C)	Maximum Rate (°C/s)
Original System	154	6.33
Original + 1% HCFC 141b	147	5.72
Original + 2% HCFC 141b	146	5.43
Original + 3% HCFC 141b	142	5.24
Original + 4% HCFC 141b	140	4.96

* Note that the foam system that was qualified for production usage has 1% more HCFC 141b than the original. The production formulation has been changed to have a total of 11.91% HCFC 141b in the total formulation.

Cell Structure

Sprayed foams produced with added HCFC 141b appeared to be overblown and had a poor cellular structure with a wide distribution of cell sizes and many larger pores. In an attempt to improve the homogeneity of the cell structure and mechanical properties, minor formulation changes including: surfactants, additives, and catalysts were investigated. Figure 3 shows the cellular structure of urethane based insulations.

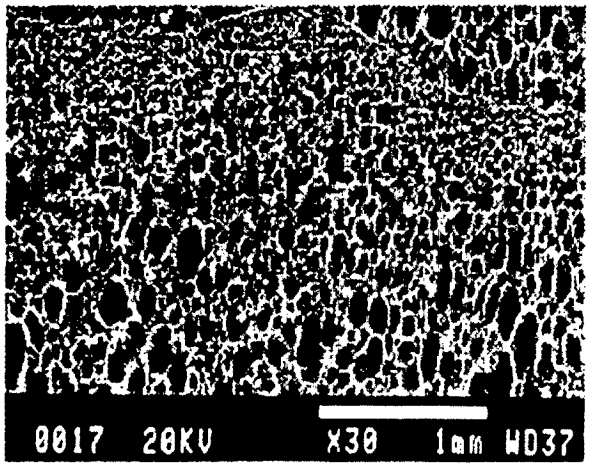
Figure 3. Scanning Electron Micrograph of Typical Cellular Structure



Surfactants, surface active agents, were investigated as a potential means to modify the cell structure. Seven organosilicone surfactants were evaluated, each was added to the formulation at 1, 2, and 3 percent levels. The surfactant level had no effect on cell structure. Three of the seven surfactants evaluated, including the current surfactant, produced foam with an acceptable cell structure, but there were no significant differences in mechanical properties. The decision was made to keep the current surfactant at a level of 2% of the formulation weight.

PF5050, a 3M product marketed as a blowing and nucleating agent, was investigated to improve cell structure. PF5050 has limited solubility in polyol and isocyanate components and must be constantly agitated to maintain an adequate emulsion. Foams produced with PF5050 had a fine cell structure immediately adjacent to the sprayed surface (knitlines) but offered little or no improvements in the core of the sprayed material, see Figure 4. This was interesting information, since previous work with PF5050 in the molding system produced a fine cell structure throughout the molded parts. Closed cell content of the panels sprayed with PF5050 dropped to 94% from 97% with no added PF5050. As a result, room temperature thermal conductivity rose from 0.16 to 0.18 BTU in/ft²h°F. The decision was made not to include PF5050 in the low density formulation.

Figure 4. Scanning Electron Microscope Photograph with PF5050 Added



Catalysts were another minor ingredient investigated. Experimental formulations incorporated higher levels of trimerization catalysts to drive the latter stage of the reaction. A statistically based experiment was designed to evaluate both the ratio of the three catalysts and the overall catalyst level. The experiment was designed to evaluate catalyst interactions and support quadratic models of the catalysts effect on reactivity. The catalyst experiment was complicated by the fact that the original formulation has an autocatalytic polyol that dominates the system reactivity. With catalyst changes of approximately 70%, the reactivity changed less than 20%.

Compression tests on hand mixed foam were used to select the best catalyst ratio for improved strength. Limited data with low output sprays indicated a possible increase in tensile strength with the catalyst adjusted systems, but in the end, although the reactivity profile was improved, there was no significant change in the mechanical strength of panels sprayed at high output.

The decision was made to further investigate the potential of a lower density insulation by altering some of the major ingredients. All TPS personnel from NASA and Lockheed Martin brainstormed and outlined a testplan to improve the mechanical properties of the low density foam by modifying the polymeric structure. The goal was to improve mechanical properties with minimal sacrifice of the thermal properties.

Polymer Structure

The major formulation changes investigated were identified as solvent effect and crosslink density. Two of the three flame retardants in the original system are non-reactive and act as solvents or plasticizers. Theoretically, high levels of these plasticizers would weaken the polymer matrix, while low levels would likely result in a brittle foam with poor cryogenic properties.

A statistically based experiment was designed to evaluate and optimize the flame retardant ratios and combined flame retardant level. This experiment was designed to determine the optimum flame retardant combination producing the insulation with maximum substrate adhesion and minimal negative effect on thermal properties. Since two of the flame retardants were non-reactive, changes in their level also altered the isocyanate index of the system. The experimental variables and ranges are identified in Table 3. Note that although isocyanate index was not a primary variable in the experiment, it did significantly vary from 335 to 440, and was analyzed as a factor contributing to foam properties.

Table 3. Variable Ranges in the Flame Retardant Experiment

Flame Retardant A (FR A):	65 - 97% of FR blend
Flame Retardant B (FR B):	0.9 - 13% of FR blend
Flame Retardant C (FR C):	1.9 - 24% of FR blend
Combined Flame Retardant Level:	6.5 - 28% of Total System weight

Thirty formulations were blended and sprayed at low output to produce test panels. Data indicated that the optimum flame retardant ratio was 5.0 FR A: 1.0 FR B : 1.7 FR C, and the optimum flame retardant level was 5.75 weight% of the total system. The original system had a flame retardant ratio of 24:1:2, with an overall level of 5.8 weight% of the total system. The optimized system had an isocyanate index of 353 versus 378 for the original formulation. The optimized flame retardant package was further evaluated and incorporated into the final low density formulation.

Crosslink density of the foamed polymer was also investigated to seek the optimum strength versus friability. Formulation variables affecting crosslink density include: *isocyanate index*, higher index foams can be stronger, but brittle and more sensitive to processing parameters; *isocyanate functionality*, higher functionality offering more reactive sites that would lead to a higher crosslink density; *water used as a co-blowing agent* simultaneously acts as a crosslinking agent producing an amine catalyst in the reaction; and *polyol functionality*, evaluated in 1985-1986 and found to improve the mechanical strength, but at the expense of severe gun build-up that resulted in the inability to process the material.

Of the many options available to change crosslink density, the two approaches selected were to incorporate a higher functionality isocyanate, and to use water as a co-blowing agent. Preliminary tests with low output sprays indicated a 20 to 30% increase in strength with these two approaches. Testing of panels sprayed at high output verified the improved strength with the water co-blown system. The average bond tension was 15 to 20% greater than that of the low density version of the original system, but still 10 to 15% weaker than the current high density system. Verification panels were sprayed with the water co-blown system. Data is presented in the following table.

Table 4. Mechanical Properties of Experimental Systems A & B with Adjusted Flame Retardant

	Original	System A	System B*
Bond Tension (psi)			
70°F, Avg.	45.9	46.4	46.3
Std.Deviation	10.7	9.5	10.9
-2 sigma	24.5	27.4	24.4
n	29	135	156
300°F, Avg.	32.3	32.3	32.3
Std.Deviation	5.1	4.6	5.3
-2 sigma	22.0	23.1	21.7
n	179	253	296
Density (lb/ft³)	2.35	2.09	2.12

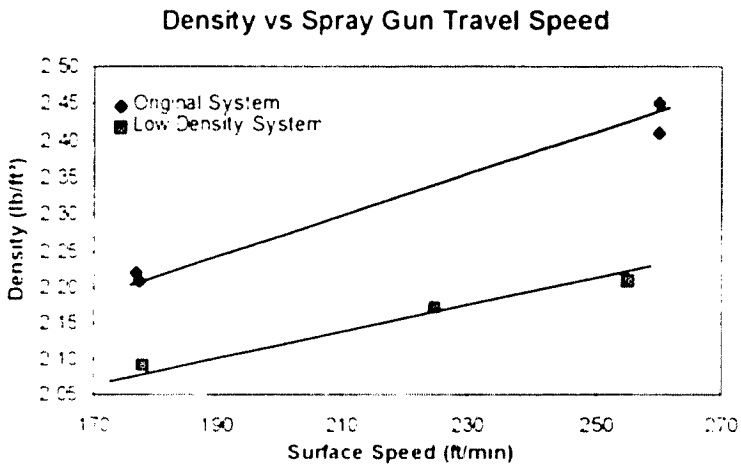
*Note System B is water co-blown and has the same flame retardant package as System A

The 2.10-2.15 lb/ft³ density of these systems was obtained by both formulation and processing adjustments. The decision was made to select Experimental System A for characterization and initial qualification testing. Data that follows is taken from test panels sprayed with System A.

Processing

Throughout this study, the changes in density that were sought were only slightly greater than the density variations that may result from typical processing adjustments. The density may vary ±0.1 to 0.2 lb/ft³ in a given spray. Figure 4 illustrates the resulting density with changes in the processing variable of surface speed or gun travel. With faster surface speeds, less material is applied per pass. This lower mass, results in reduced foam expansion and higher density.

Figure 4. Density vs. Surface Speed for the Original and Lightweight Insulations



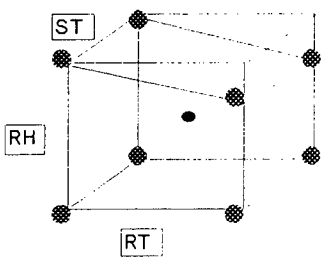
In addition to variations in gun travel (surface) speed, the process parameters of component temperature, substrate temperature, environmental temperature and relative humidity were also studied in a statistically based experiment to evaluate changes in material properties as a function of these parameters. Table 5 presents the processing conditions sprayed.

Table 5. Process Definition Test Conditions

	Application	Substrate Temp	Room Temp	Rel Humidity	Overlap Time
1	1 H2 & 1 O2 Barrels	125	85	30	30
2	1 H2 & 1 O2 Barrels	160	105	5	30
3	1 H2 & 1 O2 Barrels	125	105	5	30
4	1 H2 & 1 O2 Barrels	160	85	5	30
5	1 H2 & 1 O2 Barrels	125	105	19	30
6	1 H2 & 1 O2 Barrels	125	85	5	30
7	1 H2 & 1 O2 Barrels	160	105	19	30
8	1 H2 & 1 O2 Barrels	160	85	30	30
9	1 H2 & 1 O2 Barrels	145	94	24	30
10	Upper Ogives	145 or 160	94	24	30

The experimental system was found to have acceptable properties across the entire processing window. Test panels sprayed for qualification tests were fabricated with a faster surface speed to produce "thin" panels (1.2 to 0.7 inches thick) that are representative of the new thick-thin production spray process. By comparison developmental panels were sprayed 1.2 to 1.7" thick and had a lower density. The average density of all "thin" panels sprayed with the experimental system was 2.26 lb/ft³, compared to 2.36 for "thin" panels sprayed with the original system. The following graphs, figures 5-7, illustrate the experimental space and effects of the process parameters on material properties. Figure 8 presents the bond tensile strengths of the original and low density insulations.

Figure 5. Low Density Foam Processing Study



Low Density System Qualification
- 9 Experimental Conditions
  - 8 extreme points
  - 1 center point
- Evaluates entire processing region with fewer runs
- 2 sprays per condition (8 panels/spray), 18 total sprays

Figure 6. Density vs. Environmental Conditions

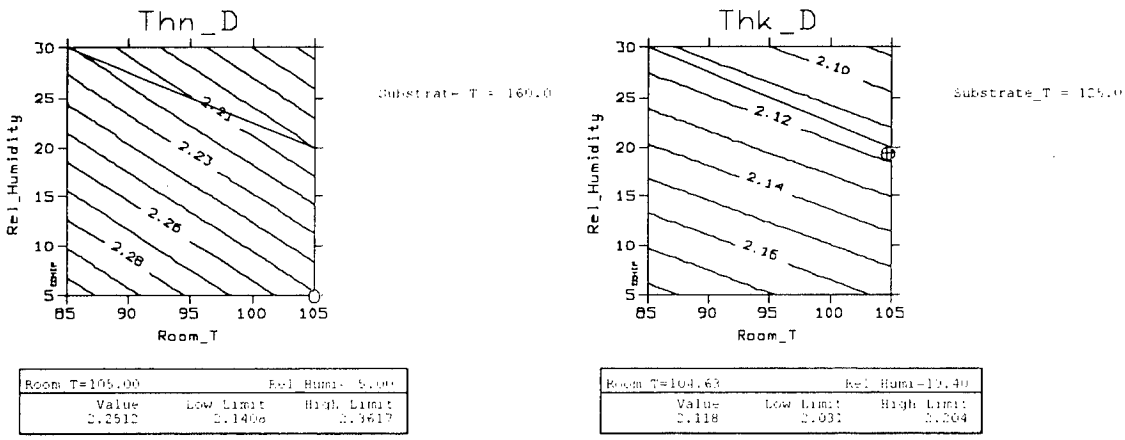


Figure 7. Bond Tension vs. Environmental Conditions

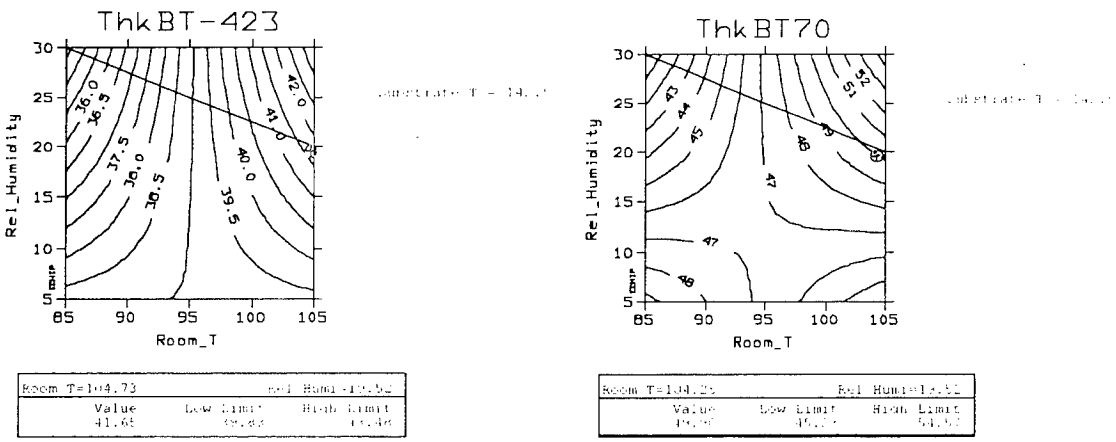
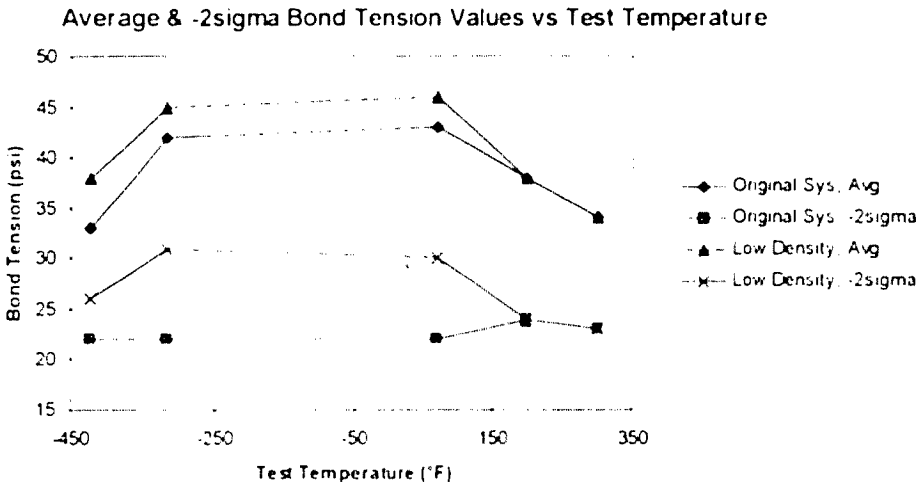


Figure 8 Bond Tensile Strength of the Low Density and Original Insulations



Conclusions

The low density insulation, with mechanical properties equal or superior to those of the original high density system, was developed using the base raw materials of the original formulation, with changes only to the flame retardant package The system reactivity was slightly faster, but was tested and found to have no negative effect on gun buildup in a duration spray Material properties were found to be acceptable across the entire processing window Based on the mechanical test data, additional thermal testing is warranted and will be completed in the upcoming fiscal year The cooperation of the development, test, and processing personnel and the incorporation of statistically based experimentation was crucial to the success of this project

Acknowledgments

All members of the low density foam development team worked tirelessly and contributed to the success of this project Team members included the system supplier, NASA, and Lockheed Martin personnel from MSFC and MAF

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Evaluation of Polyurethane Foam Insulation Blowing Agents with Zero Ozone Depletion Potential

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ABSTRACT

The MSFC Thermal Protection Systems (TPS) Materials Research Laboratory is currently investigating environmentally friendly blowing agents for use in the insulations of the Space Shuttle's External Tank. The original TPS foam materials of the External Tank were blown with chlorofluorocarbon (CFC) 11 that is now regulated because of its high Ozone Depletion Potential (ODP). Hydrochlorofluorocarbons (HCFCs), with an ODP that is one tenth that of CFCs, have been widely adopted as an interim blowing agent in urethane insulations. In FY96, Lockheed Martin completed the production qualification and validation of HCFC 141b blown insulations. Due to the expected limited commercial lifetime of HCFC 141b, research efforts are underway to identify and develop alternatives with zero ozone depletion potential. Physical blowing agents identified have included hydrocarbons, fluorocarbons, fluoroiodocarbons, hydrofluoroethers, and more predominantly, hydrofluorocarbons (HFCs). This paper will describe results from a research program with candidate HFC blowing agents.

INTRODUCTION

HCFC 141b has been widely adopted by industry as the interim blowing agent of choice for urethane based foam insulations. Even though this material has an ODP approximately one tenth that of CFC 11, it too is scheduled to be phased out in favor of materials with zero ODP. Current regulations call for the phaseout of domestic manufacture of HCFC 141b by January 1, 2003, with an exemption for continued use in insulation applications until 2030. While the use exemption to 2030 would seem to cover the insulation requirements through the end of the Space Shuttle program, lack of a domestic source after 2003 makes continued use after 2003 improbable. Furthermore, as experienced with phaseout of CFC 11, as suitable replacement candidates are identified, industry blowing agent producers may be quick to make the change to the new materials, effectively phasing out manufacture before the mandatory deadline date.

In view of the current regulations, and the uncertainties regarding the continued availability and use of HCFC 141b, research is continuing in NASA's TPS Materials Research Laboratory to identify and evaluate potential zero ODP blowing agent candidates suitable for application in cryogenic foam insulations for the Space Shuttle External Tank. Initial literature reviews and cooperative efforts with the EPA's Air and Energy Engineering Research Laboratory yielded over 200 candidate compounds for assessment as potential physical blowing agents to replace HCFC 141b. This list of candidates was screened based on such factors/properties as ODP, global warming potential, vapor phase thermal conductivity, molecular weight, boiling point, flammability, solubility, toxicity, and commercial availability. The down selected list of most likely candidates consisted of various chemicals in the following classes: hydrofluorocarbons, hydrofluoroethers, fluorinated hydrocarbons, fluorocarbons, fluoroiodocarbons, and hydrocarbons. Candidates from these classes were further screened for their applicability to cryogenic foam insulations and their expected support from industry. The most prominent candidates under consideration by US industry are hydrofluorocarbons.

In a previous paper[1], results of foaming trials in a pour-in-place foam system were presented. This paper will present the properties of the leading HFC blowing agent candidates and provide an overview of the evaluations performed to date in a sprayable foam system.

PROPERTIES OF HFC 245ca, HFC 245fa, and HFC 236ea

The three leading candidate HFC's currently being evaluated for use in ET foam systems are HFC 245ca, HFC 245fa, and HFC 236ea. A comparison of some of the key properties of these materials versus CFC 11 and HCFC 141b is shown in Table 1.

Table 1.
Blowing Agent Physical Property Comparison

	HFC 245ca	HFC 245fa	HFC 236ea	CFC 11	HCFC 141b
Molecular Weight	134	134	152	137	117
Boiling Point, °C	24.4	15.3	6.2	23.8	32.1
Heat of Vaporization, BTU/lb-mol	12,563	no data	11,537	10,700	11,200
Flammability	none	none	none	none	slight
Vapor Thermal Conductivity, BTU-in/hr-ft²-°F	0.095	no data	0.1	0.057	0.072
Vapor Pressure, psia @ 25°C	11.9	17.8	no data	12.8	10
Liquid Density, g/cc @ 25°C	1.4	1.32	no data	1.49	1.24

From this table, it can be seen that the HFC 245ca is most similar to CFC 11 in regards to molecular weight, boiling point, density, and vapor pressure. Thus, from a formulation and processing perspective, HFC 245ca would be closest to a direct substitution in existing foam systems. Use of this material, however, would be accompanied by a higher heat of vaporization and vapor thermal conductivity that might require formulation or process enhancements to compensate for reactivity effects and increased thermal conductivity. From a producibility/cost standpoint, HFC 245ca is more difficult to synthesize and thus, is a less attractive candidate to commercial producers and end users. HFC 245fa and HFC 236ea, while more economical to produce, have a boiling point lower than room temperature which may require pressurized blending and component feed systems and modified processing equipment. Thus, while HFC 245ca appears to be technically most similar to CFC 11 and HCFC 141b, market pressures may favor commercialization of HFC 245fa or HFC 236ea.

FORMULATION APPROACH

HFC 245fa, HFC 245ca, and HFC 236ea are not yet commercially available, and hence, experimental samples are relatively expensive and difficult to obtain. For these reasons, the scope of this initial effort was limited to a 1:1 substitution of the HFC candidates into an existing HCFC 141b blown urethane formulation. No catalyst adjustments or molecular weight ratio adjustments were made for this evaluation.

In preparing the experimental blends, the apparent solubility of the HFCs were noted. As in the prior effort with the pour-in-place foam system, each of the candidates were soluble to levels in excess of 30% by weight of the B component. Due to the low boiling point of the HFC 245fa and HFC 236ea, special blending and transfer techniques were devised to minimize blowing agent losses.

REACTIVITY EFFECTS

Cup reactivity tests were performed with each of the experimental HFC blown formulations as well as control formulations with both CFC 11 and HCFC 141b. Because this foam system is a fast reacting spray formulation, the foam components were cooled to 40°F for this testing. Results are shown in Table 2.

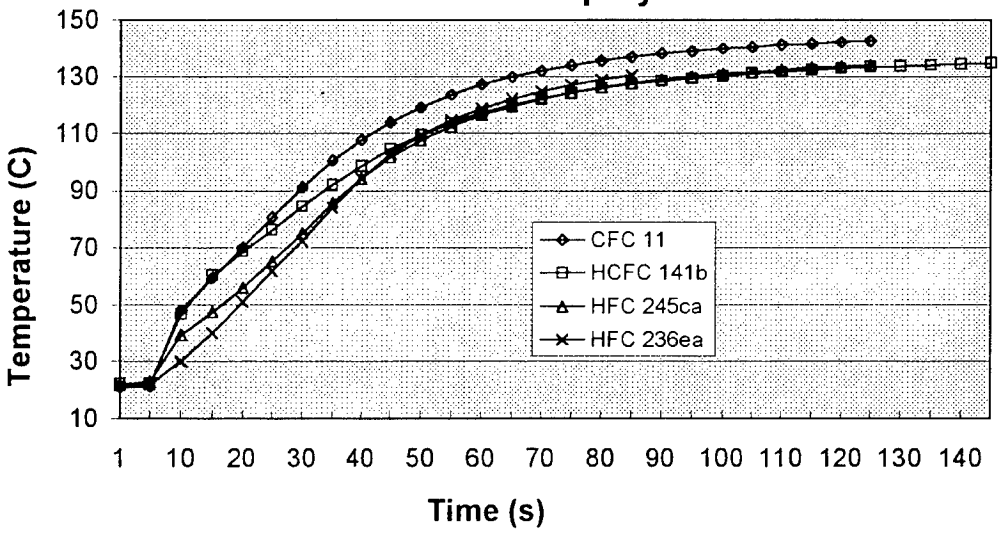
Table 2.
Reactivity Comparison - Urethane Spray Formulation

	CFC 11	HCFC 141b	HFC 245fa	HFC 245ca	HFC 236ea
Components (°F)	40	40	40	40	40
Mix(s)	3	3	2	2	2
Cream(s)	4	4	2	3	1
Gel(s)	9	9	11	8	12
Tackfree(s)	11	13	12	16	15
Rise(s)	30	36	37	37	37
Density (lb/ft^3)	1.6	1.7	1.7	1.8	2.0

Notes: No catalyst adjustment was made to normalize reactivity.

One of the first observations from this data is the relatively quick cream time of the experimental systems, particularly the HFC 245fa and the HFC 236ea blown materials. This can be attributed to the relatively low boiling point of these blowing agents. Review of the gel time, tack free time, and rise time data reveals a general trend of extended times with the experimental foam systems. This trend is most likely due to the higher heats of vaporization of the experimental materials as compared to CFC 11 and HCFC 141b. This was further supported by reaction exotherm tests, shown in Figure 1, where the temperature of the foaming masses blown with the experimental HFC's were somehwat lower than those achieved with the control foams. Core densities of the HFC 245fa and HFC 245ca experimental systems were comparable to the controls. The HFC 236ea was somewhat higher, indicating lower blowing efficiency and/or higher evaporative losses with this material.

Figure 1.
Exotherm of Urethane Spray Formulations



SPRAY FOAM PROPERTIES

After completion of the reactivity assessment with the experimental and control formulations, spray trials were performed. Initial spray trials were performed with each formulation using a Gusmer FF proportioner and Gusmer GX-7 spray gun. With the HFC 245fa and HFC 245ca formulations, only minor spray gun and process parameter adjustments were required to achieve foam panels in the target density and thickness ranges. The HFC 236ea formulation, however, exhibited high density and rough surface texture when sprayed with the Gusmer set-up.

An effort was then initiated to develop a processing method more suitable for the HFC 236ea. A dynamic mix spray gun manufactured by Edge Sweets was modified for this purpose. After several iterations, a combination of gun set-up and process parameters was achieved that yielded foam panels with a density comparable to those of the control and the HFC 245 isomers.

A summary of the mechanical and physical property results from these spray foam trials is presented in Table 3.

Table 3
Urethane Foam Spray Property Comparison

Parameter/Property	HFC 245fa	HFC 245ca	HFC 236ea	HFC 236ea	CFC 11	HCFC 141b
Spray Equipment	Gusmer	Gusmer	Gusmer	Edge-Sweets	Gusmer	Gusmer
Density (pcf)	2.6	2.2	2.9	2.4	2.4	2.3
Bond Tension (psi)	67	33	88	76	73	19*
70°F	41	36	53	37	46	19*
200°F	47	30	68	76	86	21*
-320°F						
Flatwise Tension (psi)						
70°F	83	65	95	73	68	31*
200°F	44	41	55	32	40	25*
-320°F	76	86	110	103	87	53*
Compression (psi)						
70°F	38	26	34	28	31	26
200°F	25	22	32	21	21	29
Closed Cell Content (%)	95	94	95	95	94	96
K (BTU in/h ft² °F)	0.141	0.154	0.157	0.139	0.145	0.174

Notes
* Tensile properties were unusually low for this HCFC 141b control - most likely due to use of non-optimum process conditions. Tensile values shown for CFC 11 serve as the best comparison for experimental assessment.

With the exception of the HFC 236ea formulation processed with the Gusmer spray equipment, all experimental formulations exhibited a density comparable to the control CFC 11 and HCFC 141b formulations. The HCFC 141b control panels prepared in this evaluation exhibited unusually low tensile strength values (most likely due to the use of non-optimum processing conditions for this material) and were not used as a basis of comparison. However, when compared to the CFC 11 control, tensile strength values at ambient and elevated test temperatures typically compared favorably to CFC 11. At cryogenic test conditions, in bond tensile strength tests, the experimental formulations exhibited a more pronounced departure from the control value due to the increased frequency of failures associated with the substrate. In addition, the HFC 245ca bond tensile strength was lower than the control not only at cryogenic temperature, but also at ambient and elevated test temperatures. This material exhibited a higher percentage of failures associated with the substrate at all temperatures tested. However, the flatwise tensile strength results (which measures the cohesive strength of the material) did compare favorably to the control. These results indicate that, in general, the HFC blown formulations exhibit comparable

tensile properties to the CFC 11 control, but that more extensive process development may be required to improve cryogenic capability in all cases and substrate adhesion in general with the HFC 245ca material. Review of the compressive strength and closed cell content of the tested formulations shows comparable performance for each material. Foam thermal conductivity values determined in this study were somewhat surprising in that the experimental materials were comparable to or somewhat lower than the controls. This result is unexpected due to the higher vapor phase thermal conductivity of the HFCs versus the control materials. Further, more detailed evaluation will be required to address this disparity.

SUMMARY

HFC 245ca, 245fa, and 236ea have been identified by industry as leading zero ODP candidates for the replacement of HCFC 141b as blowing agent in rigid urethane foams. The current position of fluoro chemical manufacturers favors commercialization of HFC 236ea or HFC 245fa due to their simpler commercial synthesis. These two materials have boiling points below room temperature, however, and may pose challenges in developing appropriate foam application processes. HFC 245ca, on the other hand, has physical properties most similar to CFC 11 and HCFC 141b and could provide the simplest substitution from a formulation and processing perspective.

Test results from this study with the three candidate HFCs show that there are indeed some effects of HFC substitution on both foam reaction kinetics and resulting foam properties. Foam reactivity tests indicate that catalyst adjustments would be required to maintain reactivity and processing characteristics similar to baseline foam systems. Mechanical and physical property tests, likewise, show that more thorough process development will be required to optimize both the application methods and the process constraints necessary for optimum foam properties. Overall, however, this study has shown that the three leading HFC replacement materials are indeed viable candidates for rigid urethane foam systems.

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1. Sharpe, J., D. MacArthur, T. Kollie, R. Graves, M. Liu, and R. Hendriks. 1994. "Evaluation of HFC 245ca and HFC 236ea as Foam Blowing Agents." Polyurethanes World Congress 1994, p. 134.

A Tooling Foam With Zero Ozone Depletion Potential For Composites Fabrication

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ABSTRACT

The MSFC TPS Materials Research Laboratory has developed a tooling foam for use in composites processing with mechanical and thermal properties superior to those of commercially available materials. MARCORE™ is a urethane modified polyisocyanurate foam system blown with an environmentally friendly blowing agent with zero ozone depletion potential. The patented material has the advantages of rapid prototyping, processing with unlimited cross sectional area, and compatibility with most preimpregnated composite resins and their associated cure cycles. The tooling foam is dimensionally stable at temperatures above 250°F and can withstand pressures greater than 100 psi. The chemistry, liquid properties, material properties, and applications are presented.

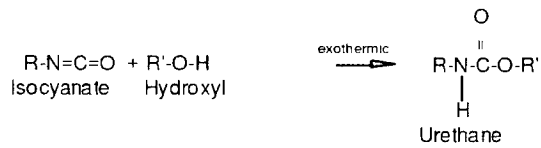
INTRODUCTION

The success or failure of an in-situ tooling foam for composites use is primarily dependent on two factors: compatibility with resin chemistry and dimensional stability at required processing temperatures and pressures. MARCORE™ is compatible with epoxy, bismaleimide and phenolic resins and meets the temperature and pressure requirements necessary to process these systems. These resin systems require cure temperatures of 350°F and pressures to 135 psi. In some cases, the laminated foam core composites require post cures at temperatures of 475°F. MARCORE™ shows a much higher resistance to chemical degradation, better thermal stability, and better machinability than presently used foam core materials.

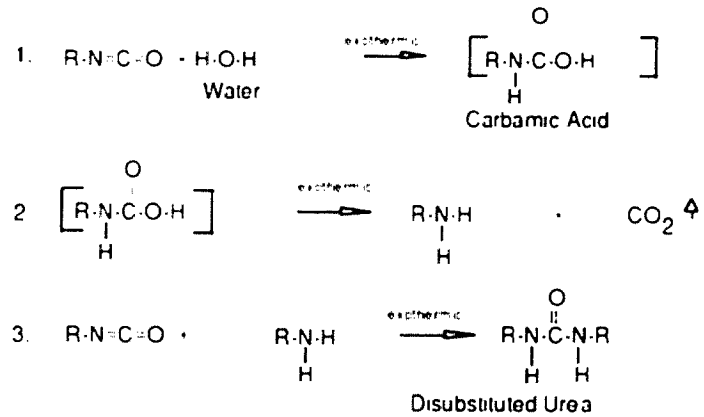
MARCORE™ CHEMISTRY

MARCORE™ is a urethane modified polyisocyanurate foam that is water blown. As portrayed below, three types of reactions are occurring simultaneously during the foaming process:

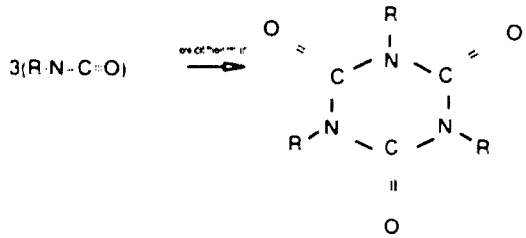
I. A urethane reaction takes place between polyols (OH groups) and isocyanates (NCO groups). The urethane linkages provide strength and toughness, however, they have the lowest thermal stability relative to the remaining two reactions.



II. Urea linkages result from the reaction between water and isocyanate. They increase strength but are also a major factor in increasing undesirable friability. The urea linkage has better thermal stability relative to the urethane linkage. The water/isocyanate reaction also generates CO, which in turn acts as a blowing agent for foam formation.



III Isocyanurate linkages result from trimerization of three isocyanate molecules to form a ring with high thermal stability but low mechanical properties



The approximate molecular segment thermal stability of the three linkages discussed is as follows:

Linkage	Urethane	Urea	Isocyanurate
Stable to	~250°F	~390°F	~520°F

The initiation and rate of these three main reactions is controlled to a large degree by catalyst type and catalyst level. Various tertiary amines and metal salts are used as catalysts. Proper catalyst choice and level are critical as they affect, not only reaction rate, but also density, strength and thermal stability.

Similarly, polyol choice is crucial in achieving desired foam properties. There are literally thousands of polyols for rigid foam production. They vary in molecular weight, functionality, monomer type, unsaturation level, amine content, ester or ether, etc. Although, the urethane linkage has the lowest thermal stability of the three types under discussion it was found that this choice is critical to achieving the desirable thermal properties of MARCORE™

FORMULATION DEVELOPMENT

A series of formulation changes were made to improve the properties of MARCORE™ for composites applications. A summary of these is presented in Table 1 below. Dimensional stability at 350°F was used as a simple screening test for each formulation iteration.

Table 1
MARCORE™ Formulation Development

	Initial Formulation	Intermediate Formulation	Final Formulation
Polymeric MDI	Medium Functionality (2.7)	**High Functionality (3.0)**	High Functionality (3.0)
Excess for Trimer Conversion	High to very high	High to very high	High to very high
Polyol 1	High Functionality Polyether (strength)	**Aromatic (thermal stability and strength)**	Aromatic (thermal stability and strength)
Polyol 2	Low Functionality Polyether (viscosity reduction)	Low Functionality Polyether (viscosity reduction)	Low Functionality Polyether (viscosity reduction)
Blowing Agent	Physical (CFC-11)	Physical (CFC-11)	**Chemical (H2O)**
Catalysts	Amine (for flow) Metal (for strength)	Amine (for flow) Metal (for strength)	**Amine (optimized for H2O rxn) Metal (for strength)**
Free Rise Density (lb/ft3)	10-12	10-12	10-12
Dimensional Stability Results (350 F)	0% pass	20% pass	100% pass
Ozone Depletion Potential (ODP)	Yes	Yes	No

As observed above, initially a physical blowing agent, CFC 11, was chosen. CFC 11 reduces the formulation viscosity without chemically reacting with any of the other formulation ingredients, thus improving the processability. Poor dimensional stability results drove further formulation development. During the intermediate formulation development, basic component changes such using a higher functionality isocyanate, aromatic polyol, and catalyst adjustments were introduced. With dimensional stability results remaining unfavorable, the replacement of CFC 11 with water was considered. Initially this was viewed as an unnecessary complication since another, very powerful, set of reactions would have to be considered. During the final stages of formulation development, water was incorporated as the blowing agent. This change to a chemical blowing agent mandated catalyst and isocyanate adjustments to control the new set of reactions. Once the proper control of these reactions was achieved, dimensional stability was improved to a pass rate of 100%. In addition to these favorable results, a future environmental issue was resolved. The ozone depletion potential (ODP) of the formulation blowing agent was reduced from 1.0 to 0.0.

LIQUID AND REACTIVITY PROPERTIES

"A" Component

The "A" component contains 4,4'-Diphenylmethane, Diisocyanate (commonly referred to as MDI) and should be handled with appropriate precautions. The viscosity of the "A" component is approximately 900 cps at room temperature which makes it easy to pour and mix. As with all isocyanates, contact with ambient air should be kept to a minimum to reduce contamination and reaction with airborne moisture. The "A" component container must be maintained with a nitrogen or dry air purge and ullage.

"B" Component

The "B" component is a mixture of polyols, blowing agent, and additives and has an ozone depletion potential of zero which makes it environmentally attractive. It is fairly viscous, 4700 cps @ room temperature.

Reactivity

MARCORE™ is a relatively slow reacting system when compared to polyurethane and urethane modified polyisocyanurate spray foams and reaction injection molding foams. The foaming reaction does not start until 30 seconds for mechanical hand mixing (with a paint stirrer) with component temperatures at room temperature. The delayed reaction start time is a cost advantage with the production of slab foam since the investment of automated pumping and mixing equipment (used with the faster reacting systems) is not necessary. Typical foam reaction times are shown below:

Ratio, A : B by weight	8.3 : 1.0
Component Temperature, °F	72
Mix time, sec	15
Start of rise, sec	30
Hard gel, sec	120
Tack free, sec	150
End of rise, sec	225
Density, lbs/ft³	9.1

The rate of exothermic reaction, along with its associated temperature, was used as a measure of the foam performance. The plots, shown in Figure 1, illustrate the occurrences of the urethane reaction and the isocyanurate reactions. The first rate peak is generated by the reaction of the isocyanate with the polyols resulting in urethane linkages. This is followed by a reduction in exotherm rate. During this period the temperature of the reacting mixture continues to increase due to the continuing isocyanate, water reaction. When the temperature reaches 260°F, in the presence of a suitable catalyst, the second, higher rate peak occurs due to the cyclotrimerization of the isocyanate resulting in isocyanurate linkages. This is also the "hard gel" point as seen above at 120 seconds.

PHYSICAL AND MECHANICAL PROPERTIES

The primary physical property goal for the MARCORE™ development was superior dimensional stability at 350° F. Additionally, in order to withstand autoclave pressure the compressive strength at 350° F had to be greater than 135 psi. Tables 2 and 3 list the physical and mechanical property test results for 11 lb/ft³ and 22 lb/ft³ versions of MARCORE™, respectively:

Figure 1. Exothermic Temperature Rise

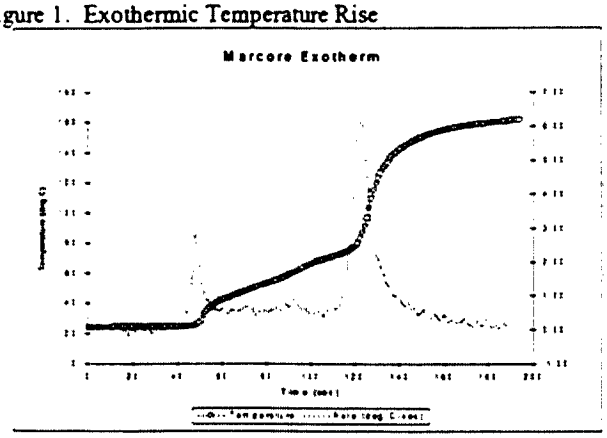


Table 2
MARCORE Physical/Mechanical Properties @ Density of 11 lbs/ft³

Dimensional Stability (ASTM D 2126)

Temperature, °F	Time, hrs	Pressure	Volume Change, %
350	24	atmospheric	-1.0
275	48	atmospheric	-0.1
250	2	vacuum, 29"	-0.1
350	2	vacuum, 29"	-0.1

Compressive Strength, psi (ASTM D 1621, proceedure A)	300 @350°F
Flatwise Tensile Strength, psi (ASTM D 1623)	120 @350°F
Coefficient of Thermal Expansion (CTE) (ASTM D 696)	3×10^{-5} (77-350°F)
Limiting Oxygen Index, % (ASTM D 2863)	26

Thermal Conductivity, BTU in/ft².hr.°F (k) (ASTM C 177):

Temperature, °F	k
-200	0.241
32	0.281
80	0.322
210	0.353

Table 3
MARCORE Physical/Mechanical Properties @ Density of 22 lbs/ft³

Compressive Strength, psi (ASTM D 1621)

Temperature, °F (Wet/Dry)	Compressive Strength, psi
Ambient/Dry	2, 060
250, Wet	1,430
365, Dry	1,330

Flat Bar Tension, psi (ASTM D 638)

Temperature, °F (Wet/Dry)	Tensile Strength, psi
-65 (Dry)	470
Ambient (Dry)	490
Ambient (Wet)	400
250 (Dry)	390
250 (Wet)	380

Glass Transition Temperature, °F (Wet/Dry)	613 (dry) 562 (wet)

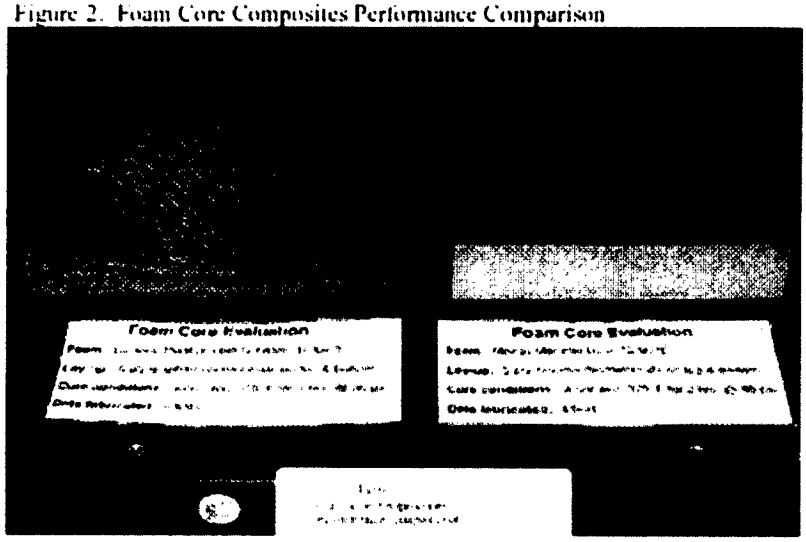
COMPOSITE APPLICATIONS

MARCORI ™ was developed as a low density tooling material for composites pre-impregnated (prepreg) lay-ups. It has been proven to be compatible with epoxy, phenolic and bismaleimide resins and their associated cure cycles. Following are the actual cure cycles used for the initial evaluation of MARCORI with prepregs based on these three resins:

Resin	Autoclave Cure Conditions	Post Cure Conditions	Result
epoxy	350°F 100 psi 4 hrs	none	successful
phenolic	350°F 100 psi 4 hrs	none	successful
bismaleimide	375°F 85 psi 2 hrs	475°F 6 hrs	successful, micro cracks in foam due to post cure

Figure 2 demonstrates the compatibility of MARCORI ™ with bismaleimide (BMI). It is compared here to a commercial urethane modified polyisocyanurate tooling foam widely used in the composites industry. These early tests were relatively small parts consisting of foam core lay ups seven inches square by two inches deep and cylinders of similar size. While this size is appropriate for many composite parts, there is a greater demand in the aerospace industry for a light weight, machinable, dimensionally stable tooling material to replace larger steel and sand mandrels which have the limitations of high cost and or high mass. For this reason MARCORI ™ process development work moved from small laboratory pours of less than one cubic foot to slabs of approximately six cubic feet.

Figure 2. Foam Core Composites Performance Comparison



These large pours were initially performed using a picture frame mold 50"x50"x4" placed in a large heated press with hydraulic clamping. Two simultaneous mixes of 38 lbs. each were made by two operators, poured in the mold and the press was then closed. Dimensional stability and compression tests at 350°F confirmed foam quality that was suitable for composite cure cycles. Figures 3 and 4 show the press with mold and the finished MARCORI ™ slab. This foam was machined to required dimensions and used to produce isolation fins for the Lockheed Martin Reusable Launch Vehicle (RLV) project cryogenic composite mini tank and as stiffener fillers in support of the RLV subscale tank development. A cure cycle of 350°F 100psi 4 hrs was used to cure the fin lay ups. In this application the

same foam tool was successfully used to make several fins, thus enhancing the cost effectiveness of this material. Figure 5 shows a photograph of the stiffeners on the RLV subscale tank.

Figure 3. Tooling Mold in Press

Figure 4. Molded 50"x50"x4" Part

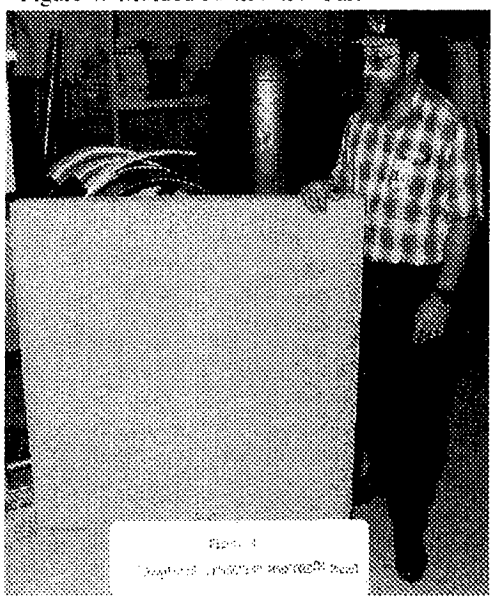
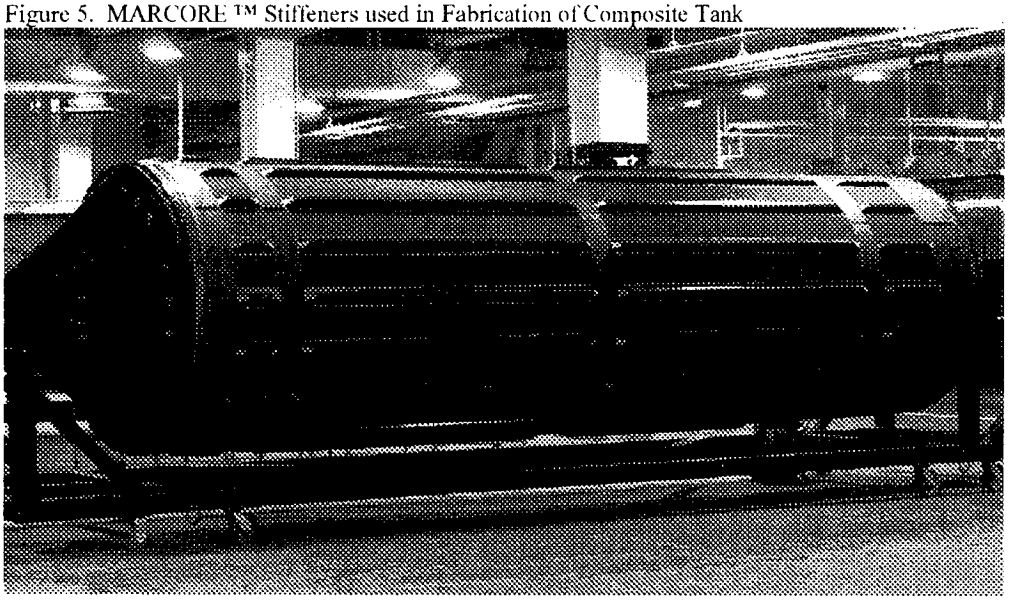


Figure 5. MARCORE ™ Stiffeners used in Fabrication of Composite Tank



Subsequent to the scale up success, another application requiring a foam slab 50"x50"x12" was demonstrated. Previous work with other tooling foams and tests utilizing MARCORE showed acceptable bond properties using high temperature epoxy adhesive. However, in order to reduce time and manpower requirements, a technique to pour on a previous pour was developed. The same four inch deep picture frame mold was used for the first slab which was allowed to cure overnight. Following the cure the slab was left in place in the press and the mold shimmed up four inches. Another pour was made on top of the first slab and allowed to cure. A third similar pour was performed the following day

which completed the final required slab size. Dimensional stability and flatwise tensile tests at 350°F confirmed foam quality across the knitlines. Figure 6 shows a photograph of the finished multiple pour slab. This slab was machined to proper dimensions for a lay up resulting in a graphite-epoxy mold for a composite access door close-out. Its outside dimensions are 49"x48.5" with a 10" draw. Figure 7 shows a photograph of the machined foam master, ready for lay-up of the composite pre-preg. It should be noted that in this case the foam tool could not be used for a second lay-up as planned because it cracked apart at the finish of the autoclave ramp down. This is thought to be caused by inadequate dissipation of internal pressure due to a failure in the vacuum bag assembly. Further evaluation is planned to resolve this issue.

Figure 6. Completed Multiple Pour, 50"x50"x12"

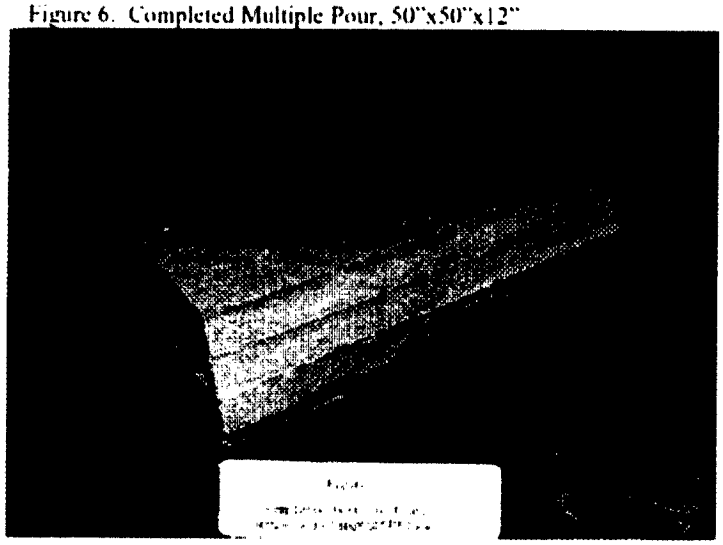
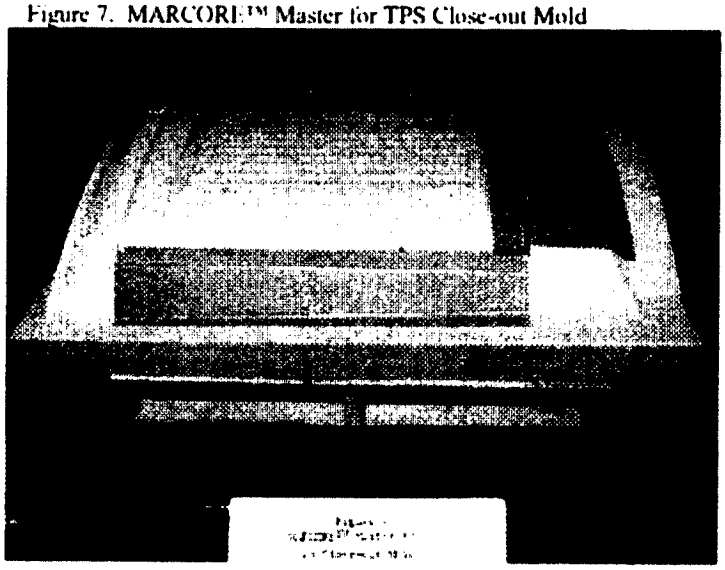


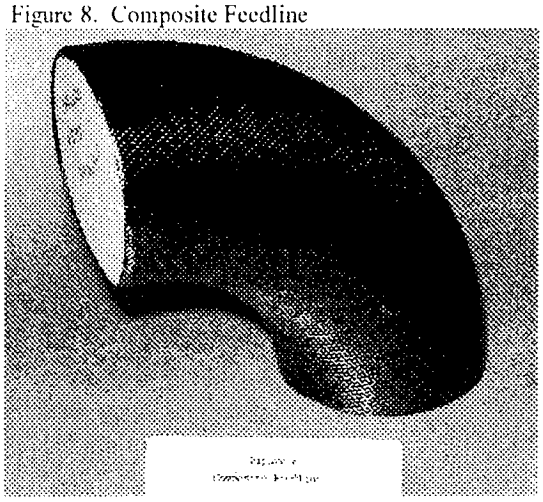
Figure 7. MARCORI™ Master for TPS Close-out Mold



MARCORI™ has also been selected for evaluation as a tooling material by Phillips Laboratories, Albuquerque, NM, for their program to develop methods of low cost manufacturing of isogrid structures. A Cooperative Research and Development Agreement (CRADA) between Phillips Laboratories, Tuskegee University and Lockheed Martin is underway to develop this technology.

A Marshall Space Flight Center program to develop composite feedlines and transfer lines for liquid hydrogen is also evaluating this foam for use as composite tooling. Figure 8 shows a photograph of the results of the first hand lay-up of a seven inch diameter elbow. The cure cycle was 350°F/100psi/4 hrs.

Figure 8. Composite Feedline



CONCLUSION

MARCORE™ has been shown to be an ideal material for many low cost tooling applications in the manufacture of composite parts. It has the unique advantages of superior physical properties, ease of manufacture, unlimited cross section and light weight. Additionally, it has been developed to be environmentally friendly, with zero ozone depletion potential. It has demonstrated that there can be technical advantages in meeting the goal of zero ozone depletion.

APPROACHES TO ENVIRONMENTAL MANAGEMENT

MANAGEMENT STRATEGIES FOR MULTI-USE GOVERNMENT FACILITIES

Maurice Hale
SAIC
Huntsville, AL

Second Conference on Aerospace Environmental Technology
August 6 - 8, 1996

Von Braun Civic Center
Huntsville, AL

Abstract

Recent base closings, privatization of government facilities, and moves toward operation of portions of government programs by private contractors have created large multi-use areas requiring efficient environmental management. A strategy is described for management of just such a multi-use government facility in which an agency (NASA) and its Occupational Safety, Industrial Hygiene, and Environmental Services service contractor SAIC (Science Applications International Corporation) implemented management of the environmental affairs for both NASA Ames Research Center and the adjacent former Moffett Naval Air Station. By cooperatively managing both facilities using one management structure and one contractor with a "charge back" system of payment for services, both NASA Ames and the newly named Moffett Federal Airfield benefit from lower fees, faster responses, and better service. This paper describes the management strategy used by NASA, federal users of Moffett Federal Airfield, and SAIC to provide seamless environmental services and payments within a multi-use facility.

Introduction

A History of Moffett Federal Airfield

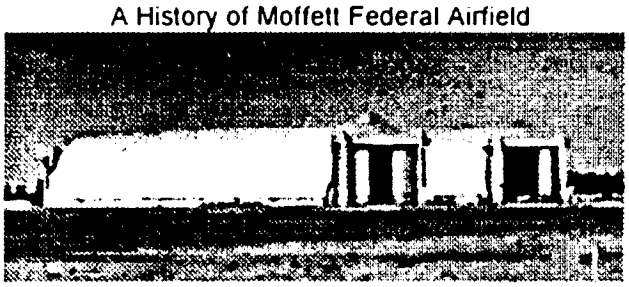


Figure 1
Hangers 2 & 3 at Moffett Federal Airfield

On April 12, 1933, the United States Government commissioned a 1000 acre parcel of land in Sunnyvale, California as Naval Air Station, Sunnyvale. It was later renamed NAS Moffett Field. The original mission of the Naval Air Station was to serve as a home base for the Navy dirigible, the U.S.S.Macon, which was lost at sea on February 12, 1935.

Several years later, in December 1939, the National Advisory Committee for Aeronautics (NACA) established the Ames Aeronautical Laboratory on 62 acres adjacent to the Naval Air Station. In 1958, when the National Aeronautics and Space Administration (NASA) was formed, the Laboratory became NASA's Ames Research Center.

Over the years, NAS Moffett Field served as an Army Air Corps training base, a home for World War II Navy dirigibles, a station for Navy jet fighters, and a center for anti-submarine warfare. At the same time, Ames Research Center continued to grow and develop into one of Silicon Valley's prime resources.

In the late 1980s, as the nation's military began to decrease, Congress called for the formation of the Base Realignment and Closure (BRAC) Commission. In 1991, the BRAC Commission recommended the closure of Moffett Field as a Naval Air Station, and the continued use of the facility to the benefit of Government and industry

Moffett Field was closed as a military base on July 1, 1994. Supervision of Moffett's two runways, three aircraft hangars, and 3.5 million square feet of facilities was turned over to NASA Ames Research Center. As the new federal custodian, NASA Ames began the operation of a shared federal facility known as Moffett Federal Airfield.

WHAT IS MANAGED

About 20% of the administrative and warehouse buildings and about 40% of the airfield capacity is currently available for use, or will be in

subcommittees, environmental activists and the California Coastal Commission have been involved in discussing the fate of the 28,000-acre army base. Contaminated with thousands of rounds of unexploded ammunition, Fort Ord will require a major cleanup. However, the land's eventual use will determine the region's economic future, so community response is essential.

There remains a significant portion of the airfield and associated facilities available for use by Government agencies, Government contractors, and for those seeking to advance research and development efforts related to NASA's missions. (See Reimbursable Space Act Agreements/Commercial Technology at Moffett Federal Airfield.) This includes administrative, warehouse and hangar space as well as airfield ramp access and airfield use. MFA is not now open for general aviation or other activities not "associated" with the federal government.

Some of the current Resident Agencies at Moffett Federal Airfield include:

* Naval Air Reserve
* Air National Guard
* Army Reserve
* U.S. Army
* Space Camp California
* Air Force, Onizuka
*Lockheed/Martin Missiles and Space
* Navy Exchange
* Bureau of Alcohol, Tobacco and Firearms
* Defense Commissary Agency
* United States Geological Survey
*Department of Veterans Affairs-Medical Center, Palo Alto
* Stanford University
* Golden Bay Credit Union
* The American Red Cross

CONTRACTS FOR ENVIRONMENTAL SERVICES

Science Applications International Corporation (SAIC) was selected as the support contractor for NASA Ames beginning in 1995. The Occupational Safety, Industrial Hygiene, and Envronmental Services contract is the instrument for implementing the environmental services for both NASA Ames and Moffett Federal Airfield. SAIC employed two principle subcontractors, Microcraft Technologies of Tullahoma, Tennessee, and USPCI (purchased later by Ladlaw).

The actual management of the inter-related environmental services is best understood by tracking the contracting and the payment for services.

(1)- Based on the agreement signed by the Resident Agencies with the Moffett Federal Airfield and NASA, each agency agrees to use the support services of NASA, except for internal reporting unique to the RA. Joint use requires careful definition of boundaries as well as cooperative interfaces regarding flows or damage across those boundaries. Basically, each agency is responsible for all generation within their boundaries. It should be noted that NASA by agreement with the US Navy did not assume responsibility for the Superfund RI/FS in place at the time of the closure, although monitoring activities of the resulting cleanup actions was continued by NASA and SAIC after the transition.

(2)- Each RA includes a monthly and yearly estimate for services in their budgets and submits this estimate to NASA. This normally includes hazardous waste pickup and disposal, training, signage, and emergency services. This information is compiled by NASA to form the budget for the service contractor.

(3)- NASA issues a Service Order to SAIC for each RA based on the budget submitted. This is normally for one year, but can be shorter depending on the amount of funding estimated by the RA and the timing of the various FYs of the agencies.

(4)- SAIC responds to NASA with a time based estimate of services and charges for the Service Order. At the same time, SAIC sets up a special charge number for the various services requested to provide timely and accurate tracking of charges. Each major sub-contractor also sets up a similar charge number for the services they are responsible for providing.

(5)- When NASA accepts the estimate, they issue budget authority to SAIC to begin services and response to requests from the RA.

RESPONSE AND PAYMENT

(6)- In addition to the scheduled pickup and training, SAIC also responds to requests from NASA to provide added services to RAs when requested. This includes emergency services including Level 1 response. At this point, both NASA and SAIC can respond based on faith the agreements will be met.

(7)- SAIC tracks the charges for each agency using an internal bi-weekly accounting and reporting policy. The tracking also includes estimates at completion and percentage expended figures.

Monthy reports (SF254, 255) are made of the integrated services.

(8)- NASA tracks compliance and audits the performance on the contract for each of the agencies. Upon approval, the costs reported to NASA are paid according to the normal policy of NASA Ames. NASA Ames then adds a very small fee to cover the cost of money and administration and bills the resident agency.

(9)- Each Resident Agency then reimburses NASA Ames for the environmental services provided. If needed, the budget for the RA is adjusted and added services are requested by the RA.

SATISFACTION OF PARTIES

A key ingredient in the success of the system is the desire on the part of NASA and SAIC to assure the satisfaction of the parties, including the cities, county, state, and federal jurisdictions. Feedback sessions are held at least monthly to review response, charges, and customer suggestions. Part of the success is the careful definition of the concept of "customer". Each party has several "customers" which have various requirements. When possible, help with customer satisfaction is provided by one of the parties to another even when the second party does not have direct responsibility to satisfy the requirement. This spirit of communication and cooperation has solved many problems.

For instance, it became embarrassing to military commanders to have to report delayed expenses in months when they did not have hazardous waste disposal. In effect, this resulted in a "division by zero" which drove "COST PER POUND" columns to infinity on some internal military reporting. To avoid this while maintaining balance of payments, the parties agreed to bill certain RAs on a three month running average for pickup and disposal services.

CONCLUSIONS

There are several advantages and a few disadvantages to this strategy for management of multi-use area. One of the strongest points is that a centralized point of contact and communication is established for City, County, State, and Federal identities, which also simplifies record keeping by assuring a central location for data. Secondly, a real gain from economy of scale can be realized by all parties, whereas multiple environmental service contracts lose from multiple boundaries, management, and reporting. The use of a single contractor is especially attractive to governmental personnel. Finally, common standards can be employed throughout the facilities.

Disadvantages include the delay in the payment for services to the central agency from the resident agencies, which adds to the cost of money if the support contractor is paid before funds are transferred to the central account. From a support contractor viewpoint, this strategy adds complication by requiring difficult tracing of labor and charges, particularly after mixing of classified waste for economical disposal. An additional negative is the potential variation in budget caused by addition or deletion of services from the resident agencies, making forecasting of resources required very complicated.

Cooperation of the parties is essential for this strategy to work. It is essential that the strategy include developing trust so that timely response to unfunded requirements can be made. This has been accomplished by a high level of communication and a sense of "customer service", throughout the organizations.

ACKNOWLEDGMENT

Sincere appreciation and acknowledgment is given to Mr. Steven G. Brisbin, Chief, Office of Safety, Health, and Medical Services, Office of Safety, Reliability, and Quality Assurance, at NASA Ames Research Center, Moffett Field, CA. for input to this paper, and to the staff of Ames Research Center and the Moffett Field Transition Office for developing the basis for this paper and for direct input of pictures and text.

ENVIRONMENTAL AND PRODUCTIVITY TECHNOLOGY INNOVATION FOR THE FOOD MANUFACTURING INDUSTRY

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TECHNOLOGY REQUIRED

The food processing industry seeks efficient and cost effective means by which to peel horticultural products.

BACKGROUND

One of the first unit operations involved in processing of many horticultural commodities, and whole peeled tomatoes in particular, is peeling. Efficient removal of peel material is required for appearance and quality purposes and also to ensure uniform heating during processing operations. However, there is a tradeoff between removal of peel material and retaining as much flesh material, which translates to yield, as possible. Both chemical (lye) and mechanical systems of peeling have been utilized for horticultural products.

Lye peeling involves the use of approximately 10-15% caustic soda (sodium hydroxide) or potassium hydroxide. The operation requires an ample water supply, lye, and a heat source. Products are passed through a heated lye solution, washed with water and typically dipped in acid to neutralize the remaining traces of caustic soda.

The objective of the mechanical peeling operation is to split or crack the peel to a sufficient degree that the entire peel will be subsequently removed when the product passes over mechanical peel eliminators, typically rubber disc rollers followed by a pinch roller bed. Products are typically "pressure peeled" which involves exposure to high pressure steam followed by a release to atmospheric pressure, or "vacuum peeled" which involves exposure to lower pressure steam followed by vacuum.

In tomato products, the removal of peel material is required to meet the quality portion of the Standards of Identity. Canned tomatoes (21 CFR 155.190) and canned stewed tomatoes (21 CFR 155.190) are defined in the Standards of Identity issues under the Federal Food, Drug and Cosmetic Act. These Standards state that peel per kilogram of the finished product must cover an area of not more than 15 cm^2 (6.8 cm^2 per pound) based on an average of all containers evaluated.

PROBLEM AND IMPACT OF SOLUTION

Efficient peeling requires that processors have an understanding of raw material characteristics, in particular the maturity and variety, and process operations that optimally remove peel material. Presently when loads of horticultural products arrive at a processing facility there may be information recorded in terms of grower, field location and variety but even this is not always known. In addition, although variety has tremendous impact on peeling efficiency, another important factor is maturity. Mature products are typically peeled more easily than immature products, but processors must take more care not to over-peel, which may happen in mature fruit. Fruit texture changes with maturity and this will affect both peelability and ultimate yield.

Time and temperature of exposure, and vacuum pressure specifications, are all factors which are currently manipulated on site to optimize peel removal. Very little information exists on the effects of these factors on peel removal and ultimately yield. In a study carried out in our laboratory we evaluated the effects of the following steam temperatures and exposure times on tomato peel removal: 212°-250°F fpr 30 seconds to 2 minutes. It was determined that peelability and yield were optimal under the highest temperature conditions (250°F) and that exposure time depended on variety but in general at least 45 seconds were required. Optimization of peeling conditions result in a significant increase in yield of canned whole, sliced and diced products.

STATE OF THE ART

In the early 1900s, tomatoes and other products were blanched in ambient pressure steam or in boiling water, immersed or sprayed with cold water to crack the skin and then the peel was removed by hand. Beginning in the 1960s, the use of hot lye (sodium hydroxide or caustic) solutions and peeling aids allowed for more efficient peel removal.

In the 1970s, there began a move away from the use of lye due to waste disposal problems, lower product recovery and the complexity of recovering peel and pulp tissue. During this period a number of studies were carried out to investigate the use of hot calcium chloride solutions, application of freeze-heating, high pressure or superheated steam and flame or infrared treatments on peeling efficiency. In recent years, the application of high pressure steam (7 to 10 bar) for short dwell times (5 to 15 sec) in combination with mechanical peel eliminators has replaced lye peeling operations in most horticultural product processing operations.

Efficiency of tomato peel removal by high pressure steam has been shown to depend upon steam pressure, dwell time, variety and presence of disorders such as yellow shoulder disorder (YSD). Subjecting the tomato to too much heat may result in softening and/or removal of excessive amounts of tomato pericarp and a reduction in yield.

Optimization of the peeling operation to achieve adequate peel loosening without excessive yield loss is a challenge, and will depend to a large part on variety, maturity, and fruit size. Horticultural product processors should be aware of the genetic identity of incoming raw fruit and determine the optimum combination of steam pressure and dwell time to maximize product recovery, throughput and quality. In addition, pre-sorting of incoming loads may allow for much better targeting of raw materials for selected end products. Presently, variability within product loads and between loads of what may be mixed varieties requires processors be continually changing peeling time/temperature conditions.

TECHNOLOGY SPECIFICATIONS AND CONSTRAINTS

Existing peeling technologies in food operations may be improved by better understanding of raw materials and the factors that govern peel removal. The use of high pressure steam followed by mechanical peel eliminators is common. To date, however, very little work has been systematically carried out to elucidate the effect of time, temperature and vacuum pressure on peel removal. The technology sought might pre-sort tomatoes according to maturity and/or textural properties. In addition, technology that specifies time, temperature and vacuum conditions based on raw material characteristics is desirable.

The Needs Statements have been prepared by university and industry experts under the direction of the National Food Processors Association's technical staff according to the outline and format prescribed by the systems implementer, R. J. Philips & Associates, Inc.

Sponsored by U. S. Department of Agriculture Rural Business—Cooperative Service, U. S. Department of Agriculture/Cooperative State Research, Education and Extension Service, and the U. S. Environmental Protection Agency. Partnering with National Food Processors Association, American Bakers Association, American Meat Institute, Food Processing Machinery & Supplies Association, International Dairy Foods Association, Snack Food Association, and United Egg Association. Hosted by University of Nebraska-Lincoln Food Processing Center.

Title: Solar Cell Assembly Defluxing Using Ozone Depleting Chemical Replacements

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Abstract

Studies to identify trichlorotrifluoroethane (Freon TF - used at TRW in alcohol & stabilizer mixture formulations such as Freon TES and Genesolv DES) replacement cleaning agents for solar cell defluxing applications have been ongoing at TRW since 1992. Though initial studies identified some promising aqueous and semi-aqueous cleaning agents, they were eliminated as replacement candidates in 1994 due to process control, substrate corrosion, and manufacturing floor space concerns. All scale-up testing since 1994 has concentrated on warm (60 °C) isopropyl alcohol (IPA), hydrochlorofluorocarbon (HCFC) (AK-225), and hydrofluorocarbon (HFC) (Vertrel SMT, an azeotrope of Vertrel XF HFC and dichloroethylene) technologies as replacement candidates for solar array manufacturing applications. Based on the results of the scale-up test efforts, the SMT and pure AK-225 materials cleaned as well as the existing process, but both materials attacked the substrate's silicone solar cell-to-coverglass bond region more aggressively than the existing Freon TF based cleaning agents. The AK-225AES (an azeotrope of AK-225, ethanol and stabilizer) material was identified as a drop in replacement for the existing process, however this HCFC will only see limited implementation because of its production cut-off date in the year 2015, high cost, and increased health risk (50 ppm Threshold Limit Value) compared to the Freon TF (1000 ppm Threshold Limit Value).

The warm IPA spray process, on the other hand, cleans as well as the existing process yet appears to less aggressively attach the silicone bond region of the solar cells than the SMT, AK-225, AK-225AES or existing Freon TF mixtures. Based on laboratory tests, the selected IPA process will out-perform the present cleaning process, but IPA's flammability rating (Class 1B) introduces new safety concerns that were not an issue in the past and do not need to be addressed with the HCFC and HFC products. At a cost of approximately $400,000, TRW has purchased custom designed equipment and is making the necessary facility modifications to safely handle the new IPA spray process for solar cell module strings up to 2 x 4 feet in dimension. The new equipment is scheduled to be operating in November of 1996, and AK-225AES is presently under evaluation as an intermediate replacement should the IPA system implementation schedule slips outside of TRW's Freon TF use schedule. In addition, a smaller degreaser with AK-225AES is presently under consideration as a temporary replacement cleaning agent for solar cell defluxing operations prior to coverglass bonding, and additional IPA capital equipment will be evaluated in 1997 as the long term replacement for the precoverglass cleaning operation.

Introduction

Depending on production levels, between 400 and 660 gallons of chlorofluorocarbons (CFCs) are utilized by TRW's Power Systems Department each year to remove flux residues from solar cells during the fabrication of spacecraft solar arrays. Studies were initiated in 1992 under a cost-share program between TRW's Safety Health and Environmental Affairs Department, the South Coast Air

Quality Management District (SCAQMD), and California Manufacturers Association (CMA) to target possible aqueous and semi-aqueous cleaning systems suitable to replace Freon TF in TRW's solar cell defluxing applications. The visual and ionic measurement results of the 1992 study identified one aqueous and several semi-aqueous solutions as possible replacement candidates.

After 1992, TRW's Space and Technology Division (S&TD) continued to fund several Ozone Depleting Chemical (ODC) replacement efforts within the Division. As part of a 1994 effort, scale-up testing was performed on cells cleaned using various aqueous cleaning and rinsing operations. In addition, tests were performed using isopropyl alcohol (IPA) cleaning procedures. Due to corrosion concerns, limited floor space, operating issues, and suspicious data scatter in the power loss measurements of the aqueous cleaned cells, aqueous and semi-aqueous cleaning of solar cells was dropped from evaluation after 1994. Warm IPA spray cleaning replaced aqueous and semi-aqueous cleaners as the better defluxing agent candidate.

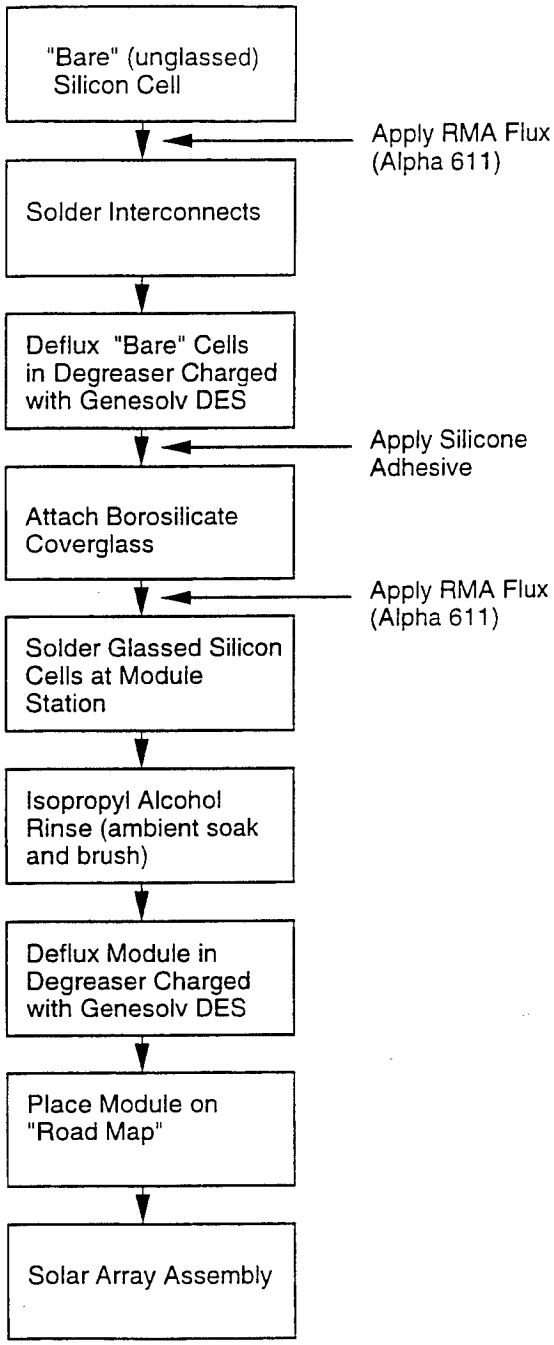
Further testing was initiated in 1995 using warm IPA spray, straight AK-225 and perfluorocarbon/isopropyl alcohol solvent system cleaning procedures. After review of the material and facility costs, and assessment of substrate damage, corrosion and power results, a warm isopropyl alcohol spray cleaning process developed by TRW was selected as the primary replacement candidate. At the end of 1995, an equipment specification was written to solicit quotes from vendors qualified to custom design and build a piece of equipment to safely handle the selected cleaning process.

As a result of 1995 and 1996 test efforts, TRW's Electronic System & Technology Division (ES&TD) approved and is implementing AK-225AES for printed circuit board (PCB) defluxing applications. Since large quantities of AK-225AES will be available at TRW for printed circuit board applications, a small S&TD effort was pursued in 1996 to qualify the AK-225AES and Vertrel SMT cleaning materials as back-up or alternate cleaning solutions for solar cell assembly applications. Based on the results of power and cleanability tests, AK-225AES is under consideration as an acceptable alternative for solar cell defluxing applications. Due to the high AK-225 material costs, the warm isopropyl alcohol system is being pursued as the long term solution to the solar cell defluxing effort, but alternative non-flammable cleaning agents are still under consideration for some repair and small scale solar cell cleaning applications.

Body

TRW uses Genesolv DES (a mixture of Freon TF, ethanol, isopropyl alcohol and stabilizer) to clean residual rosin mildly activated (RMA) flux from solar cells during the fabrication of spacecraft solar cell modules and panels. As can be seen in the solar cell fabrication process flow diagram (*Figure 1), solar cells are defluxed twice during the fabrication process (once, after the interconnects are soldered on/before the coverglass is bonded to the solar cell; and again after the solar cells have been soldered together to form modules/before bonding the solar cell modules to the solar array substrate). The interconnect and coverglass operations of the solar cell process are automated. The cells are transported through the automation line in solar cell carriers designed to handle and transport up to 25 cells at a time. The cells in the cell stack carrier format are individually separated but are spaced close enough to present cleaning and

Figure 1 - Solar Cell Process Fabrication Flow Diagram



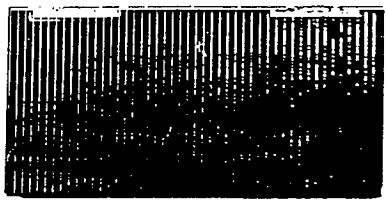


Figure 1 - "Bare" Silicon Cell

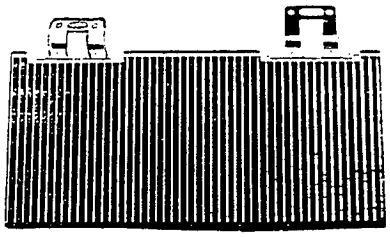


Figure 1 - "Bare" Silicon Cell with Interconnects

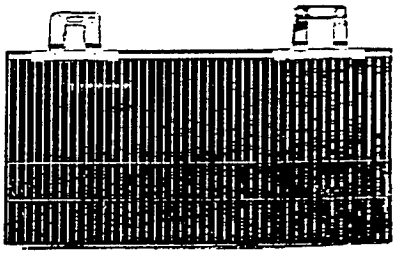


Figure 1 - Silicon Cell with Coverglass (Cell Stack)

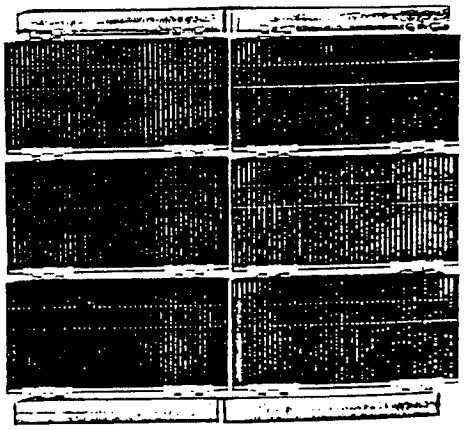


Figure 1 - Six Cell Stack Module

Table 1 - Solar Cell Power Test Results

Cleaning Agent	LAPSS or CSSS Source Power Method	14 or 30 Day Humidity Exposure	% Power (Watts) Change After Humidity Exposure	Notes
ALPHA 2110	LAPSS	30	-26.8 to 23.58	Some cells showed visual signs of corrosion/discoloration
Ambient IPA	LAPSS	30	-5.51 to -4.12	No signs of corrosion
60 °C IPA	LAPSS	30	-3.87 to 2.97	No signs of corrosion
Genesolv DES	LAPSS	30	-9.8 to 9.8	No signs of corrosion
No Cleaning	LAPSS	30	-20.13 to 49.09	Cells were visually corroded and delaminating
Genesolv DES ('95 Run)	CSSS	14	-5.5	Cells showed signs of worming corrosion
60 °C IPA ('95 Run)	CSSS	14	2.04	Cells showed minor worming corrosion
AK-225	Not Performed	N.A.	N.A.	Caused greater coverglass delamination than Genesolv DES.
Genesolv DES ('96 Run)	CSSS	14	-0.58	No signs of corrosion, minor coverglass delamination
60 °C IPA ('96 Run)	CSSS	14	-0.54	No signs of corrosion, No coverglass delamination.
AK-225AES	CSSS	14	-0.60	No signs of corrosion, equal coverglass delamination to Genesolv DES
Vertrel SMT	CSSS	14	-0.49	No signs of corrosion, Slightly more coverglass delamination than Genesolv DES

Even though there was considerable data scatter in the 1994 power test results, visual examination of the tested cells supported previous corrosion concerns regarding the use of aqueous and semi-aqueous cleaning agents for solar cell defluxing. The power results of the Alpha 2110 cleaned samples exhibited more scatter than the IPA and Genesolv DES cleaned specimens, and the Alpha 2110 samples showed more signs of visual corrosion that the IPA and Genesolv cleaned cells. In addition to the corrosion concerns, the Alpha 2110 process (wash, one to two rinses plus a drying operation) was viewed as more cumbersome than the single step IPA and Genesolv DES processes. As a result of the corrosion and process floor space issues, scale-up testing on aqueous and semi-aqueous cleaning agents was discontinued after 1994.

drying challenges for the first defluxing operation. After the solar cell cover glasses are bonded, the cells are soldered together in strings to form solar cell modules as large as 2 x 4 feet in total dimension. The solar cells in the flat module format require a large cleaning chamber and are difficult to handle and clean without causing substrate damage.

TRW's Power Sources Manufacturing Department uses 400 to 660 gallons of Genesolv DES each year to remove flux residues from solar cells during the fabrication of spacecraft solar arrays. Studies were initiated in 1992 to target possible aqueous and semi-aqueous cleaning systems suitable to replace Freon TF mixtures in TRW's solar cell defluxing applications (Reference 1). The aqueous and semi-aqueous cleaning agents were screened by visually inspecting the cells for flux removal and substrate damage. The ionic residue of cleaned cells were also measured using an ionograph. One of the cleaning agents tested visually did not completely remove the flux from the solar cells and was eliminated early from the 1992 study. All of the remaining cleaning agents cleaned well enough in the ionograph screening tests to reduce the ionic residue below 1.5 milligrams/square inch, but two of the cleaning agents were dropped as candidates due to substrate compatibility problems. The two agents attacked the silicone coverglass and solar cell bond and caused the coverglass to partially delaminate from the solar cell. Upon completion of the 1992 study, one aqueous (Alpha 2110) and three semi-aqueous cleaners (Loncoterge 155, Aquanox 101, and Ionox FC) were identified as candidate replacement cleaning agents. After reviewing the health, safety and handling issues related to the selected cleaning agents, it was determined that the aqueous cleaner (Alpha Metal's Alpha 2110) presented the fewest implementation issues and was selected as the primary candidate to test in the 1994 scale-up testing.

As part of the 1994 effort, scale-up testing was performed on cells cleaned using various aqueous cleaning and rinsing operations. Though the 1992 screening tests were promising, continued concerns were expressed regarding the possible corrosion impact that aqueous and semi-aqueous cleaning could have on the solar cells given their inherent galvanic properties. As a back-up candidate for the solar cell application, isopropyl alcohol (IPA) and AK-225 cleaning procedures were added to the 1994 test matrix. Humidity and power testing where also introduced into the test plan in order to determine the possible long term corrosion and performance effects that the cleaning agents might impose on the cells. Either a Large Area Pulse Solar Simulator (LAPSS) or a Continuous Source Solar Simulator (CSSS) source was used to measure the power output of solar cells both before cleaning and after exposure to a warm, humid (45 °C 95% relative humidity) environment for 14 or 30 days. The results of all of the solar cell power tests can be found in Table 1.

All of the Alpha 2110 cleaned cells were cleaned using a 4% (by volume) mixture of Alpha 2110 sprayed at 60 °C. The 6-cell modules were then spray rinsed in deionized water (at 13 MΩ·cm resistance & 60 °C) followed by air or oven drying, or were subjected to a second rinse operation using an ambient IPA spray and air drying operation. Two IPA cleaning processes (ambient spray and 60 °C spray) followed by ambient air drying operations were also tested using the 6-cell LAPSS source power test and visual examination procedures. In addition, a 6-cell standard cleaned in the existing defluxing system was tested as part of the 1994 test matrix. Straight AK-225 was eliminated from the test matrix prior to power testing, because the solvent caused more solar cell/coverglass delamination than the Genesolv DES solvent.

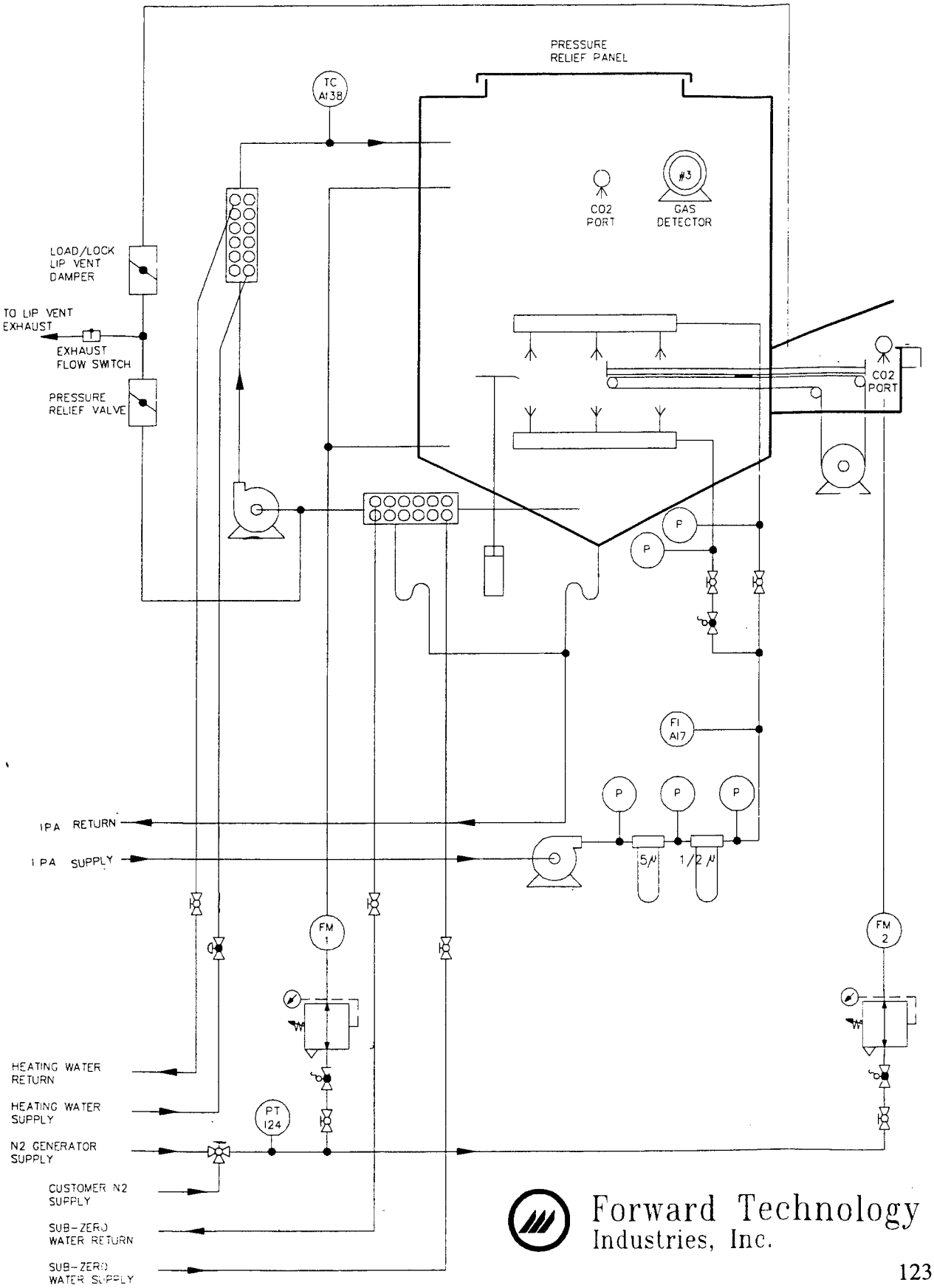
Because the 1994 scale-up power/corrosion test results (performed using LAPSS source power testing procedures on 6-cell modules) were scattered, a review of the test procedures was performed prior to continuing 6-cell LAPSS source power testing in 1995. Upon review of the testing procedures, it was determined that some of the data scatter was the result of poor solar cell quality combined with variations caused by the 6-cell module configuration and extended exposure to the humid test environment. To resolve these issues, the 1995 and 1996 power testing procedures were changed to single cell power tests using CSSS source power test procedures, flight qualified solar cells, while limiting the humidity test exposure to 14 days. To compensate for varying solar cell quality, base-line samples cleaned in Genesolv DES and warm IPA were run with each '95 and '96 test lot in order to obtain relative comparison data of the proposed cleaning materials, and the Genesolv DES and IPA test results for the '95 and '96 test runs are reported separately in Table 1.

In an attempt to eliminate the solar cell cleaning operations, the viability of using "no-clean" flux materials was also investigated in 1994. The results of the 1994 no-clean flux residue study showed that no-clean flux residue left on the solar cell surfaces inhibited the cure of the coverglass adhesive. Though the "no-clean flux" material was renamed to "low-residue flux", the investigation also identified IPA as an acceptable cleaning agent for the low-residue flux. At the present time, low-residue fluxes have not been qualified for TRW soldering applications. If the low-residue flux materials are qualified, they are expected to have limited implementation and are not expected to completely replace RMA flux for all of TRW's soldering operations. As a result, RMA flux was the only base contaminant used for the Genesolv DES replacement study. Since IPA was identified as an acceptable low-residue flux cleaning agent, it is assumed that any system qualified to clean the RMA flux will also be able to sufficiently clean solar cells contaminated with the low residue flux materials if they are qualified at a later date.

In 1995, CSSS source power testing was used as a final check to qualify warm IPA prior to proceeding with equipment quote requests for the required capital equipment. Based on the 1994 and 1995 visual and power test results, neither the ambient or warm IPA systems pose a corrosion hazard. Due to drying problems, the ambient IPA process was shown to have a greater tendency to leave drying spots on solar cells than the warm IPA spray process. Based on the visual results, the warm IPA spray process cleaned as well as the existing Genesolv DES vapor process. Unfortunately, warm IPA cleaning posed fire safety hazards and environmental concerns that never had to be addressed with the existing non-flammable process.

Due the flammability of IPA (NFPA Class 1B Flammable material) the existing Genesolv DES vapor degreasing equipment could not be used to implement the selected IPA cleaning process. In addition, equipment was also needed to control IPA emissions, because it is also classified as a Volatile Organic Compound (VOC). An equipment specification was generated and a procurement activity initiated in late 1995, to identify a source of equipment which would safely handle the warm IPA spray process and would limit IPA emissions to the environment (not to exceed 14 gallons/month). A purchase order was placed in February of 1996 for a system designed to handle the cleaning of 2 x 4 feet solar cell modules. A piping diagram of the proposed cleaning chamber is shown in *Figure 2.

Figure 2 - Chamber Piping Diagram of Proposed IPA Spray System



Forward Technology Industries, Inc.

The solar cell modules will be loaded into the loading drawer area of the equipment and the equipment loading area door will be closed. Upon initiation of the cleaning cycle, the loading area will be purged with nitrogen before the parts rack is automatically transferred into the cleaning chamber. The solar cells will then be sprayed for up to 2 minutes on both sides with warm IPA, followed by a circulating IPA vapor drying and condensing operation. Once the IPA concentration within the cleaning chamber falls below 0.2 %, the loading rack is transferred back into the loading chamber and the cleaning cycle is completed.

As a result of parallel 1995 and 1996 test efforts, TRW's Electronic System & Technology Division (ES&TD) approved and is implementing AK-225AES for printed circuit board (PCB) defluxing applications. Since large quantities of AK-225AES will be available at TRW for PCB applications and the mixture was thought to less aggressively attack to silicones than the straight solvent, a small effort was pursued in 1996 to qualify the AK-225AES and Vertrel SMT cleaning materials as back-up or alternative cleaning solutions for solar cell assembly applications. Visual examination of the solar cells under ultraviolet light (*Figure 3) was used determine if flux was removed using the candidate cleaning processes, and CSSS source power testing and humidity testing were performed on single cells cleaned in the noted cleaning agents. Based on the results of the power (Table 1) and cleanability tests, the AK-225AES material is under consideration as an acceptable alternative for solar cell defluxing applications.

Due to high cost and to the future production cut-off date of the AK-225 products, the warm isopropyl alcohol process is being pursued as the long term solution to both of the solar cell defluxing operations. Because of the configuration of the solar cells in the cassettes, it is questionable whether the module cleaning equipment will be able to clean and dry the cells in the cassettes sufficiently such that the coverglass bonding operation can be performed without having to spot check and hand wipe the cells. Visual examination of cells cleaned in standard IPA vapor drying systems have shown that higher operating temperatures of this type of equipment will clean and dry the solar cells in the cassettes equally as well as the Genesolv DES vapor cleaning system. Due to limited floor space it is hoped that the incoming solar cell module IPA spray cleaning system will be able to handle both defluxing operations, but representative solar cell cassette tests will not be able to be performed until the equipment is on line. An investigation is presently underway to determine how to implement the use of AK-225AES in a small degreasing system within the solar cell production area for the solar cell cassettes until either the new system or an alternative system is identified.

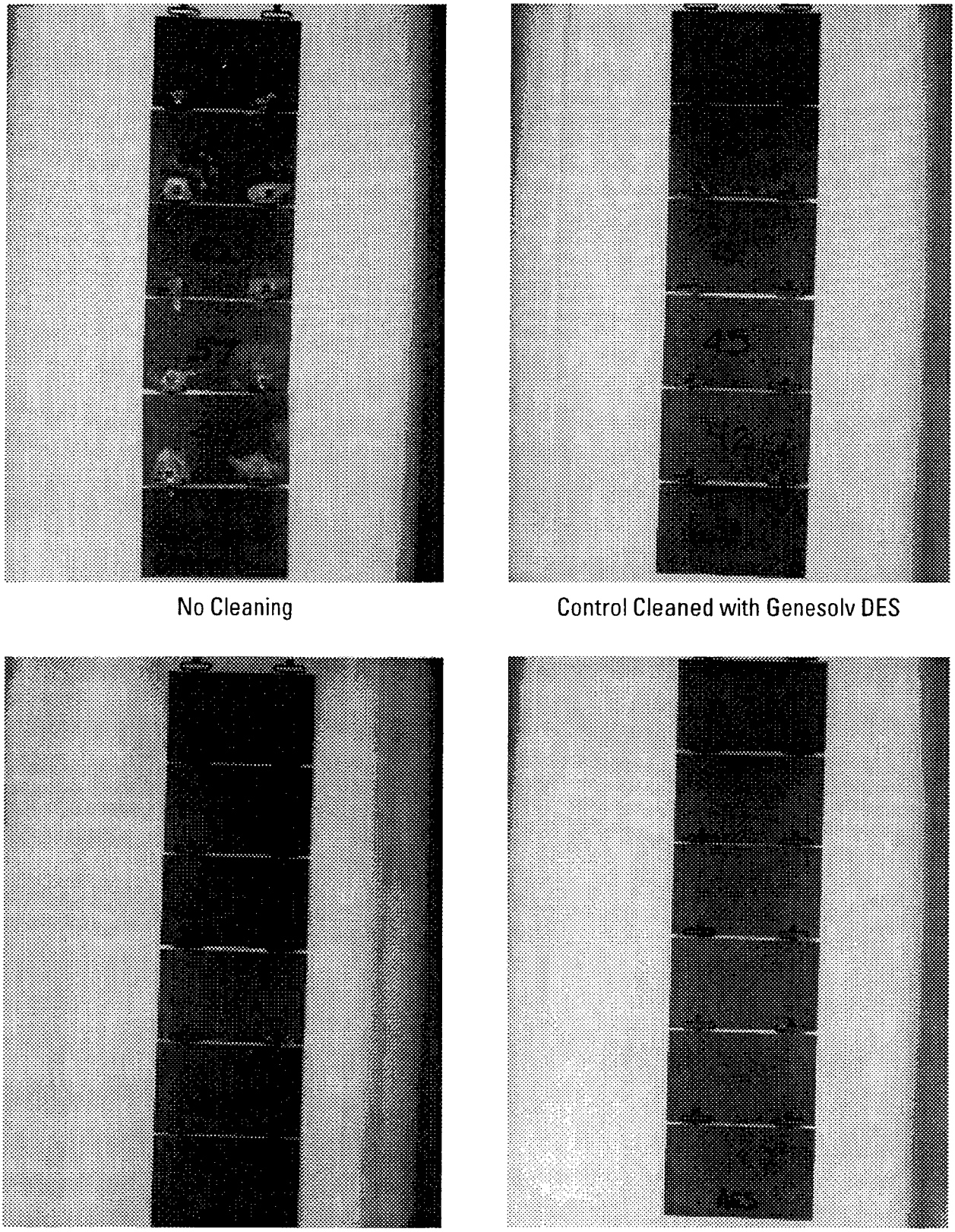


Figure 3. Visual Inspection of Solar Cells Under Ultraviolet Light

Conclusions

Warm IPA, AK-225AES, and Vertrel SMT are all possible replacement candidates for solar cell defluxing operations. Though the initial capital costs are higher for the warm IPA process, it was selected as the replacement cleaning process for the following reasons: 1) it cleans as well as AK-225AES, and Genesolv DES solvents; 2) it less aggressively attacks silicone coverglass bonds than Vertrel SMT, AK-225AES, or Genesolv DES; 3) it is significantly cheaper than CFC, HCFC, and HFC products and 4) it presents fewer substrate corrosion and process implementation concerns than aqueous or semi-aqueous cleaning systems. The selected warm IPA spray cleaning process is expected to clean solar cell modules as well as the existing Genesolv DES vapor cleaning process with fewer substrate damage concerns. Until the new equipment is on line and is available for testing, it is presently planned to use an AK-225AES spray and vapor cleaning process to clean solar cells prior to coverglass bonding. If it is determined that the module spray system cannot be used to effectively clean the solar cells in the stack carriers, separate IPA capital equipment will be pursued for cell cassette cleaning configuration.

Acknowledgments

Special thanks and recognition are due to the following individuals and organizations for their support of this project since 1994:

Don Laverty for his diligent work in coordinating and implementing capital and facility modifications for at least four different ODC replacement processes within S&TD's Manufacturing Center. Marshall Cannady of S&TD staff and Linda Kovalcik, Cliff Beggin, & Gailyn Small of the Power Sources Manufacturing Department for documentation support, testing and sample preparation. Forward Technology Inc. of Minneapolis, Minnesota for the supporting equipment diagrams used for this report and presentation. TRW's SHEA Department for coordinating all SCAQMD permitting issues. Mary A. Mercer, James Filar, Tom Estes, and Debbie Lopez of TRW's Materials, Processes & Manufacturung Department for documentation and technical support.

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The Use of IVD Aluminum Coating to Replace Cadmium Platings

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ABSTRACT

The McDonnell Douglas Corporation's (MDC) Ion Vapor Deposition (IVD) of Aluminum coating process is a viable substitute for cadmium plating finding wide use throughout the DoD repair/maintenance community. Cadmium is a toxic metal, a suspected carcinogen, and on the EPA 17 hazardous materials list for reduction or elimination from the workplace. Cadmium waste streams arise from several maintenance operations: paint stripping (depaint media contaminated with cadmium), cadmium stripping, and cadmium plating. Once cadmium escapes into the environment, it can find its way into the water supply or food chain. In September 1992, OSHA issued an Expanded Standard which restricted the permissible exposure limits (PEL) to cadmium dust thereby increasing regulatory record keeping, medical surveillance, and cost for protection of workers above the Expanded Standard's action level. In contrast, aluminum and the IVD aluminum coating process are environmentally clean and worker friendly. Aluminum dust is nontoxic and is regulated only at the "nuisance dust" level by OSHA. To eliminate cadmium usage, MDC has assisted the Air Force, Navy, Marine, and Army repair/maintenance facilities with equipment recommendations, equipment installation, and operator and maintenance training on both the coating process and equipment. In addition, MDC contracted with the Sacramento Air Logistics Center (ALC) and with the Warner Robins-ALC to eliminate the use of cadmium. The Ogden-ALC has contracted MDC to evaluate IVD aluminum coating, zinc-nickel platings, and a SermeTel coating for replacement of cadmium plating in landing gear overhaul operations. Currently, MDC is evaluating cadmium replacement with IVD aluminum on the C-17 and has started a program to improve IVD aluminum coating process affordability through process cycle time reduction and updating equipment to state-of-the-art configuration. The MDC presentation will discuss program activities and accomplishments directed at cadmium elimination.

INTRODUCTION

McDonnell Douglas Aerospace (MDA), a division of MDC, pioneered the development of the IVD aluminum coating process. In the mid-1960's MDA began experimenting with a new vacuum coating concept initially studied by Mr. D. M. Mattox, Sandia Corporation. As a result of MDA's equipment and process refinements and extensive testing of the IVD aluminum coating process, MDA was awarded a contract in 1973 to fabricate a production coater for use at the Naval Air Rework Facility at North Island, California. During this contract, MDA upgraded the coating process/equipment from a small laboratory 18-inch bell jar coater with two evaporators to a large production coater 4 feet in diameter by 8-feet long with multiple evaporators. The coater was successfully installed in 1974.

In 1977, MDA completed an IVD aluminum coater for the Air Force Materials Laboratory, Manufacturing Technology Division. This coater was 6 feet in diameter and 10-feet long and was used to optimize parameters and fixturing for coating both aircraft and engine parts. This coater was successfully installed at the Ogden-ALC (OO-ALC) for the coating of landing gear components.

During this time, MDA was a major contributor to the development of the Tri-services Mil-Spec (MIL-C-83488) for both application and inspection of the IVD aluminum coating. MIL-C-83488 was issued in August 1977.

During the mid-1970's, MDA introduced the coating process into our production shop as an alternative to cadmium plating on steel and anodize on aluminum. Production utilization of the IVD aluminum coating process started in September 1977 and continues uninterrupted to the present. The first production coater had a coating zone

nominally 10-feet long by 6-feet wide by 12-inches deep. The coater had twelve evaporators and was used for many years coating such large diverse parts as F-15 aluminum wing skins measuring about 9 feet tip-to-tip by 5.5-feet wide, 10-foot long F-18 wing spars, and F-18 bulkheads nominally 8-feet long by 5-feet wide and 7-inches deep.

In the late 1970's, IVD aluminum had established itself as a better coating process than anodize on fatigue-critical, high-strength, aluminum-alloy parts. Unlike the anodize process, the IVD aluminum coating process does not decrease the fatigue strength of high-strength, aluminum-alloy parts. Therefore, it was selected to replace anodize on fatigue-critical components for the new Navy F-18 aircraft. In addition to eliminating the fatigue debit associated with the use of anodize, the aluminum coating provided good corrosion resistance and paint adhesion on these high-strength, aluminum-alloy parts. For the F-18 program, MDA redesigned the production coating equipment utilizing the lessons learned from the Navy, Air Force, and MDA's first production coater. The new coater was 6 feet in diameter and nominally 12-feet long. The coater utilized a removable parts-holding rack with a coating area of 50 square feet (5-feet wide by 10-feet long) and capable of coating parts up to 14-inches deep, or even larger in diameter with a rotary rack. The new coater utilized seven evaporators instead of 12. Other features included better evaporator cooling, pressure control system, pressure gauges and monitors, and improved electronic controls. All of these factors improved the coating quality, equipment reliability, and overall productivity.

Beginning in the late 1970's, MDA began marketing the IVD aluminum coating process/new coater to both industry and military repair/maintenance facilities. To eliminate cadmium usage, MDA assisted the Air Force, Navy, Marine, and Army repair/maintenance facilities with equipment recommendations. Then, MDA fabricated the coaters, installed them, and trained operator and preventative-maintenance personnel on the use of the IVD aluminum coating process and equipment operation/trouble-shooting/repair. During the subsequent years, MDA successfully installed over 60 IVD aluminum coaters worldwide. In November 1987, MDA sold the manufacturing rights to the equipment and process to Abar Ipsen, Bensalem, PA and provided technical assistance and training for Abar Ipsen personnel for about a year. As MDA did, Abar Ispen provides service to existing owners of the equipment, provides modernization packages, and continues a program for developing improvement to the process equipment. Now, all Air Force, Navy, Marine, and most Army repair/maintenance facilities have one or more IVD aluminum coaters.

Although MDA is no longer involved with manufacturing of the equipment, MDA has remained active in promoting usage of the environmentally friendly, IVD aluminum coating process as a direct substitute for the hazardous, waste-generating, cadmium plating process. In February 1988, MDA was awarded a three-phase contract, C87-101602 titled "The Substitution of IVD Aluminum For Cadmium," from the Air Force Engineering and Services Center, Tyndall AFB, FL. This effort demonstrated IVD aluminum coating as a direct replacement for cadmium plating with full implementation at the Warner Robins ALC (WR-ALC). In May 1993, MDA was awarded a two-year contract, F04699-92-R-0114 titled "Ion Vapor Deposition Aluminum Qualification Tests," to qualify IVD aluminum coating as a replacement for cadmium platings at the Sacramento ALC (SM-ALC). This contract was completed successfully in 1995. In addition, smaller service/training contracts were awarded for IVD activities at the OO-ALC, San Antonio ALC (SA-ALC), and WR-ALC. In October 1993, MDA was awarded a contract, F08635-94-C-004 titled "Determination of the Effectiveness of Non-Chromated Conversion Coatings For Use With IVD Aluminum Coatings." This effort was completed successfully in June 1995.

Currently, MDA is working on an Air Force/Systems Research Laboratories, Inc. (SRL) contract, F33601-94-DJ018 titled "Elimination of Environmentally Hazardous Materials from the Landing Gear Overhaul Process." This effort will evaluate IVD aluminum coating, zinc-nickel platings, and a SermeTel coating for replacement of cadmium plating in landing gear operations at OO-ALC. Also, MDA is evaluating cadmium replacement with IVD aluminum on the C-17 and has started an in-house program to improve IVD aluminum coating process affordability through process cycle time reduction and updating equipment to state-of-the-art configuration. This paper will discuss the above contracts and program activities and accomplishments directed at cadmium elimination. However, all discussions of necessity will be brief. The reader is encouraged to contact the writer for additional details/discussions concerning any program or for copies of reports on contract activities.

BACKGROUND

Cadmium is a toxic metal, a suspected carcinogen, and on the EPA 17 hazardous materials list for reduction or removal from the workplace. In September 1992, OSHA restricted the PEL to cadmium dust which greatly increased regulatory record keeping, medical surveillance, and cost for protection of workers above the Expanded Standard's action level. On the other hand, both the aluminum coating and IVD coating process are environmentally clean. Aluminum is low in toxicity and safe to handle, store, and dispose of with standard shop practices. Aluminum dust is nontoxic and is regulated only at the "nuisance dust" level by OSHA.

There are inherent advantages to the substitution of IVD aluminum for cadmium, in addition to hazardous waste reduction and safe worker exposure. IVD aluminum outperforms cadmium in preventing corrosion in acidic environments and actual service tests. Also, aluminum coatings can be used at temperatures up to 950°F, whereas cadmium is limited to 450°F. IVD aluminum coatings can be applied to high-strength steel without fear of hydrogen embrittlement. Aluminum coatings can be used in contact with titanium without causing solid-metal embrittlement, and they can also be used in contact with fuels; cadmium is prohibited for these applications. Additionally, IVD aluminum can be used in space applications, whereas cadmium is limited because of sublimation.

The soft, ductile IVD aluminum coating has properties almost identical to pure aluminum. Therefore, the use of IVD aluminum is also well suited for aluminum-alloy details providing excellent corrosion resistance, good electrical conductivity, and elimination of the fatigue debit associated with anodize coatings. MDA uses IVD aluminum to protect hundreds of different, aluminum-alloy parts on the F-15, F/A-18, and AV-8B aircraft. IVD aluminum is highly conductive and remains so in service when treated with a standard chromate conversion coating. IVD aluminum-coated fuel and pneumatic line fittings provide a conductive path across bonding joints dissipating static electrical charges generated by fluid or air flow. IVD aluminum replaces electroplated tin to provide a low-resistance path at the interface with other components for electromagnetic interference capability (EMIC).

The IVD aluminum coating is applied in production coating equipment called Ivadizers®. The basic equipment consists of steel vacuum chamber, a pumping system, fixturing to hold the parts, an evaporator power supply, and a high-voltage power supply, Figure 1. A typical IVD coater with IVD aluminum parts suspended from hooks on the substrate holder, parts rack, is shown in Figure 2. In this figure, the parts rack has been moved partially out of the coater onto the parts rack air-flotation dolly in front of the open IVD aluminum coater.

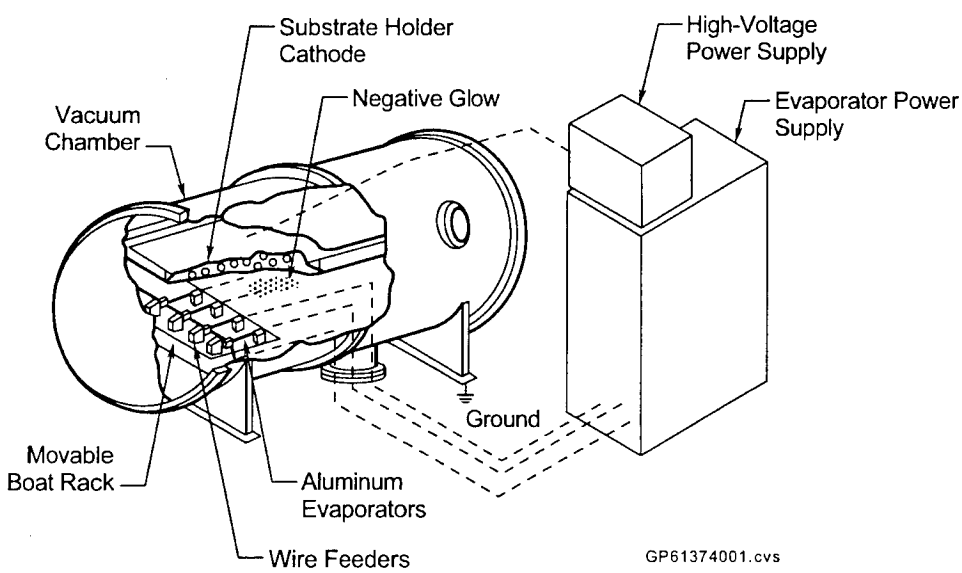

Figure 1. Schematic of an Ion Vapor Deposition System

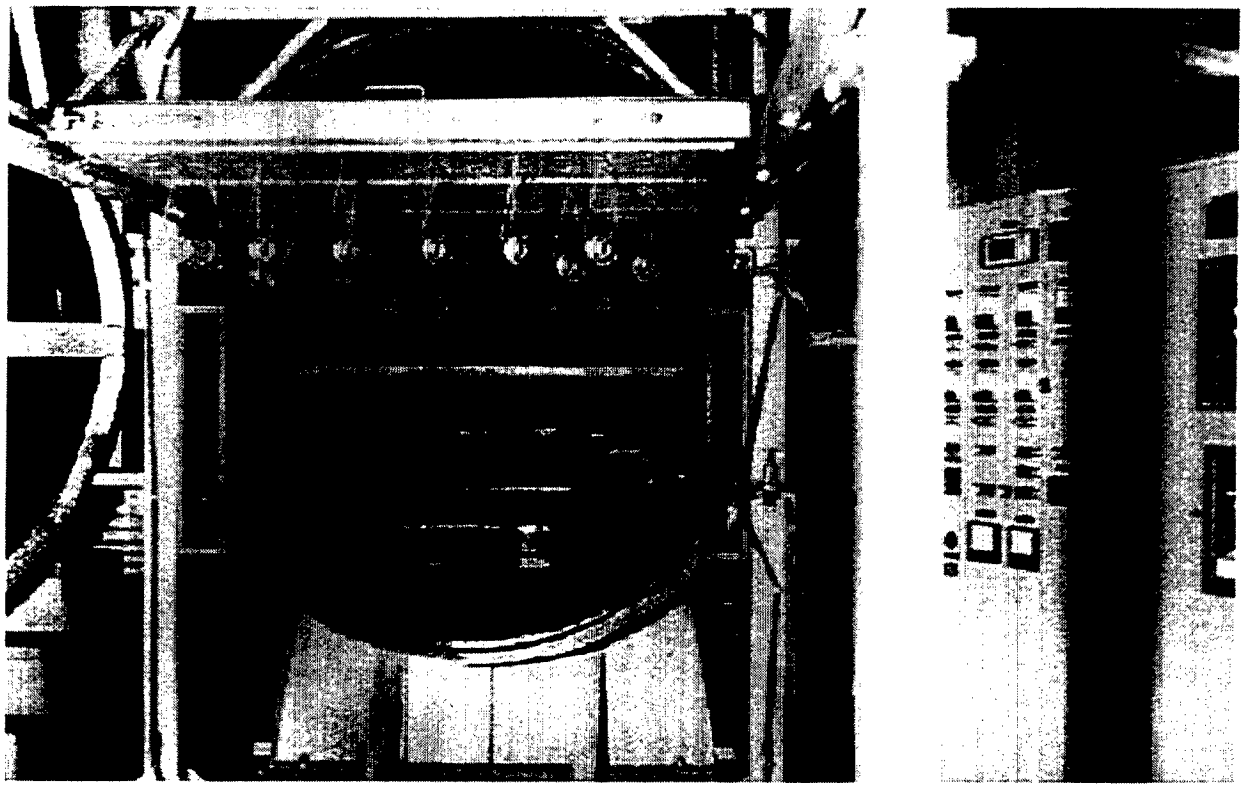

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Figure 2 - Typical IVD Aluminum Coater With IVD Aluminum-Coated Parts Suspended From the Parts Rack

The IVD processing sequence consists of pumping the vacuum chamber down to about 9 x 10 Torr. The chamber is then backfilled with argon gas to about 1.0 x 10 Torr, and a high negative potential is applied between the parts being coated and the evaporation source. The argon gas becomes ionized and creates a glow discharge around the parts. The positively-charged gas ions bombard the negatively-charged surface of the parts and perform a final cleaning, which contributes to good coating adhesion.

Following glow-discharge cleaning, aluminum wire is evaporated by being continuously fed into resistance-heated crucibles. As the aluminum vapor passes through the glow discharge, a portion of it becomes ionized. This, in addition to collision with the ionized argon gas, accelerates the aluminum vapor towards the part surface, resulting in excellent coating adhesion and uniformity.

The coating requirements for IVD aluminum are specified in MIL-C-83488, the Tri-service Specification for pure aluminum coatings. Table 1 defines the coating thickness classes and minimum corrosion resistance requirements for these classes per MIL-C-83488. After coating, the parts are chromate-treated in accordance with MIL-C-5541. This provides additional protection against corrosion, forms a good base for paint adhesion, and is a common treatment for aluminum-alloy and cadmium-plated surfaces. In virtually all applications, IVD aluminum can replace cadmium of equal thickness. It can also be applied thicker than cadmium where part tolerance permits; this results in additional corrosion resistance.

Table 1- Minimum IVD Aluminum Coating Thickness Classes and Corrosion Resistance Requirements Per MIL-C-83488

Class	Minimum Aluminum Coating Thickness		Corrosion Resistance in Five Percent Neutral Salt Fog	
	(Inch)	(Microns)	Type I (Hr)	Type II (Hr)
1	0.0010	25.4	504	672
2	0.0005	12.7	336	504
3	0.0003	7.6	168	336

Type I: Without Chromate Conversion Coating
Type II: With Chromate Conversion Coating

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IVD ALUMINUM COATING - REPLACEMENT OF CADMIUM PLATINGS

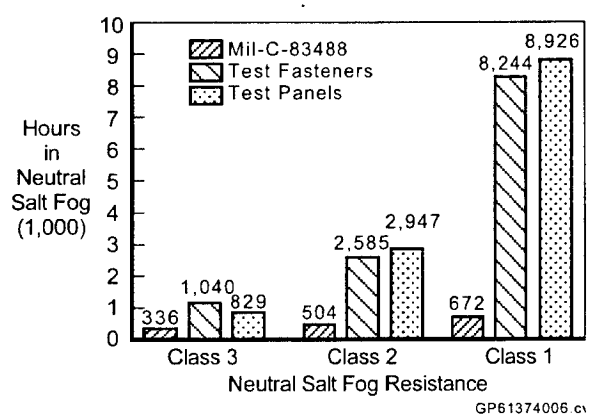
The objective of the Air Force Contract C87-101602, "The Substitution of IVD Aluminum for Cadmium," was to verify that IVD aluminum can replace cadmium processing across-the-board at the Air Force Air Logistics Centers. The thrust of this effort was to reduce hazardous waste generation. This contract was performed in three phases extending from February 1988 to August 1992.

In Phase I, technical information pertaining to IVD aluminum coating and cadmium platings, gathered from both MDA's extensive testing and other military/industrial test sources, was compiled into a database handbook for use by ALC personnel (Reference 1). The database handbook primary sections included:

- Coating Properties
- Corrosion Resistance
- Effect on Mechanical Properties (Substrate)
- Fastener Installation Characteristics
- Coating Versatility
- Rework and Field Repair
- Processing Cost
- Environmental Impact

Each primary section had several subtropics for an in-depth discussion comparing IVD aluminum coating and cadmium platings. As an example, the corrosion resistance of IVD aluminum versus Mil-Spec requirements, Figure 3, shows the average times to failure, red rust, for both IVD aluminum-coated panels and fasteners in a neutral salt fog environments per ASTM B117. For the test panels, there are 148 data points for Class 1, 167 for Class 2, and 56 for Class 3. For the test fasteners, there are 13 data points for Class 1, 257 for Class 2, and 284 for Class 3. An IVD aluminum coating thickness can be selected to meet demanding corrosion resistance requirements. Also, in Phase 1, MDA determined that IVD aluminum could replace cadmium processing without concern for about 80 percent of the ALCs' parts. (Later contracts have shown this percentage to be very conservative with 90-95 percent being more likely.) The database handbook provides the engineer or designer with a valuable tool for a comprehensive comparison between aluminum and cadmium plating for any cadmium replacement purpose.

Figure 3 - Average Test Results Versus Minimum Requirements of MIL-C-83488



In Phase II, data was generated and process development was directed at "area of concern" applications (Reference 2). These include coverage of internal surfaces, lubricity, and, to lesser extent, erosion resistance. Although the IVD aluminum process is not confined to line-of-sight applications, it does have limitations regarding the ability to coat into deep recesses. Generally, the process can be used effectively to coat into a bore or recess for a distance equal to approximately one times the diameter of the opening. Therefore, for parts with a length-to-diameter ratio greater than 1:1 (or 2:1 if open at both ends), the IVD aluminum coating coverage on portions of the internal surface may be inadequate. MDA demonstrated the effectiveness of both sacrificial-type and barrier-type supplemental protection systems for internal surfaces where the IVD aluminum coating thickness could be marginal or inadequate.

During Phase II, NAS1308-10 bolts and 47FLW-820 nuts were used to generate generic torque-tension data for wheel tie-bolts. Torque-tension data was generated for 15 installation cycles of reuse for various IVD aluminum/cadmium bolt finish-nut finish-lubricant combinations. Twenty lubricants/lubricant combinations were

evaluated on the 1/2-inch diameter bolts and nuts either IVD aluminum coated or cadmium plated. MDA did not find any lubrication that performed as well by itself as the baseline MIL-T-5544 synthetic graphite-petrolatum lubricant or MIL-T-83483 molybdenum disulfide-petrolatum lubricant. Then, MDA evaluated the torque-tension characteristics of the baseline lubricants alone and with supplemental dry-film lubricants on actual 5/8- to 3/4-inch diameter wheel tie-bolts for 15 reuse cycles. The torque-tension data demonstrates the acceptability of the use of IVD aluminum on threaded parts with proper lubrication.

MDA also supported the procurement and acceptance of a state-of-the-art IVD aluminum coater for the WR-ALC during Phase II for the Phase III demonstration effort.

In Phase III, MDA demonstrated the acceptability of IVD aluminum coating to replace cadmium platings across-the-board at the WR-ALC (Reference 3). MDA employed a "hands-on" approach working with the responsible departments at the WR-ALC to replace the use of cadmium with the use of IVD aluminum for all parts that were cycled through the WR-ALC plating shop during a 12-month period. The replacement of cadmium with IVD aluminum was accomplished by: assuring all processing equipment needs were available; defining thickness classes and processing steps; establishing Quality Assurance guidelines and tests; verifying environmental compliance; and demonstrating the feasibility of applying IVD aluminum to all parts that had been processed with cadmium. For example, the C-130 Propeller Barrel Assembly is composed of two barrel halves, front and rear, shown IVD aluminum coated in Figure 4. The front barrel half, nominally 16 inches in diameter by 7-inches deep, was coated on the stationary parts rack. However, the larger rear barrel half could not be coated on this rack. These high-volume details had been identified by WR-ALC as an application where special fixturing would improve productivity. Therefore, MDA designed and fabricated a fixture for the rear barrel half, Figures 5 and 6. The fixture attaches the part to the rotary parts-holding rack and masks areas on the part which are not to be coated. To meet production demand, additional fixtures were fabricated by WR-ALC to coat up to eight parts simultaneously on the rotary parts-holding rack.

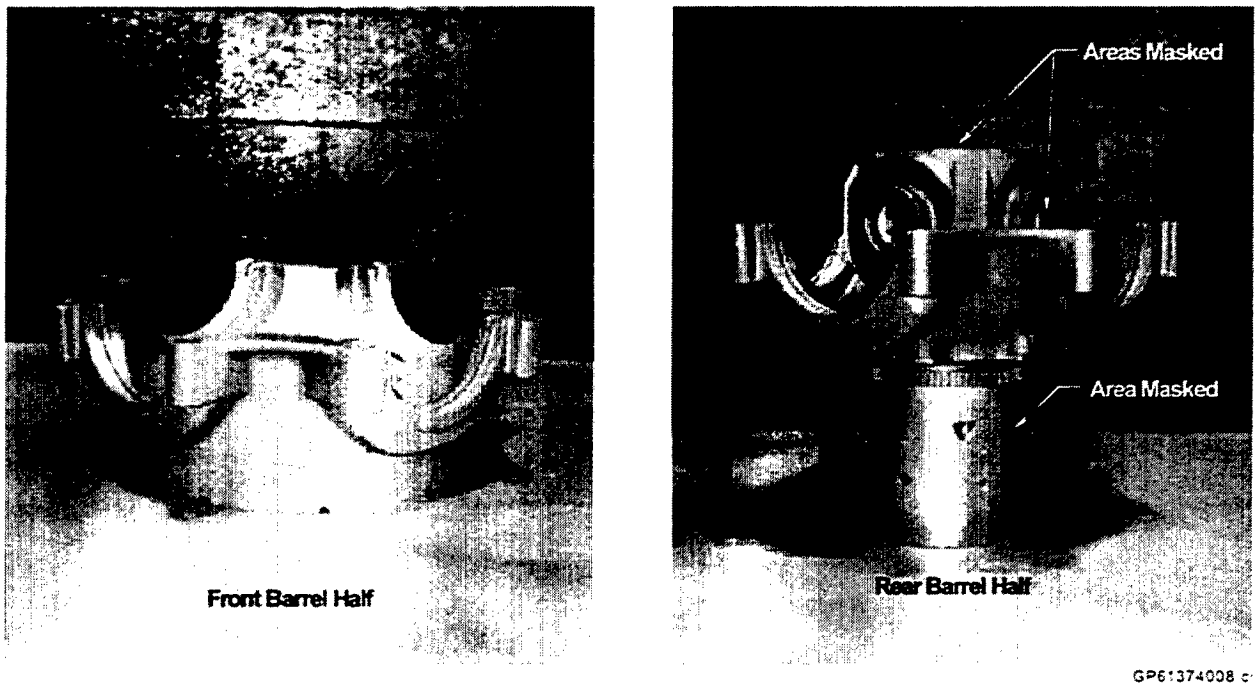


Figure 4 - C-130 Propeller Barrel Halves

During Phase III, the full implementation of IVD aluminum coating at WR-ALC was successfully demonstrated by IVD aluminum coating all parts that were previously cadmium plated and then verifying the coating conformed to the quality assurance of MIL-C-83488. Over 100 cadmium-plated parts were converted to

IVD aluminum coating. As a result of this program, the WR-ALC cadmium plating line was closed on a permanent basis eliminating this hazardous waste stream and its associated problems.

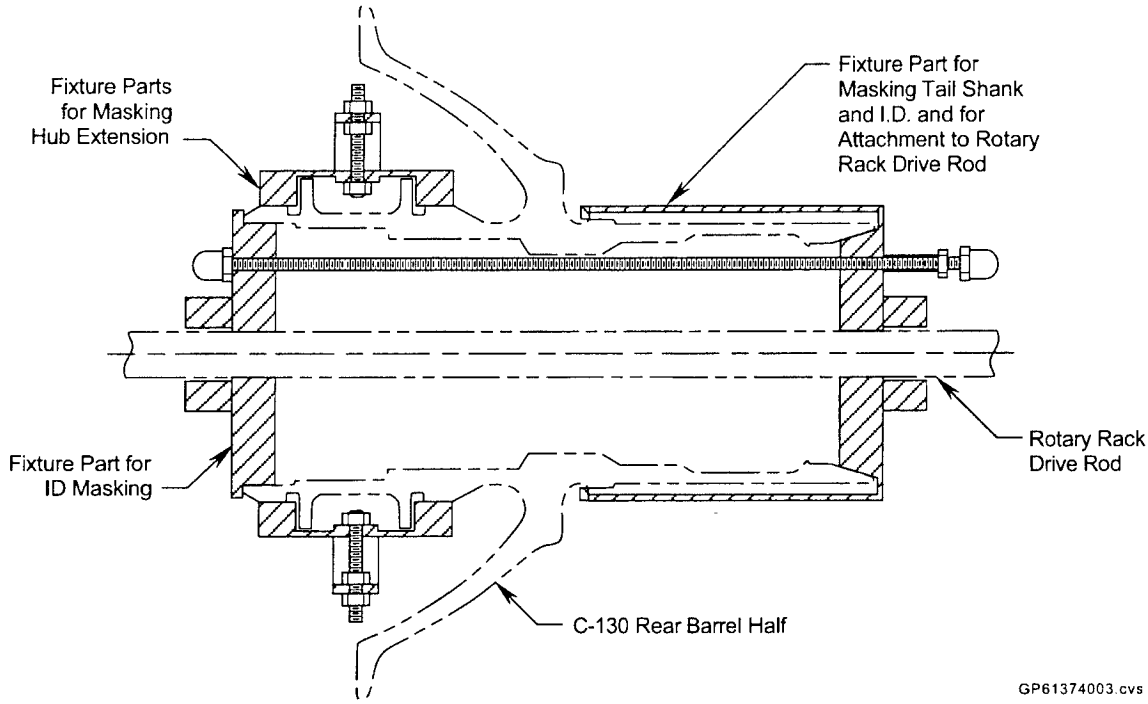


Figure 5 - Fixture/C-130 Propeller Rear Barrel Half Installed on the Rotary Rack

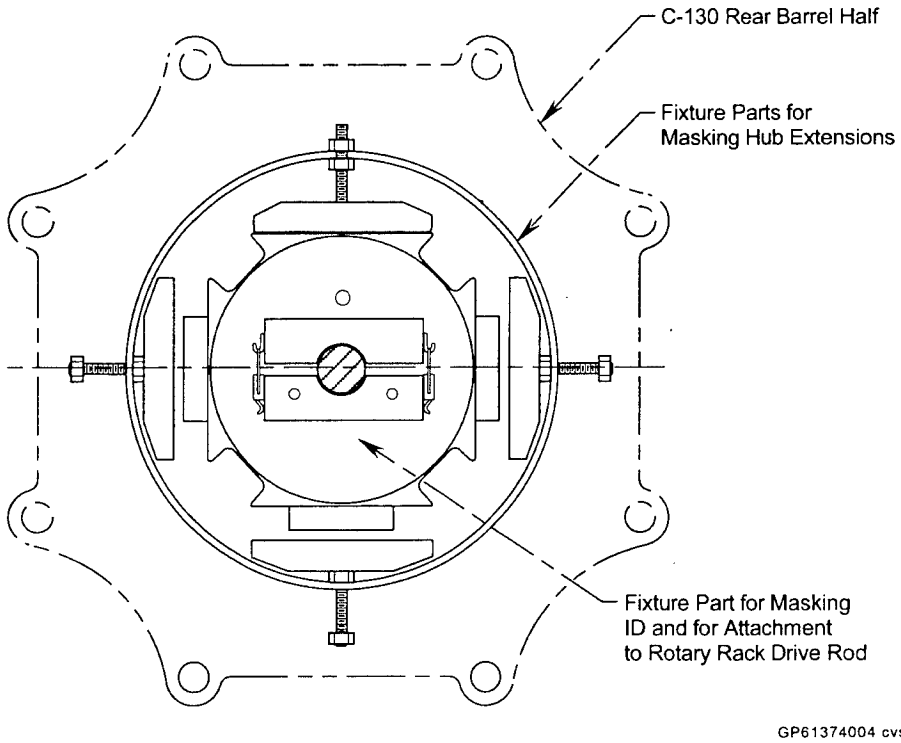


Figure 6 - End View of Fixture/C-130 Propeller Rear Barrel Half Installed on the Rotary Rack

The primary objective of the SM-ALC contact F04699-92-R-0114 titled "Ion Vapor Deposition Aluminum Qualification Tests," was to assist SM-ALC qualification of IVD aluminum coating for the various applications that now require cadmium plating (Reference 4). A secondary objective of this program was to implement the use of IVD aluminum coating on selected aluminum-alloy parts. Accomplishment of these objectives reduced hazardous waste generation by eliminating the waste streams associated with both the application of cadmium and handling of cadmium-plated parts. The program started in May 1993 and was successfully completed in May 1995.

Five tasks were directed at qualifying IVD aluminum for the replacement of cadmium plating at the SM-ALC: (1) evaluating the need for additional support equipment; (2) establishing coating thickness needs for each part's function/operating environment and guidelines for masking, fixturing, and prototype testing; (3) defining Quality Assurance acceptance performance requirements and providing orientation for operator and preventative-maintenance personnel; (4) demonstrating the feasibility of applying IVD aluminum to all detail parts that had been previously processed with cadmium; and (5) verifying environmental compliance.

An important aspect of demonstrating the feasibility of applying IVD aluminum to cadmium-plated parts was to establish production Procedure Cards for each part. High quality finishes result from controlled processes. Control of the IVD process is achieved by eliminating operator variance by having a detailed written procedure for each production part that specifies any specialized cleaning, masking needs/techniques, fixturing directions for part orientation and spacing, and coating parameters. These procedures are recorded in a simple Procedure Card format for operators to review prior to processing the part. Procedure Card use ensures common processing of each individual production part regardless of coater operator or processing frequency.

SM-ALC also requested the Procedure Card information on each part be installed into a computer database in Ashton-Tate dBASE III Plus. SM-ALC created the initial database, screen, and report files for the Procedure Cards. During this contract, MDA wrote and combined five dBASE III Plus computer programs to produce a menu driven program which easily searches the computer Procedure Card database for a specific part. All of the information in the database for a specific part can be viewed at the computer terminal or printed. The database can be searched by the IVD operator and does not require prior knowledge about computer operation or dBASE III Plus. A step-by-step search procedure was written to assist the operator in how to turn on the computer; call up the main Procedure Card Menu; and then proceed to view (or print) the procedure for a specific part number, part name, control number, or all of the Procedure Cards in the database; and then turn off the computer.

The full implementation of IVD aluminum at SM-ALC was successfully demonstrated by IVD aluminum coating virtually all parts that were previously cadmium plated and then verifying the coating conformed to the Quality Assurance requirements of MIL-C-83488. All 214 parts prototyped were coated successfully and released for production coating.

MDA has been awarded several service/training contracts to assist the OO-ALC, SA-ALC, and WR-ALC with specific problems and to train personnel. In June 1994, the WR-ALC contracted MDA to assist them in the process design of fasteners coated with IVD. WR-ALC found that cadmium-plated fasteners were not satisfying the latest dimensional requirements of fastener specifications. Internal and external cadmium plating sources were unable to meet their exacting dimensional thread tolerance requirements. Problems arose because cadmium tank plating is known to build up in high-current-density areas, crest of threads, and thin-out in low-current-density areas, roots of threads. IVD aluminum was demonstrated as being able to satisfy WR-ALC's exacting dimensional thread tolerance needs. Coating techniques were mathematically derived, coating techniques developed, and coating thickness verified by both photomicrograph and beta-backscatter thickness measurements. MDA assisted OO-ALC with the correction of pressure control/coating adhesion problems. MDA demonstrated correct evaporator installation and operation at the SA-ALC solving a major evaporator breakage problem. IVD operator and preventative-maintenance personnel received intensive training on the IVD process at all three ALCs.

The IVD aluminum coating and process is environmentally pristine. For good corrosion resistance and for paint adhesion, the IVD aluminum coating needs a chemical conversion coating as does cadmium plating. However, conversion coatings per MIL-C-5541 contain hexavalent chromium, a known carcinogen. MDA was awarded a contract, F08635-94-C-004, titled "Determination of the Effectiveness of Non-Chromated Conversion

Coatings For Use With IVD Aluminum Coatings," to determine the effectiveness of the use of non-chromated conversion coating with IVD aluminum coating (Reference 5). Following a comprehensive survey for the identification of non-chromated conversion coating, screening tests of candidate coatings were made to identify those having acceptable corrosion resistance, primer adhesion, and contact electrical resistance for additional long-term tests and pilot processing. This effort identified sealing steps II and III of the Sanchem-CC process as functionally acceptable as an alternative to chromate conversion coating and appears to be a viable production process for replacement of the hazardous hexavalent chromium. Alodine 2000 was also a satisfactory alternative to chromate conversion coating, except its performance in acidic salt fog was not as good as the Sanchem process. This 20-month program extended from October 1993 to June 1995.

The Clean Air Act Amendments of 1990 severely restrict emissions of hazardous pollutants such as chromium, cadmium, and volatile organic compounds (VOCs). Since chromium and cadmium present health hazards, PELs and requirements for disposal of hazardous wastes are tightly controlled by OSHA and the Environmental Protection Agency (EPA), respectively. Costs associated with disposal of hazardous waste are extremely high, as are potential liabilities. Unfortunately, the aerospace industry still relies mainly on chromium and cadmium to protect landing gear parts from wear and corrosion.

MDA was awarded SRL contract F33601-94-DJ018 titled "Elimination of Environmentally Hazardous Materials from the Landing Gear Overhaul Process" in October 1995 to identify and evaluate environmental compliant processes to eliminate hazardous waste and personnel safety concerns.

Cadmium is widely used as a sacrificial coating for corrosion protection of steel alloys, and landing gears in particular. It provides excellent corrosion resistance. However, cadmium is easily removed during paint stripping operations, resulting in contamination of stripping media and large volumes of hazardous waste. Because low embrittlement cadmium is a soft, easily removable coating, it contaminates virtually everything it physically contacts (e.g. wiping rags, hydraulic oil, masking materials). The Expanded OSHA Standard for Cadmium is already in effect and puts nearly all overhaul operations at risk of violating action levels and/or PELs for cadmium requiring the use of more stringent overhaul process control, worker surveillance, and record keeping.

One major objective of this program is to investigate, demonstrate, and recommend environmentally acceptable materials and processes that would significantly reduce hazardous waste associated with landing gear manufacturing operations, especially for chrome usage, cadmium plating, and stripping operations. Briefly, only cadmium replacement will be discussed. Cadmium replacements being evaluated are:

IVD Aluminum and Iridite 14-2 chromate-conversion coating
Acid Zn-Ni and Corroban chromate-conversion coating
Alkaline Zn-Ni and Zinic IZ-268S Iridescent chromate-conversion coating
SermeTel CR984-LT and CR985 chromated-seal coating

Low embrittlement cadmium plating, chromate conversion coated, will be the control for comparison of the replacement finishes. Corrosion resistance tests will consist of scribed and unscribed finished panels evaluated in neutral salt spray per ASTM B177 and unscribed finished panels evaluated in acidic salt spray per ASTM G85, A4. Adhesion will be evaluated by bend-to-break tests or appropriate scribed tests. Additionally, any possible hydrogen embrittling potential or fatigue debits associated with the replacement processes will be determined, as well as the repairability, torque-tension characteristics, and paint adhesion of the finishes. Tests have begun.

In the second quarter of 1996, MDA was awarded three C-17 Pollution Prevention projects dealing with cadmium elimination. The projects are: (1) C-17 Pollution Prevention - IVD Aluminum Replacement of Cadmium, (2) C-17 Pollution Prevention - Ion Vapor Deposited (IVD) Aluminum Applicability Improvements, (3) C-17 Pollution Prevention - Non-IVD Aluminum Replacement of Cadmium. Work has just started on these projects.

Project (1) will demonstrate the applicability of the IVD aluminum process as the general replacement for cadmium processing to a sufficient degree for subsequent product implementation for C-17 applications at both OEM and depot locations. This project will also identify those applications, if any, for which IVD aluminum is not feasible. This project will identify and characterize cadmium-plated C-17 parts, define the needs of an implementation plan, perform a production evaluation, and a risk assessment report to use IVD aluminum.

Project (2) will investigate methods to improve IVD aluminum applicability/functionality addressing both C-17 OEM and depot utilization. The project will include the investigation of coating chamber size/C-17 parts size compatibility; evaluate coating densification, internal surface coverage, and surface sealing; optimizing performance with a non-chromated conversion coating; and perform a risk assessment.

Project (3) will investigate non-IVD aluminum replacement processes for cadmium plating for only those applications for which IVD aluminum is not a feasible/suitable replacement or additional alternate solutions is desirable. These applications include: oversize parts, parts with internal surfaces to be plated, and standard parts.

Currently, MDA has a in-house program to improve IVD aluminum coating process affordability through cycle-time reduction efforts, updating existing IVD coaters to state-of-the-art configurations, and adding a larger coater for future production needs.

CONCLUSIONS

The environmentally compliant IVD aluminum coating process is a qualified, demonstrated across the board replacement for topic cadmium plating processes at the WR-ALC and SM-ALC. Full qualification and implementation of IVD aluminum coating has allowed closure of the cadmium plating lines at these two ALCs. IVD aluminum, in addition to other cadmium replacement finishes, contributed to closure of the cadmium plating line at the Oklahoma City Air Logistics Center. In addition, IVD aluminum is finding ever increasing utilization at the OO-ALC and the SA-ALC. Although other cadmium replacement finishes are available, IVD aluminum is expected to be the major contender for replacement of cadmium plating for current program specific efforts directed at identifying environmentally compliant solutions applicable to the landing gear industry and to the C-17. These efforts will most likely accelerate the use of IVD aluminum. Current investigations and equipment modernization efforts are expected to improve process efficiency and meet needs for anticipated production requirements. The development and use of IVD aluminum production Procedure Cards for individual parts and coating verification to the performance requirements of MIL-C-83488 ensures consistent, high-quality coatings that meet or exceed the functional capability of cadmium. The use of IVD aluminum produces a pristine, environmentally friendly, safe finishing system for both today's and the future's demanding corrosion resistant requirements.

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CLEANING: DEVELOPMENTS IN AQUEOUS MEDIA

PROGRAM DEVELOPMENT FOR AN AQUEOUS CLEANING SYSTEM

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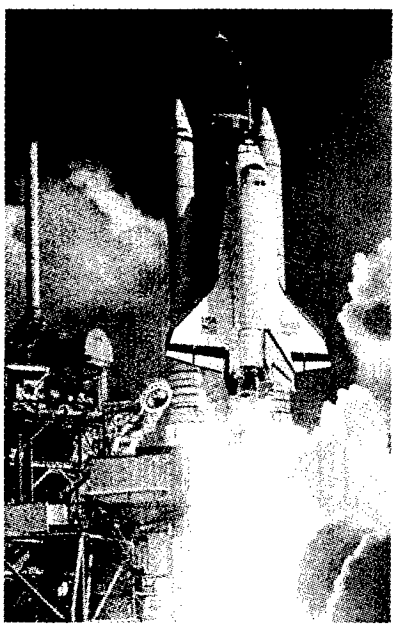
August 1996



ABSTRACT

Process parameters, bath life tests, scale-up parameters, and disposal in municipal water treatment systems were determined for an aqueous cleaner, Brulin 1990GD®. The aqueous cleaner had been selected for cleaning space shuttle reusable solid rocket motor (RSRM) components through a battery of screening tests. Optimized process conditions were determined with a designed experiment program. It was estimated that the cleaner would clean approximately 2.7 RSRM motors with grease and over 10 RSRMs without grease. The cleaner performed well with the adhesives tested and small variations in cleaner concentration did not significantly increase the presence of residual contaminants on test surfaces. Scale-up parameters provided for both small parts and large RSRM components showed that approximately 10 gal/ft^2 of cleaner solution is required to remove grease. Biodegradation tests showed that the cleaner was acceptable in a municipal-type waste water treatment facility.

INTRODUCTION

Thiokol Space Operations manufactures the RSRM at its Promontory, Utah, plant. Past processes have used vapor degreasers with methyl chloroform (TCA). An aggressive program to eliminate TCA was started shortly after the 1990 amendments to the Clean Air Act which mandated the phaseout of TCA production.

The RSRM depends on effective adhesive bonds to ensure quality performance. The largest parts to be cleaned, the RSRM cases, are 12 ft in diameter and 13.5 ft high. Clean surfaces prior to adhesive bonding are essential to robust bonds such as insulation-to-case, insulation-to-liner, and the many other bondlines that hold insulation and instrumentation to the case and nozzle components.

Early investigations of many types of cleaners showed that Brulin 1990GD performed best in subscale simulations of Thiokol's degreasing processes. Process definition for full-scale processes was the next step.

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In addition, it was necessary to know how long the cleaner would perform in the intended application and what chemical changes would occur before the cleaner bath failed. Also, the best method of disposal for the spent cleaner was needed for implementation of the new process.

PROCESS OPTIMIZATION

The process study was conducted to determine which process parameters significantly affect the ability of Brulin 1990GD to remove contaminants. It was found that the following parameters significantly affect one or more of the response variables measured:

- Cleaner concentration
- Cleaner temperature
- Wash pressure
- Wash flow rate

Other parameters varied were not significant or produced mixed signals.

Table 1. Statistically Significant Results Summary

Significant (95% confidence level) Variables and Direction of Effects

Response	Surface	Clean Temp	Clean Conc	Wash Pressure	Wash Flow	Clean Time	Pre-Rinse	Rinse Time	2-Variable Interactions
TDCB Fracture Energy	Steel		↑	↓					
	Aluminum	↑							Temp x Concentration
Panel Tensile	Steel								
	Aluminum	↑	↑	↓	↑		↑		Temp x Concentration Temp x Pressure Concentration x Pressure Temp x Pre-rinse
TDCB Fracture Mode	Steel	↑	↑	↓	↑	↑			Temp x Concentration Temp x Flow Concentration x Pressure Temp x Pre-rinse
	Aluminum	↑	↑						Temp x Concentration Flow x Rinse Time Temp x Flow Concentration x Rinse Time
Panel Failure Mode	Steel						↓		Temp x Concentration Temp x Pre-rinse Concentration x Pre-rinse
	Aluminum	↑	↑						
TDCB Conscan	Steel		↓						Temp x Rinse Time
Panel Conscan	Steel	↓	↓					↓	Temp x Rinse Time
NVR	Steel			↑					Press x Flow
	Aluminum	↓							
%Fe	Steel ESCA								
%C			↓			↓			Temp x Time Concentration x Rinse Time
Si/Zr			↑						Concentration x Pre-rinse
%Al	Aluminum ESCA				↑				Temp x Concentration Temp x Flow
%C		↓	↓	↓					Temp x Flow Concentration x Rinse-Time Concentration x Pre-rinse
Si/Zr		↑	↑						

Early tests showed that cleaning ability increased with cleaner concentration up to 10 percent. Additional tests were conducted with cleaner concentrations up to 30 percent because of the strong correlation of concentration to cleaner performance. A summary of other significant results is included in Table 1.

Process parameters were investigated with tests defined by a one-quarter replicate matrix for process variables which were thought to affect cleaner performance. The following parameters were varied in the process study:

- Temperature
- Concentration
- Cleaner spray pressure
- Flow rate
- Cleaning time
- Pre-clean rinse vs no rinse
- Post-clean rinse time

Steel samples were treated with standard concentrations of Barochem C430®, Magnaglo 20B®, and WA-4®. Both steel and aluminum samples were then coated with a thin film of Conoco HD-2® grease (0.010 $\pm$ 0.002 in.).

Specimens included panels, tapered double cantilever beams (TDCBs), and coupons for electron spectroscopy for chemical analysis (ESCA). Test specimens were then washed in a laboratory parts washer with wash parameters varied according to the test matrix.

A summary of the statistically significant main effects and two-way interactions is presented in Table 1. In Table 1, an upward pointing arrow (↑) means that the response variable (i.e., fracture energy) is increased as the process variable (i.e. cleaner temperature) is increased. A downward pointing arrow (↓) indicates that the response variable decreases as the process variable is increased. Table 1 also lists significant 2-variable interactions.

The data indicate that increased cleaner temperature, increased cleaner concentration, and increased wash flow rate increased adhesive bond strength. Increased wash pressure tends to decrease adhesive bond strength.

Increases in cleaner temperature and cleaner concentration increased the silicate level on the surface as shown by the Si/Zr ESCA response and decreased the organic and grease level as shown by the %C ESCA response.

The minimum rinse time was adequate to remove the detergent from test specimens and additional rinsing showed no benefit. Variations in other parameters produced either mixed responses or affected properties in only one of the 18 response variables.

A pre-clean rinse of greased panels with deionized water at 225 psi removed the majority of grease from the surface of the panel but did not leave a water-break-free surface. A thin film of grease was still detectable when the panels were inspected with black light.

Recommended process parameters are listed below. Although the process study included tests at 110° and 180°F, a cleaner temperature of 150°F was recommended due to equipment and facility considerations. The small magnitude of the effect of cleaner temperature was also a factor in the decision to recommend a lower temperature.

A 3-minute wash time was also recommended over the 6-minute wash time because of the small magnitude of any positive effects for the longer wash time. The longer wash time showed a small positive effect on the steel TDCB failure mode.

- Cleaner temp: 150°F
- Concentration: 10%
- Wash pressure: 70 ± 10 psi
- Flow rate: 2.5 gpm/nozzle
- Cleaning time: 3 minutes
- Pre-rinse yes/no: No
- Post rinse time: 3 minutes
- Nozzle type: Quick VeeJet® 4020
- Nozzle stand-off: 8.5 ± 0.5 in.
- Rinse temp: Ambient (77-113°F)

Additional tests were run with the above parameters at 10, 20, and 30 percent cleaner concentrations to determine the effect of a more concentrated cleaning solution. The panels cleaned with a 20 percent solution showed higher bond strength and fracture toughness. Tests at 10 and 20 percent were conducted in the aging study, but the results were not repeated. The aging study showed a decreased fracture energy at 20 percent cleaner concentration and no significant difference with tensile specimens.

BATH LIFE TESTS

Tests were conducted to determine the number of cycles Brulin 1990GD wash solution can be used before it is no longer able to remove contaminants from RSRM hardware. Tests were conducted both with inspection fluids and with grease to simulate different manufacturing situations.

The Brulin 1990GD bath effectively cleaned 440 cycles of non-greased hardware, or the equivalent to 10 RSRMs. The simulation which included HD-2 grease as a contaminant showed that Brulin 1990GD cleaned 143 cycles before faint black-light indications were apparent on the cleaned panels at cycle 144, the equivalent of 2.7 RSRMs. The presence of the grease in the cleaner did not affect the quality of the adhesive bonds after cleaning. Addition of Brulin 1990GD concentrate to increase overall concentration to 15 percent did not significantly extend the bath life of the spent solution.

Phosphate and grease concentration in the bath of the greased-hardware simulation may be an indicator of imminent bath failure. Chemical parameters to predict the impending failure of a bath with inspection fluids were not identified since the bath did not fail after 440 cycles.

INSPECTION-FLUID TEST

One steel and one aluminum witness panel per cycle were prepared with Barochem C430, Magnaglo 20B, and WA-4 applied to the panels to parallel contaminants in the RSRM refurbishment process. Cleaning of the panels was performed with wash parameters as had been optimized in the process study. Panels were rinsed with deionized water outside the washer and inspected for corrosion, water-break, and with black light.

The test plan was to continue with contamination and cleaning steps until the panels consistently (five cycles in sequence) failed either the water-break test or the black-light inspection. The bath was also to be considered to be depleted if corrosion or excessive foaming was noted. After 399 cycles the cleaning solution was not depleted, the final bond cycles were performed, and the M-52 simulation terminated.

The cleaning solution had been cycled 440 times by the time the final bond samples were cleaned and a total of 10 RSRMs were had been simulated.

Bond specimens were prepared every 25 cycles with Hysol EA 913NA® adhesive. Specimens included one D6AC and one 7075 tensile test panel, one D6AC and one 7075 surface energy coupon, and four pairs of 7075 TDCBs. Bond tests showed that there was no reduction in bond strength throughout the test. Figure 1 is a plot of the fracture energies for aluminum TDCBs for the first 375 cycles. Failure modes were nearly 100 percent cohesive in the adhesive and tensile strengths demonstrated that the surface preparation was generally good for the first 375 cycles.

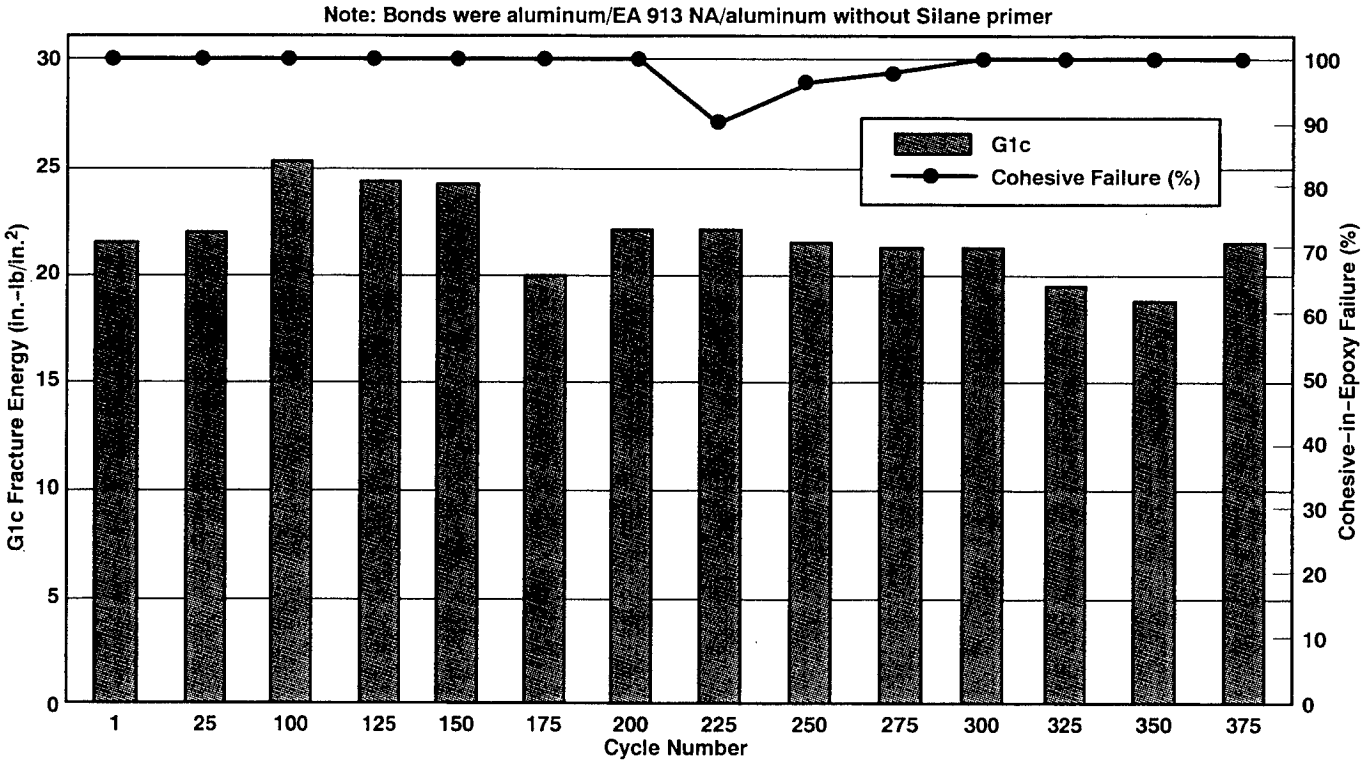


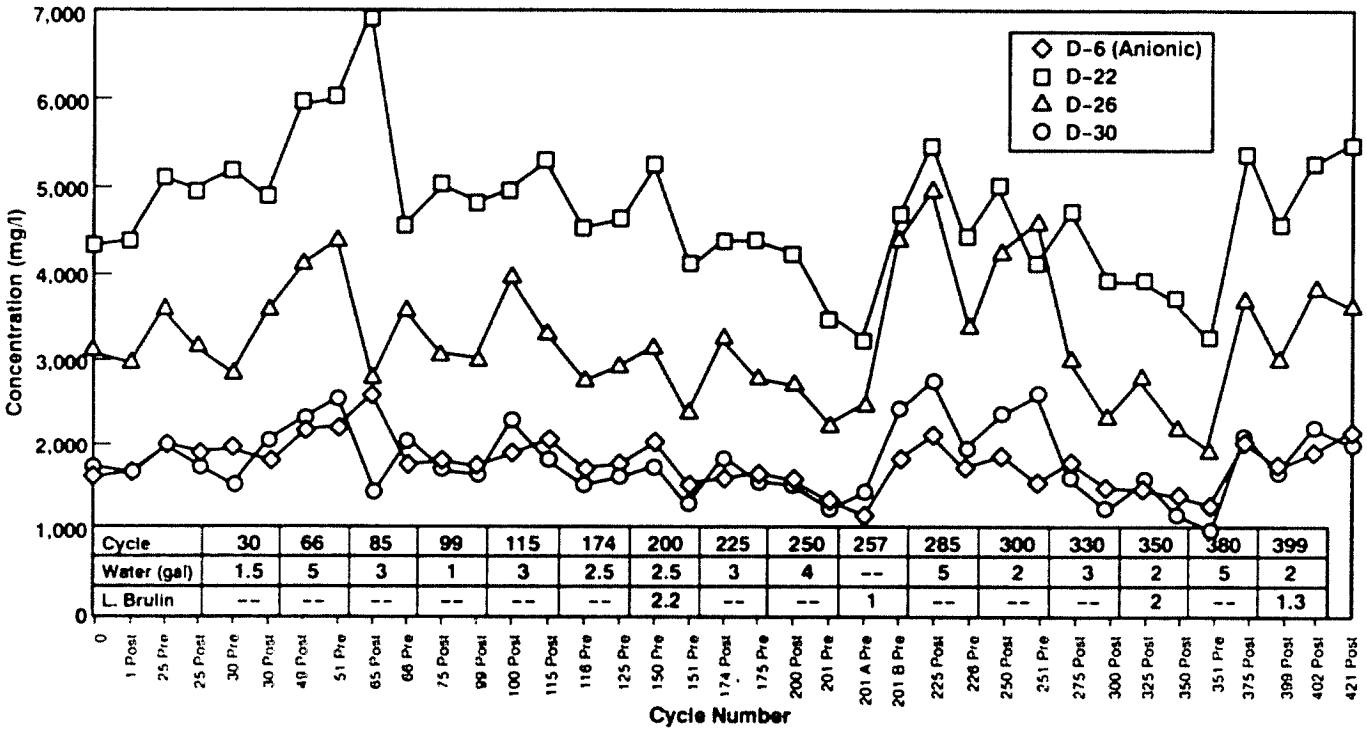
Figure 1. TDCB Bond Data for First 375 Cycles of Inspection Fluid Test

Initially, periodic bond samples were prepared after every 25 cycles, then final bond samples were prepared beginning with cycle 400. Bond values for the final cycles of the simulation showed that the cleaner performed acceptably on the test specimens. Bond and fracture energy values for epoxy adhesives are in the range that would be expected for the adhesives on a clean surface.

NBR insulation panels for the final cycles were cleaned and some coated with 25 mg/ft^2 and others with 50 mg/ft^2 of HD-2 grease before bonding. The addition of the grease to the bondline was to determine if the Brulin 1990GD had increased the sensitivity of the bondline to contaminants.

Failure modes for the NBR panels were 100 percent cohesive in the nitrile butadiene rubber (NBR), as is normal for NBR vulcanized bonds. The aqueous cleaning and Chemlok®-NBR bond process remained robust even with the grease added to the bondline. Data for the ethylene-propylene-diene monomer (EPDM) insulation bondline were also satisfactory.

The detergent concentration varied significantly during the 440 cycles as can be seen in Figure 2. The water level and surfactant concentration of the bath were maintained with deionized water and Brulin 1990GD concentrate, as needed, to compensate for losses.



Cycle	30	66	85	99	115	174	200	225	250	257	285	300	330	350	380	399
Water (gal)	1.5	5	3	1	3	2.5	2.5	3	4	--	5	2	3	2	5	2
L. Brulin	--	--	--	--	--	--	2.2	--	--	1	--	--	--	2	--	1.3

Figure 2. Constituent Concentration for Inspection Fluid Wash Simulation

The addition of surfactant was based on the concentrations of D-8 and D-22 surfactants. The D-8 and D-22 concentrations were good benchmarks for the concentration of the Brulin 1990GD as other components followed the D-8 and D-22 concentrations. Note that codes are used to identify the surfactants in order to protect the manufacturer's proprietary information.

Concentrations of the elements varied consistently throughout the cycles and matched the surfactant peaks of the high-pressure liquid chromatography (HPLC) data. The concentration of silicon, which represents the sodium metasilicate in the cleaner, remained relatively constant throughout the test and was not depleted.

GREASE-LOADING TEST

Panels were treated with Diala Oil®, Mi-glo Mag Fluorescent Particle Solution®, and coated with 10 mils of Conoco HD-2 grease. The test specimens were cleaned as before, with parameters determined in the process study. Black-light indications began to appear in cycles 144-148 in the form of streaks on the

panels, after cleaning. Bond cycles were performed on cycles 149–152 and the Brulin 1990GD concentration increased to 15 percent, based on the concentration of the D–8 and D–22 surfactants. The increased cleaner concentration provided only sporadic cleaning and the test was stopped at cycle 168 after five consecutive failures of the black–light test.

The total amount of grease cleaned off the panels was 3,969 grams, or about 0.6 lb of grease per gallon of cleaner. Analytical tests indicate the cleaner contained about 47,000 ppm of grease. An equivalent of 2.7 RSRMs were simulated in the H–7 process before the cleaner failed.

Skimming to remove oil and grease was not necessary as the grease remained emulsified, even when allowed to cool overnight. It was necessary to change the filters as emulsified grease collected on the filter and caused the pressure differential across the filter exceeded the filter manufacturer's maximum of 30 psi.

Black light was the only inspection which showed that the cleaner had failed in the grease–loading test. All panels passed the post–wash water–break tests. The water–break test did not predict failure of the black–light inspection and is therefore a less sensitive test of cleaner health in this situation.

Foam on the surface of the bath generally did not exceed 0.5 in. as long at the temperature of the bath was maintained above 110°F. No corrosion was noted on the panels and there were no other unusual occurrences.

The 100 percent cohesive failure modes and high fracture energies of the final TDCBs show that the Brulin 1990GD can provide a good bond surface even when the wash solution is so heavily laden with grease that specimens do not pass black–light inspection. Again, the fracture energies and failure modes are well within the range that would be expected for a freshly cleaned surface which was bonded under optimum conditions.

Concentrations of the constituents generally followed the same trend except for the sodium tripolyphosphate (STP). The STP is depleted by the calcium in the grease and was near zero, 33 ppm, when the solution began to fail to clean panels sufficiently to pass black–light inspection (Figure 3).

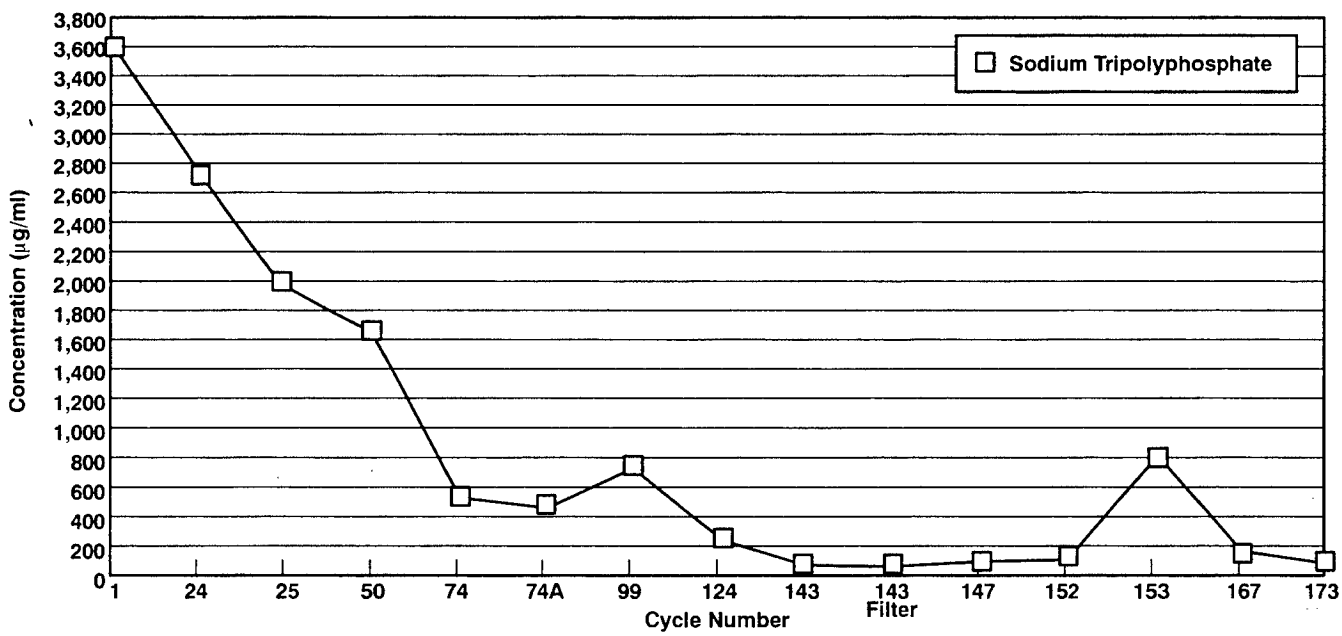


Figure 3. STP Concentration for Grease–Loading Simulation

The alkalinity showed a steady increase due to the calcium soaps that accumulated in the bath with the HD–2 grease. Alkalinity dropped due to the buffering ability of the cleaner constituents when the Brulin concentrate was added to provide a 15 percent solution.

SCALE-UP PARAMETERS

Subscale wash parameters had been established for a single panel 8 by 12 in. It was desired to use data gathered to estimate operational parameters for a larger machine.

The wash parameters temperature, pressure, and concentration were assumed to remain the same for initial runs in the midscale machine. The only parameters which were adjusted were the flow rate and number of nozzles. The number of nozzles was increased to be able to cover the larger part size and the flow rate was adjusted to ensure that the larger parts received the same amount of solution per unit area as the test panels. The flow rate was expressed in terms of wash density was calculated to be 0.070 gal/in.^{2} or about 10 gal/ft^2.

The cleaning time for various parts could be calculated based on the size of the parts and the number of nozzles which would be directed at the part.

DISPOSAL

It was important for Thiokol to determine the treatability of Brulin 1990GD in a sewage treatment plant as all of Thiokol's sewage is treated in on-plant facilities. No large municipal sewage treatment facilities are available for Thiokol's Promontory plant due to the remote location. The concern of treatability is increased because of the relatively low flow in the Thiokol treatment plant and the elimination of the dilution benefit of larger systems.

Thiokol contracted with C.R.M. of Draper Utah to perform a study (Okey, 1995) on the treatability of Brulin 1990GD surfactants in a sewage treatment plant. The biodegradation study included the Brulin 1990GD surfactants D-26, D-22, D-08, and D-30. C.R.M. found that the surfactants were all degraded to beyond detection limits (0.5 mg/l) in 7 days.

An activated sludge system was developed and later switched over to wastewater from Thiokol. The surfactants were tested on the biological system in concentrations of 1.0 to 10.0 mg/l. It was found that the surfactants had half-lives of 0.5 to 2 days with the system.

The half-life of the surfactants may be longer than hydraulic detention time of the wastewater treatment plant, but this should not be a concern because the low residual surfactant concentrations will most likely be associated with cell tissue and not with the aqueous phase.

There was no foaming or other problems noted in the study. The presence of modest levels of surfactants did not appear to have any impact on the chemical oxygen demand removal of the system and all materials were biodegraded.

REFERENCE

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AQUEOUS TUBE CLEANING ADVANCES AT MCDONNELL DOUGLAS AREOSPACE

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ABSTRACT

McDonnell Douglas Aerospace produces tubing for a variety of aerospace uses. Typically these tubes, made from aluminum, stainless steel, and titanium range from 1/4" to 6" in diameter, with lengths up to 40 feet. Prior to 1996, tube bending lubricants were removed using 1,1,1 trichloroethane in a vapor degreaser to flush the tubing. Because of the 1996 deadline for the phase-out of ozone depleting substances (ODC's), an aqueous tube cleaning system was developed using a tank immersion system, which was later changed to an enclosed cabinet system. The design change from the tank system to the enclosed cabinet system provided a savings of $500,000. The enclosed cabinet system operates by connecting tubing to a manifold located inside of the cabinet. Aqueous cleaning solutions are then pumped from enclosed tanks though the tubes at high velocities, and are also sprayed on the outside of the tubes inside the cabinet. The solution then drains through the bottom of the cabinet back to the tank. The cleaning process uses hot water as a pre-rinse, a hot aqueous cleaning solution, hot deionized water as an initial rinse and a final rinse, and a drying stage with warm purified air. Between cycles, clean compressed air purges the remaining solution out of the tubes to prevent solution cross contamination. This system takes operator error out of the tube cleaning procedure. The operator simply loads the tubing into the washer and removes clean dry tubing when the cycle is complete.

This paper discusses: 1) Current tubing configurations and problems, 2) lubricant and cleaner selection considerations, 3) cleanliness level requirements, 4) a comparison between immersion tank and cabinet systems, 5) the performance parameters used in the design process, 6) cabinet system operating sequence, 7) waste treatment, 8) laboratory test data.

INTRODUCTION

The McDonnell Douglas Aerospace (MDA) Tube Manufacturing Center of Excellence in Huntington Beach, CA performs the tube bending, swaging, and tube cleaning operations for a variety of aerospace programs including space vehicles, military aircraft, and commercial aircraft. Tubing to be used for fuel, hydraulic, oxygen or other fluid lines is fabricated, sometimes with multiple bends and complex shapes. The precision bent tubing is installed as flight hardware on space vehicles and aircraft, and must be thoroughly cleaned following processing, and prior to filling the lines with the service fluid. The tubing is usually aluminum, stainless steel or titanium ranging in size from 1/4 inch to 6 inches in diameter, with lengths up to 40 feet. The tubes are bent with a tube bending machine and mandrel using a tube bending lubricant known as Drawsol CW-50 (aka honey oil). CW-50 is a chlorinated parrafin oil that is extremely viscous and difficult to remove. Prior to 1996, tubing bent with CW-50 was cleaned in a vapor degreaser using 1,1,1-trichloroethane (TCA).

Vapor degreasing with TCA was an effective method for cleaning tubing, but the cleanliness of the tubing was strictly dependent on operator effort. The operators had to flush each tube thoroughly with TCA using a hand held spray wand to ensure cleanliness. There were many instances where inspection tagged tubing for not being clean, and the tubing had to be re-cleaned.

Environmental Protection Agency (EPA) regulations prohibited the manufacture of Class 1 ozone depleting compounds (ODC's) like TCA as of December 31, 1995. During 1994 a tube cleaning process team was organized at MDA to develop and implement a new method of cleaning tubing that did not involve the use of TCA or other ODC's. MDA had to decide whether to pursue aqueous cleaning, or to develop a solvent tube cleaning system using another substance. Environmental regulations in southern California dictate that solvent cleaning systems must be completely enclosed. Enclosed solvent systems usually involve the use of toxic chemicals, and require a South Coast Air Quality Management District (SQAMD) permit. Enclosed solvent systems are also, by nature, more difficult to maintain, and are more susceptible to failure than conventional systems. Aqueous cleaning was the most desirable method to pursue from an environmental standpoint. Aqueous cleaning technology has been proven for aluminum parts with simple geometries. Tube cleaning however, is inherently more difficult. The tubes must be thoroughly flushed to remove all contaminants. In an aqueous system they must also be dried. In order to properly flush the tubing, the tubes must be hooked up to a manifold prior to cleaning. Manifolding can be a labor intensive task, since each tube must somehow be connected securely to the manifold. Despite these potential problems, MDA decided to pursue aqueous cleaning rather than solvent cleaning for safety and environmental reasons.

MDA performed a survey of other aerospace tube cleaning processes and determined that aqueous cleaning was possible. Laboratory experiments also indicated that cleanliness levels as good or better than vapor degreasing with TCA could be achieved. The aerospace companies surveyed were in the process of getting all of the bugs worked out of their systems, and tube hookup to a manifold still presented a major problem. It was up to MDA to design an aqueous tube cleaning system that would meet the cleanliness requirements of < 5 mg /sq. ft. of non-volatile residue (NVR) (< 1 mg /sq. ft. NVR for O_2 tubing) for all shapes and sizes of tubing.

Concurrently, an MDA contract engineer was developing a manifold device that would accept any diameter of tubing, and did not require manual tightening. This manifold design was tested on a laboratory and production scale with impressive results. The first aqueous tube cleaning system design was developed around this patent pending manifold concept.

Some of the issues associated with developing an aqueous tube cleaning system included cleaning long runs of tubing, cleaning tubes with odd configurations, cleaning and drying tubes with multiple loops, loading tubes with very different shapes into the same manifold, and cleaning large diameter tubing.

Another issue at the core of the development of an aqueous tube cleaning system was the selection of a tube bending lubricant and cleaner. CW-50 is extremely viscous and yields successful bends in all sizes of tubing, even titanium. CW-50 is also very difficult to clean off of parts. Water soluble tube bending lubricants are much easier to clean, but they present problems bending larger diameter tubing, especially titanium tubing. The tube bending lubricant selected had be able to bend all diameters of tubing, including titanium, without degrading the quality of the tubing. The cleaner selected had to be able to clean a wide variety of soils, including CW-50, and could not corrode aluminum.

IMMERSION TANK SYSTEM

The MDA tube cleaning process team began designing an aqueous tube cleaning system around the patent pending manifold device. The immersion tank system consisted of a series of cleaning tanks, a manifold and pump connected to a parts basket, and an overhead crane. The manifold was configured to connect to one end of the parts basket (See Figures 1 & 2). Tubing loaded into the manifold rests on the floor of the parts basket, or on stabilizing rods located in different positions across the parts basket. A pump located at the top of the parts basket at the manifold end pulls solution through the tubing, through the manifold, and returns the solution to the cleaning tank via a return pipe located at the top of the parts basket.

The immersion tank system consisted of a load/unload station, a pre-rinse tank, an aqueous cleaner tank, an initial rinse tank, a final rinse tank, and a drying station. Tubing loaded into the manifold in the parts basket travels on an overhead crane from tank to tank. Pneumatic connections are made using guide rails and quick disconnects as the basket is lowered into the tank. The tank cleaning solution is pumped through the tubing for a specified time, then the basket travels to the next tank, repeating the process. Brulin 815GD was chosen as the cleaner for this system based on laboratory tests and previous production experience in removing Krytox greases from swaged tube ends in an ultrasonic bath. CW-50 was chosen as the tube bending lubricant because it performed well in bending all sizes and types of tubing. CW-50 is a heavy oil, more dense than water, and sinks to the bottom of the aqueous cleaning tank, thus preserving the tank chemistry for a longer period of time.

After the tubing is loaded into the parts basket at the load/unload station, the parts basket is lifted by an overhead crane and placed in a pre-rinse tank full of water. The water is pumped through the tubing for a specified amount of time, removing the bulk of the tube bending lubricant. Laboratory tests demonstrated that the pre-rinse step was effective in eliminating up to 90% of the CW-50 bending lubricant from tubing. The basket then travels to the aqueous cleaner tank containing a 15% solution of Brulin 815GD. The lubricant and soils not removed during the initial rinse step are removed in the cleaner tank. The parts basket then travels to an initial rinse tank filled with D. I. water, and then to a final rinse tank filled with >100,000 ohm D. I. water. Counter flow systems were designed between the final rinse and initial rinse tanks to conserve D. I. water. Following the final rinse, the parts basket travels to the drying station where the tubing gets dried with heated, filtered air (See Figure 3).

The issues involved in the design and development of the immersion tank system include tank manifold design, hookups, installation of an overhead crane, and tank sizing. Another critical part of the design involved the movement of the parts basket from tank to tank while maintaining the necessary electrical and pneumatic connections. Engineering students from Harvey Mudd College were contracted to help with the traveling integrated parts basket/manifold hookups from tank to tank as one of their engineering clinic projects. Bentley Engineering Company was contracted to help write the procurement specification[1] for the tank immersion system, less the manifold and parts basket, to go out to bid to local contractors.

At the end of 1994, the MDA tube cleaning process team was ready to place an order for the immersion tank cleaning system. The system had been specified, bids were received and evaluated, and the purchase order was due to be released. At a question and answer session with one of the bidders, the sales representative showed the team a drawing of a completely different type of cleaning system. The drawing was of a prototype

enclosed cabinet system being built for another aerospace company. The operation of this system was similar to a dishwasher, but was designed to do tube cleaning. The engineering staff was not impressed, but the manufacturing representatives were very interested in the idea of a turnkey tube cleaning system. The tube cleaning process team was then contacted by another vendor (Proceco Inc.) who made a more commercially viable enclosed cabinet system, and more importantly, answered all of the engineering questions in detail and was willing to work with the team to develop an enclosed cabinet system that would meet MDA's tube cleaning needs. Even though the team had already gone to bid, and were ready to place an order for the immersion tank system, they proceeded to do the necessary research to write a whole new specification for an enclosed cabinet tube cleaning system.

ENCLOSED CABINET SYSTEM

The enclosed cabinet system (See Figure 4) operates on the same principle as the immersion tank system. But, instead of immersing the tubing in separate tanks of cleaning solutions, the tubing is placed in a single cabinet and the different cleaning solutions are brought from the tanks to the tubes, cleaning the interior and exterior of the tubing in a manner similar to that of a large industrial dishwasher. All of the cleaning and drying is performed in one location. The enclosed cabinet system has four separate cleaning tanks, and each solution is pumped into the tubing with 25 horsepower vertical pumps. When the first wash cycle is complete, a diverter valve switches over to the next tank and the tubing is washed with the next solution.

The advantages of an enclosed cabinet system over an immersion tank system are numerous. The enclosed cabinet system takes up much less floor space than an immersion tank system. There are no open tanks, no need to dig pits to house the tanks, no indoor humidy problems, no safety concerns of people falling in the open tanks, and no need for a moving crane or parts baskets. The enclosed cabinet system comes complete with enclosed reservoir tanks and tube connectors. The operator simply loads the tubes into the machine, closes the lid, pushes one button, and 1/2 hour later removes clean, dry tubing from the machine. The final advantage of the enclosed cabinet system is that it provided a $500,000 savings in equipment, installation, and construction costs over the immersion tank system.

The specifications[2] required by MDA for the enclosed cabinet system are as follows:

Metals to be cleaned - Aluminum, stainless steel, titanium, Inconel.
Contaminants - Oils, grease, metal chips, bending lubricants, dye penetrants, dirt.
Throughput - 65 tubes per 8 hour shift.
Pumps - Vertical type centrifugal, CRES 316, 350 GPM @ 70 psig, minimum 25 HP TEFC motor.
Solution Heating - Resistance heaters with a maximum heat up time from 65°F to 180°F of four hours.
Electrical - 480 volts, 3 phase, 60 cycles.
Materials of Construction - All wetted surfaces shall be CRES 316L.
Cleaning Chamber - The chamber shall be 36" x 36" x 240" with removable floor grate.
Cleaning Solution - Must use a low foaming, sprayable cleaner.
Noise Level - Shall not exceed 85 decibels.
Thermal Insulation - Shall be provided on solution storage tanks.
Manual Spray Lance - Equipment shall include a pressure spray wand to clean odd shaped parts. The wand shall be fed with 5-10 GPM @ 40-80 psig by a pump from wash or rinse.
Spray Nozzles - Cleaning chamber shall be equipped with spray nozzles on top of the chamber to clean the exterior of the tubing, and the cleaning chamber.

One manufacturer, Proceco Inc., was able to meet all of the MDA specifications for the enclosed cabinet system at a competitive price.

SYSTEM OPERATION

The tubing to be cleaned is placed in special clamping fixtures in the Proceco enclosed cabinet tube cleaning system (See Figure 5). The clamping fixtures hold several small diameter (1/4"-1/2") tubes or one larger diameter tube (1"-3"). Ducting larger than 3 inches in diameter is cleaned using the manual spray lance. The clamping fixtures are connected to one of eight available ports inside the cleaning chamber with a flex hose and quick disconnect coupling. After the tubes are loaded into the machine, the lid is closed and the machine is started. A pre-clean cycle of water @170° F is flushed through the tubing for five minutes to remove the bulk of the contaminants. Following the first cycle, air is purged through the tubing for 20 seconds to remove the excess water from the tubes and prevent dilution of the cleaner tank (Tank #2). The diverter valve switches to tank #2 and a wash cycle consisting of a 5% solution of a low foaming, sprayable aqueous cleaner @135°F is flushed through the tubing for six minutes to remove the rest of the contaminants present. Following the second cycle, air is purged through the tubing for 30 seconds, and the chamber is allowed to drain for 225 seconds to prevent cross contamination from the cleaner tank to the initial rinse tank (Tank #3). The diverter valve switches to tank #3, and an initial rinse of >7000 ohm D. I. water @ 170°F is is flushed through the tubing for six minutes. Following the third cycle, air is purged through the tubing for 20 seconds to preserve the integrity of the final rinse tank. A final rinse of >100,000 ohm D. I. water @ 180°F is is flushed through the tubing for 30 seconds. The final rinse tank (Tank #4) is fed by a deionized water bank and counterflows into tank #3 after rinsing to help maintain the quality of the initial rinse tank. Tank #3 overflows to drain. Tanks 1 and 2 are equipped with a 10 micron bag filter. Tank #3 is equipped with a 5 micron bag filter. Tank #4 is equipped with a 0.2 micron cartridge filter. These filters prevent the accumulation of particulates and sludge in the cleaning tanks. Following the final rinse stage, the tubing is blown dry with heated (~130°F) filtered air for five minutes. Tubes that are larger than one inch in diameter are inverted end to end and re-run following the final rinse stage. At the end of the cleaning cycle the operator removes clean, dry tubing from the enclosed cabinet tube cleaning system.

WASTE TREATMENT

Following several months of use, tanks 1 and 2 will accumulate soil from the tube cleaning process. At the time of tank dump, clean, and recharge (DCR) the contents of tanks 1 and 2 are transferred to a large 2000 gallon waste holding tank. The waste solution consisting of water, oils, sludge, dirt, and particulates is processed through a Mars 2 ultrafiltration unit. The ultrafiltration unit collects and concentrates the oils, sludge, dirt, and particulates present in solution. The effluent from the process, which contains less than 50 ppm of oils and grease, is discharged to the sewer. The oil and sludge collected from the waste treatment process are sealed in drums and disposed of as hazardous waste.

LABORATORY TESTING

Tube Bending Lubrican Evaluation - Candidate water soluble tube bending lubricants were tested on a shop trial basis. Tubing was bent using these lubricants and tested for ovality, material condition, and orange peel. Test materials included aluminum, stainless steel, and titanium tubing ranging in size from 1/2 inch in diameter to one inch in diameter. The candidate lubricants were tested against the baselined CW-50 tube bending lubricant used in the daily tube bending operations. The tube bending lubricants tested were Amberlube EP, Amberlube EC-98, Amberlube SP, Chemtool CT-3307, Houghto

Draw 7007, Lubegard, and Tower Draw TC-88. Of the lubricants tested, only Chemtool CT-3307, Lubegard, and Tower Draw TC-88 were able to successfully bend all diameters of the three types of tubing. Many of the water soluble lubricants could not withstand the stresses of bending large diameter titanium tubing. Chemtool CT-3307 was selected as the water soluble tube bending lubricant. In laboratory cleaning tests Lubegard, and Tower Draw TC-88 were difficult to remove 100% because they left behind a residue. Further analysis showed that the stearic acid component of the Lubegard product turned into sodium stearate when immersed in the aqueous cleaners, leaving behind a residue that was difficult to remove.

Sprayable, Low Foaming Cleaner Qualification Tests[3] - Reference: M&PE Report #52,831, 11-30-95. Six different low foaming, sprayable, aqueous cleaners were tested for foaming, cleaning ability, total immersion corrosion[4], sandwich corrosion[5], salt spray corrosion[6,7], and paint adhesion[8] (See Table 1). The cleaners tested were Brulin 1990GD, Rebound 7, Daraclean 232, Daraclean 257xx, Ardrox 6333A, and Chemclean 1055. Four of the six cleaners tested passed all of the qualification tests. Daraclean 232 and Ardrox 6333A did not pass because they foamed more than any of the other products tested, and they did not clean Chemtool CT3307 (baselined water soluble tube bending lubricant) effectively. Of the four cleaners that passed, the two with the lowest pH at a 5% concentration, Brulin 1990GD and Rebound 7, were selected and approved for use in the enclosed cabinet tube cleaning system.

NVR Tube Analysis - Following system start up, and at periodic intervals thereafter, Non-Volatile Residue (NVR) analyses were performed on tubing cleaned in the Proceco enclosed cabinet tube cleaning system to define operating parameters. The NVR results of tubing cleaned in the Proceco unit are shown in Table 2. The results are reported in milligrams of contaminant per square foot of tubing. Results of <5 mg/Sq.Ft. indicate satisfactory operation of the system. Since production start up in May of 1996, the results indicate that the Proceco aqueous tube cleaning system is effectively meeting the tube cleanliness requirements.

CONCLUSION

By implementing an aqueous tube cleaning process at MDA, ozone depleting compounds such as TCA are no longer required to clean tubing. The hazards associated with chemical cleaning, potential environmental fines, and the high cost of using regulated ODC's or a replacement equivalent are no longer concerns. Furthermore, in the development of the aqueous tube cleaning system, process improvements have been made that remove the human factor from the processing sequence. Dirty tubing is simply loaded into the machine, and at the end of the cleaning cycle, clean, dry tubing is removed. The improved tube cleaning process has been accomplished without impact to the environment.

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2. MDC Procurement Specification for the Cabinet-Type Aqueous Tube Cleaning System II - Building 21, Project 6151-29-S-01, Rev. D, October 23, 1995.

3. Adam, S.J., "Qualification Testing of Sprayable, Low Foaming, Aqueous Cleaners, M&PE Report #52,831, November 30, 1995.

4. ASTM D930-89, "Total Immersion Corrosion Test of Water-Soluble Aluminum Cleaners", May 26, 1989.

5. ASTM F1110-90, "Sandwich Corrosion Test", January 26, 1990.

6. ASTM B117-94, "Standard Practice for Operating Salt Spray (Fog) Testing Apparatus", February 15, 1994.

7. Mil-C-5541E, "Chemical Conversion Coatings on Aluminum and Aluminum Alloys", November 30, 1990.

8. Federal Test Method Standard No. 141C, Method 6301.2, "Adhesion (Wet) Tape Test", January 24, 1986.

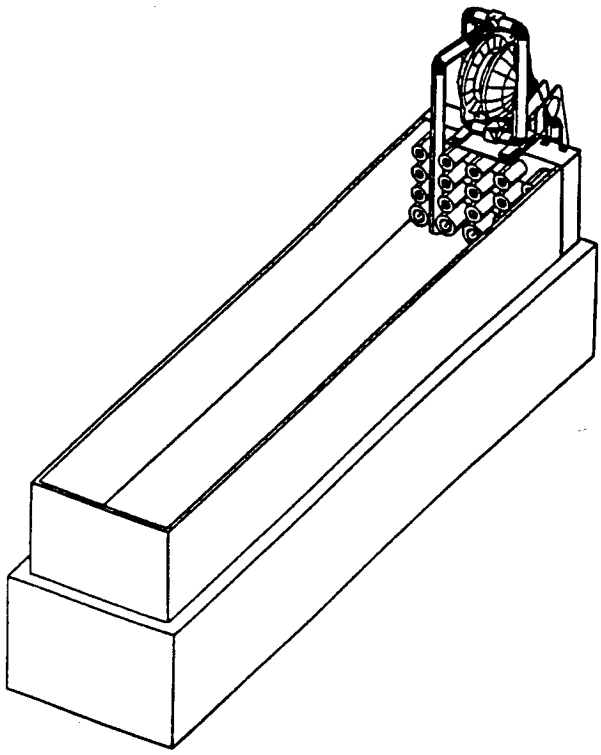

Figure 1 - Manifold with Basket Sitting Over Tank

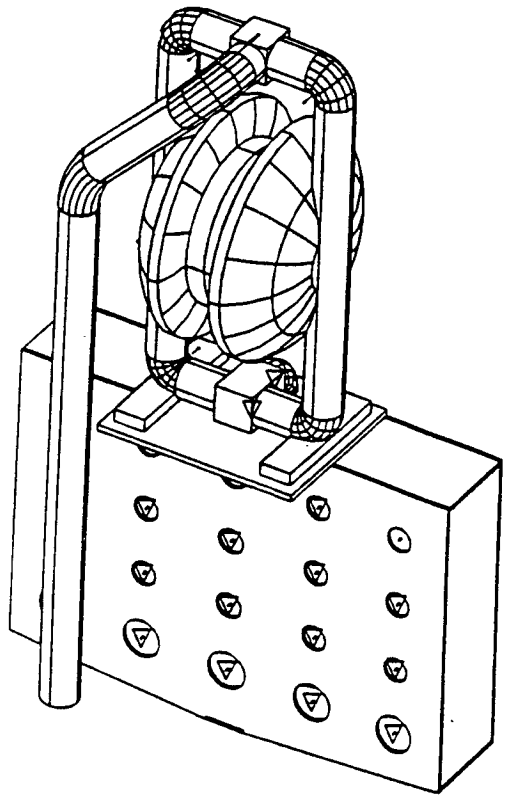

Figure 2 - Manifold with Pump, Front View

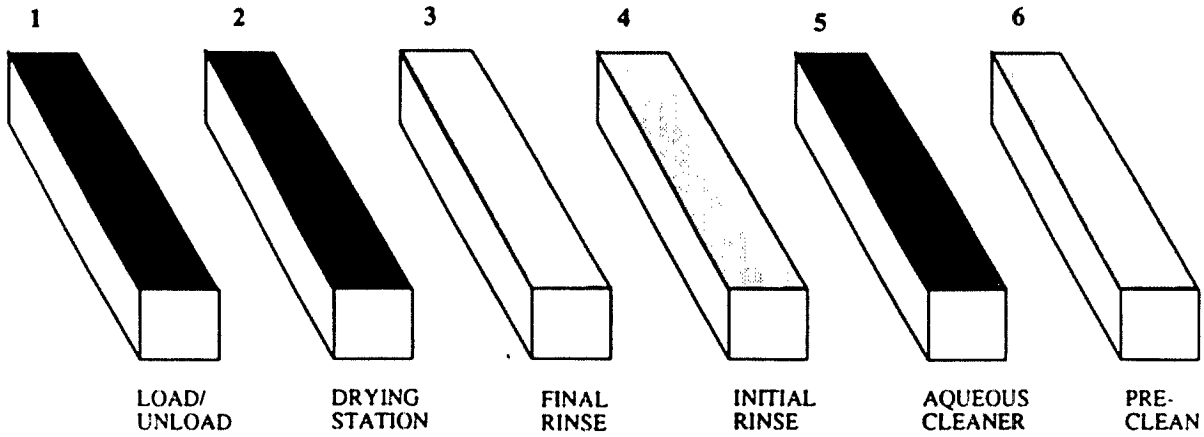

Figure 3 - Tank Immersion System Processing Sequence

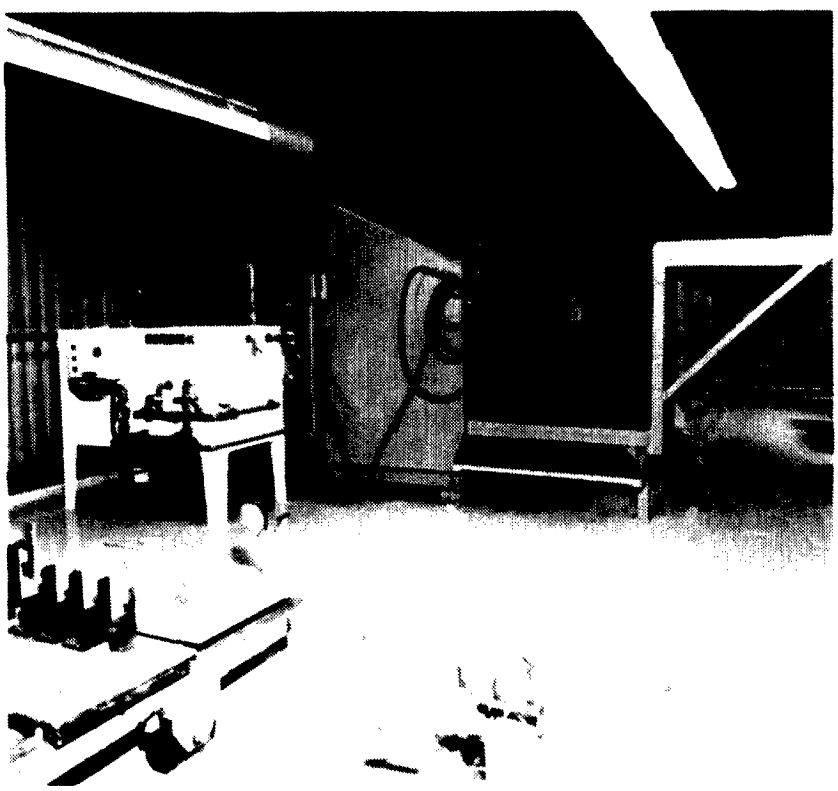

Figure 4 - Proceco Enclosed Cabinet Tube Cleaning System

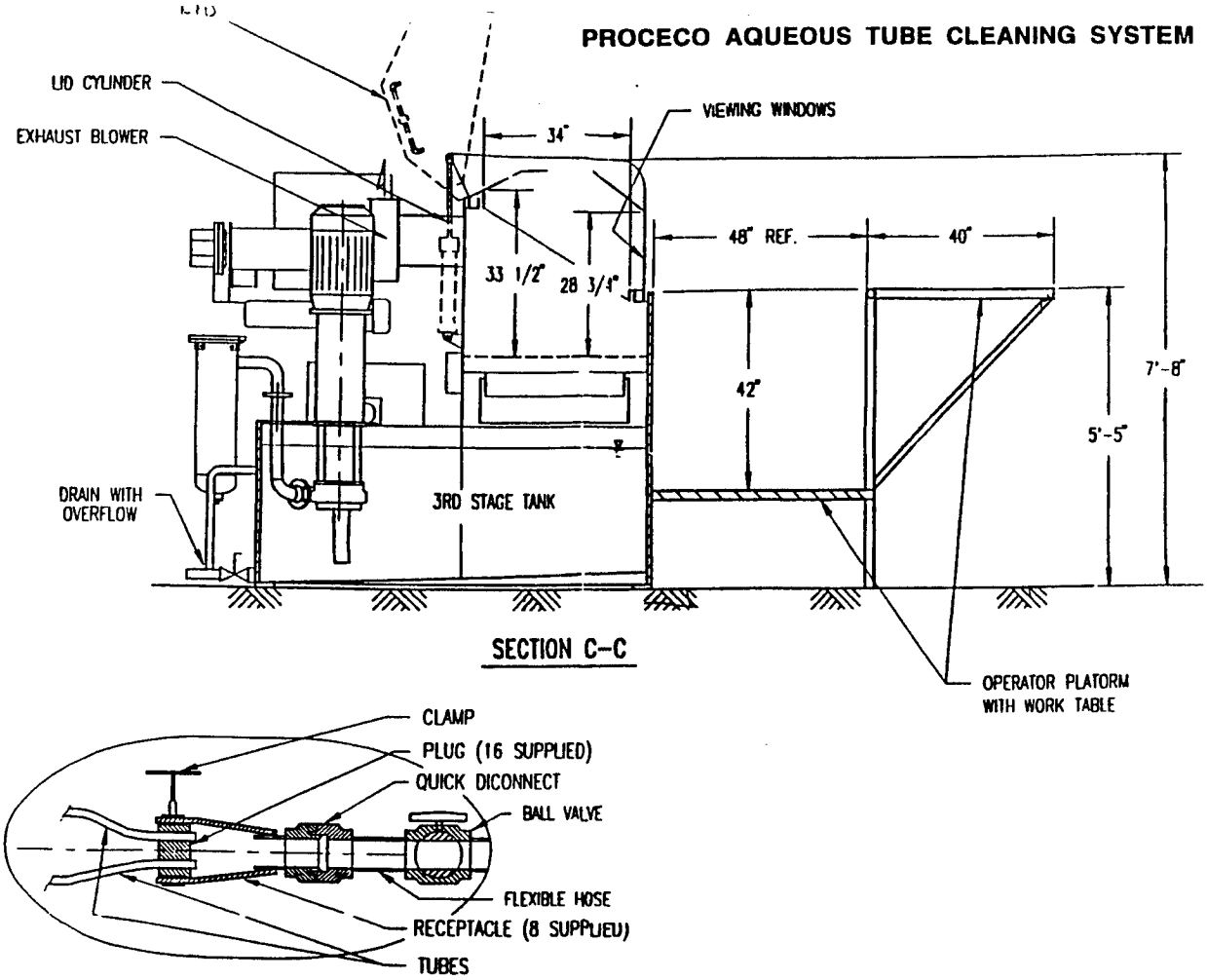

Figure 5 - Proceco Enclosed Cabinet Tube Cleaning System - Schematic

TABLE 1 - AQUEOUS TUBE CLEANER QUALIFICATION TESTING

				TEST							
	FOAMING		CLEANING	%	TOTAL IMMERSION		SANDWICH	CORROSION	SALT	SPRAY	
CLEANER	5% at 180°F	CW-50	CT-3307	TC-88	1%	5%	1%	5%	ALODINE 1200	ALODINE 1500	PAINT ADHESION
Brulin 1990 GD	No Foam	91.74	100	98.91	Fail	Pass	X	Pass	Pass	Pass	Pass
Rebound 7	A Little Foam	94.19	100	94.67	Fail	Pass	X	Pass	Pass	Pass	Pass
Daraclean 232	Lots of Foam	93.57	81.17	96.30	X	Discontinued Testing...		X	X	X	X
Daraclean 257xx	No Foam	96.75	92.13	95.24	X	Pass	X	Pass	Pass	Pass	Pass
Ardrox 6333A	Moderate Foam	100	70.96	94.57	X	Discontinued Testing...		X	X	X	X
Chemclean 1055	No Foam	98.86	99.70	94.43	X	Pass	X	Pass	Pass	Pass	Pass

Requirements:
1. Foaming - Cleaner should have little or no foam at 180°F.
2. Cleaning - Cleaner must exhibit greater than 99% cleaning of Chemtool (water sol tube bend lube).
3. Total Immersion - Cleaner should not corrode or show greater than 0.003 mg wt. loss with 2024-T3 or 7075 T6 Aluminum.

Discontinued Testing On:	Reason
Daraclean 232	Req'ts 1&2
Ardrox 6333A	Req'ts 1&2
1% Conc. Tests	Corrosive, Mfg. does not recommend use at 1% Conc

TABLE 2 - NVR RESULTS, TUBE CLEANING

DATE	DIAMETER (in)	LENGTH (in)	NVR (mg/sq. ft)	COMMENTS
03-05-96	0.75	46	0.86	1st Tube Run O_2 Clean!
03-13-96	2.5	66	1.39	2 ports closed each side Tube flipped and re-run
03-20-96	1.5	60	4.35	All ports open
03-20-96	2.5	66	1.65	All ports open Tube flipped and re-run
03-23-96	0.75	66	24.92	All ports open Short program - 3,4,3 mins.
03-27-96	0.50	36	2.37	All ports open New controller chip
04-03-96	1.5	74	0.51	New Chip, All ports open Tube flipped and re-run
04-04-96	2.5	66	0.41	New Chip, All ports open Tube flipped and re-run
04-04-96	1.5	27	11.06	>1" Dia. - Not flipped
04-05-96	1.5	27	8.35	Tube flipped and re-run
04-08-96	0.312	24	0.00	Changed program - Times incr. to 5,6,6 mins
04-08-96	2.5	66	0.20	O_2 Clean!
04-12-96	1.5	57	4.5	Super gooped up dirty tube D. I. Water Down
04-15-96	1.5	57	10.0	Tanks becoming soiled Tank 3 >400 mmohs
04-22-96	------	------	------	DCR TANKS 1, 2,&3
05-07-96	1.5	102	0.283	Fresh Tanks - Start Up Production runs start
05-21-96	2.5	48	?	QC Tube not run Shop won't bend tubes
6-04-96	1.5	20	4.17	Production tube
6-04-96	2.5	48	4.09	No DCR's since 5-07-96 QC Tube
6-14-96	2.5	48	2.82	No DCR's since 5-07-96 QC Tube
6-25-96	2.5	48	4.65	No DCR's since 5-07-96 QC Tube

AQUEOUS PRECISION CLEANING OF ENGINE COMPONENTS

by

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Abstract

Prior to 1996, precision cleaning of engine components was performed using 1,1,1-trichloroethane (TCA). Its use was banned at Rocketdyne as of 31 December 1995 due to its classification as an ozone depleting chemical. Conversion to all aqueous cleaning at Rocketdyne has been completed. Precision cleaning is performed in the Aqueous Fine Clean Facility which consists of three ultrasonic cleaning tanks, two spray rinse tanks and one immersion tank without ultrasonics. The tanks can accommodate hardware up to three feet in each dimension; flushing capabilities exist for larger hardware. A total of nine aqueous precision cleaning processes are available through the pairing of three different process options with three distinct cleaning methods. The process parameters were developed based upon earlier experiments using small test samples. Production hardware from different programs has been processed through the facility and has met particulate and nonvolatile residue (NVR) cleanliness requirements. These results demonstrate aqueous precision cleaning to be as effective as the previous TCA method.

INTRODUCTION

With the elimination of 1,1,1-trichloroethane (TCA) at Rocketdyne targeted for 1996, an alternate precision cleaning method needed to be developed, tested and eventually implemented in the new facility. With the commitment to use aqueous cleaning techniques, it was realized that the majority of cleaning would be through mechanical action rather than through chemical action as was with TCA. The mechanical technique selected for the precision cleaning process was ultrasonic cavitation using a three-step cleaning process. A study was conducted to choose the most effective ultrasonic cleaning system for the precision cleaning requirements at Rocketdyne. The system selected for use at Rocketdyne consisted of the following: 25 kHz for cleaning steps 1 and 2 in which removal of most of the soil was achieved, and 40 kHz for step 3 to remove the last microlayer of soil in the final cleaning step for enhanced cleaning effectiveness. The power levels were 4.2 watts/in^2 at the radiating plate with 43 watts/gal for each tank.[1]

In order to implement cleaning of hardware in the newly constructed facility, processing parameters had to be selected. To make these selections, a Continuous Process Improvement (CPI) Team was established and the Taguchi testing methodology was utilized for the selection of a robust process. The team was comprised of members from Manufacturing, Manufacturing Technical Support, Quality Assurance, Quality Engineering and Materials Engineering & Technology. The team's goal was to provide an efficient, controlled process of aqueous ultrasonic cleaning methods to both quality and manufacturing groups to enable them to meet contractual obligations. Taguchi testing was employed as the strategy for identifying the most effective use of key operating parameters to achieve quality, cost and schedule requirements.

BACKGROUND

The general capabilities of the facility are shown in Figure 1. Selection of the aqueous cleaning agents was based upon previous testing performed by the Materials Engineering & Technology Department. Testing consisted of evaluating agent cleaning effectiveness on typical Rocketdyne soils as well as compatibility of the various alloys which comprise Rocketdyne hardware. The cleaning agents selected consisted of the following: 1) the emulsion degreaser, Turco 3878 LF-NC; 2) the mild alkaline cleaner, Turco 4215 NC-LT; and 3) the nonionic detergent, Turco 4215 Additive.

Cleaning Line Equipment

- Tank Capacity
  - 665 gallon capacity
  - accommodates hardware 3 ft x 3 ft x 3 ft
- Ultrasonic Cleaning Tanks
  - 2 tanks equipped with 25 KHz transducers
  - 1 tank equipped with 40 KHz transducers
  - adjustable power level to 43 watts/gal maximum
- Rinsing Capabilities
  - 2 spray rinse tanks with 270° spray coverage
  - 1 immersion rinse tank without ultrasonics
- Built-in Versatility
  - hand held spray rinse wands
  - hose attachments to tooling for flushing

Figure 1. Aqueous Precision Clean Facility Equipment Capabilities

The general cleaning process for which the facility was established is provided in Figure 2. This cleaning procedure was established as the maximum requirement as it was anticipated that all three cleaning steps would not be required except under extreme conditions of hardware complexity and/or hard to remove soils.

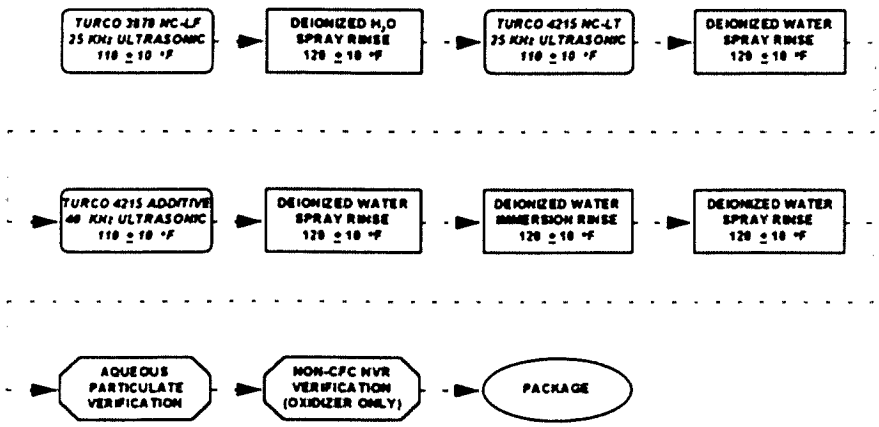

Figure 2. Aqueous Precision Clean 3-Step Procedure

The facility was designed to provide several process parameters which could be adjusted or varied for optimization of the cleaning process. The parameters were as follows: A) rinse temperatures; B) ultrasonic power levels; C) soak time prior to ultrasonic cleaning (presoak); D) ultrasonic cleaning cycle time; E) soak time after ultrasonic cleaning (recirculation); F) number of cleaning steps required; G) cleaning solution temperatures; and H) rinse times. Due to the inavailability of large numbers of scrap hardware, in order to process a large number of pieces per test, standard complex test specimens were utilized. The test specimens were fabricated from alloys commonly used at Rocketdyne and were designed with through holes, blind passages and threaded holes to simulate hardware complexity. The contaminants selected to be used consisted of the following soils: 1) Cool-Tool manufactured by Monroe Fluid Technology, Hilton, NY; 2) CRC 3-36 manufactured by CRC Industries, Inc., Warminster, PA; 3) metallic fines obtained from cutting operations in the ME&T laboratory; and 4) DTE 26 manufactured by Mobil Oil Corp., New York, NY. One test set consisted of three test specimens contaminated with the same lubricant applied to specified areas (Figure 3). Metallic fines were then applied on top of the lubricant and the specimens were then baked to simulate soils resulting from a machining process.

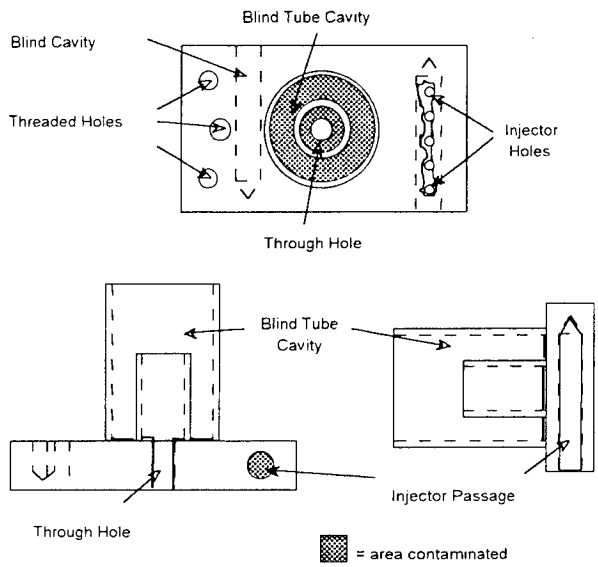

Figure 3. Standard Complex Test Specimen Configuration and Placement of Contamination

The parameters described above were identified as control factors A through H for the Taguchi test method. As recommended by Taguchi, the control factors were arranged into an L_{18} array (Table I). Each of the control factors was assigned three levels , except for rinse temperature, which was originally assigned two levels. Of importance were the measured results for particulate matter (fibers and particles) count and nonvolatile residue (NVR). These were used to evaluate cleaning effectiveness by measuring the remaining amount of soil on the test specimens. Both were evaluated separately for each test run. The results from each set of test specimens for each test run were averaged and the corresponding signal-to-noise (S/N) ratio for "smallest is best" for both NVR and particle count were calculated. The S/N ratio is a measure of the precision of the results as recommended by Taguchi. The goal was to select the processing parameters which would provide the lowest average and the highest S/N for NVR and particle count.

In any process system, there are parameters which are beyond the operator's control. These parameters are defined by Taguchi as noise factors. In a robust process system, noise factors need not be considered, as the results are obtained without controlling them. The noise factors identified for the

aqueous ultrasonic precision cleaning process were as follows: 1) type and amount of soil, 2) hardware geometry; 3) alloy type, 4) orientation in the tank, and 5) location in the tank.

The test plan was designed to include two test phases. If needed, a third phase would be designed for confirmation of a robust process with the parameters chosen. The first phase was to include two test conditions and the first three noise factors listed above. One test was to be set up with all of the control factors at their lowest settings, or the least aggressive cleaning condition. This test was to be performed in addition to those in the L_{18} array since it did not include a trial which included all the lowest settings. The second test of the first phase consisted of setting up all the control factors at the highest settings or at the most aggressive cleaning condition. This was Trial 1 of the L_{18} array. Each of these tests included varying the measured amount, type and placement of soil on the test specimens. Both nickel alloy 718 and titanium alloy specimens were evaluated. The areas contaminated are shown in Figure 3. This purpose of this test phase was to determine if the type, amount and placement of soil and specimen alloy were factors which had to be controlled in order to produce a robust process or they could be ignored due to their lack of influence on the results. In addition, the sensitivity of the measurement for soil removal was measured. Without a sensitive method, there was no reason to continue testing.

Trial	Control Factors							
	A	B	C	D	E	F	G	H
1	1	1	1	1	1	1	1	1
2	1	1	2	2	2	2	2	2
3	1	1	3	3	3	3	3	3
4	1	2	1	1	2	2	3	3
5	1	2	2	2	3	3	1	1
6	1	2	3	3	1	1	2	2
7	1	3	1	2	1	3	2	3
8	1	3	2	3	2	1	3	1
9	1	3	3	1	3	2	1	2
10	2	1	1	3	3	2	2	1
11	2	1	2	1	1	3	3	2
12	2	1	3	2	2	1	1	3
13	2	2	1	2	3	1	3	2
14	2	2	2	3	1	2	1	3
15	2	2	3	1	2	3	2	1
16	2	3	1	3	2	3	1	2
17	2	3	2	1	3	1	2	3
18	2	3	3	2	1	2	3	1

Table 1 Aqueous Precision Clean Process Development Experimental L_{18} Array

Providing there was a sensitive method for the determination of soil removal, and there were significant differences between the two test extremes in the first phase, testing was to continue with the second phase. The goal of the second phase was to complete the entire L_{18} array test matrix. This consisted of seventeen additional processing test runs with varying the levels of the test control factors for each test run. In addition, if the noise factors appeared to influence the results of the first test phase, they would be included in the second phase of testing.

In order to baseline the new aqueous precision cleaning process with the current vapor degreasing method, test specimens were precision cleaned by vapor degreasing and then analyzed for NVR and particle count using the same methods as for the aqueously cleaned specimens.

TEST PROCEDURE

The procedure to evaluate the cleaning effectiveness of the various adjusted parameters of the new facility can be summarized by the following steps: 1) contaminate test specimens; 2) preclean and dry; 3) arrange in the processing basket; 4) precision clean by the test process; 5) blow dry following clean; 6) oven dry; and 7) evaluate for cleanliness level with TCA. The details for each of these steps are given below. Test specimens were processed in groups of three specimens per set representing a total of 1 ft^2 of surface area.

The test specimens were contaminated by applying a machining lubricant of either Cool Tool, CRC 3-36 or DTE 26. Metallic fines were added on top of the lubricant and then baked at 200 °F for 1 hour. For only the first phase tests, the amount of lubricant applied to the specimens was weighed. The same lubricant was applied in identical locations for each set of three test specimens. Once contaminated, the test specimens were precleaned and dried in the Typhoon parts washer with a solution of Turco 4215 NC-LT. A visually clean condition was used to determine a satisfactory preclean.

Test specimens were arranged in the processing basket using one configuration for the entire cleaning process per test. During the first half of the first two test phases, the test specimens were wired in place to prevent potential movement during processing. In all subsequent testing, including the third test phase, the specimens were not wired in place as it was determined there was very little movement during processing. For Tests 1 and 2, only the lower basket was used, with the test specimens arranged around the basket perimeter. All tests following the first two were arranged in two baskets, with the same specimen arrangement in the lower basket as done previously. A schematic of specimen placement in the upper basket (for all tests beginning with #3) and in the lower basket (for all tests) is given below in Figure 4.

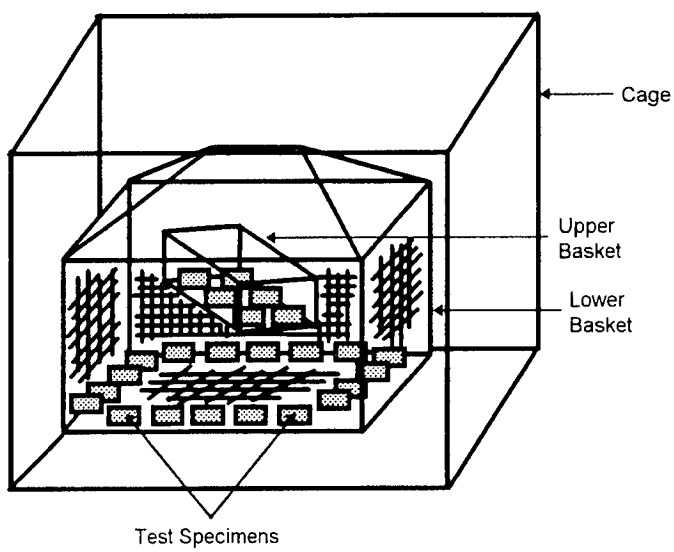

Figure 4. Process Basket Arrangement

The cleaning test process was to be performed according to the Taguchi L_{18} array (18 tests) and Taguchi Final L_4 array (4 tests). However, this was was not the case. The actual test conditions are discussed in the following section. For the first seventeen tests, the test specimens were blown dry with clean gaseous nitrogen after the final rinse.

For the first two tests, the test specimens were dried in the newly modified vacuum oven. The test specimens from all subsequent tests were dried in smaller ovens which were tested for particulates and met the requirements of less than five particles from 100 to 175 microns and none greater than 175 microns

Measurement of soil removal consisted of a modified method from the industry standard which was in use at Rocketdyne A set of three test specimens evaluated together represented one data point for the particular test process Each set of specimens, representing approximately one square foot of surface area, was grouped by the same alloy, contaminant and location of contaminant. A measured 500 ml of TCA was flushed over each set of test specimens The effluent was collected, filtered through a 0.45 micron filter and the filter evaluated for particulate matter The filtrate was evaporated to dryness and the weight of the residue determined (gravimetric NVR procedure). All equipment used during cleanliness evaluation was cleaned and verified to contain less than one mg per 500 ml of solvent.

RESULTS AND DISCUSSION

Cleaning effectiveness for the different process parameters was based on NVR and particulate matter measurements NVR is an indirect measurement of the amount of hydrocarbons remaining on the specimen following the cleaning process. It can be affected by the original soil applied and the cleaning process utilized Measurement of particulate matter was separated into two categories, particles and fibers The particle measurement typically represents what is remaining on the test specimen. However, it should be noted this measurement can be influenced by solution cleanliness, equipment used in the cleaning and evaluation process and room cleanliness On the other hand, the fiber measurement is mainly influenced by solution cleanliness, the equipment, activity level of operators working in the room and room cleanliness

The results from each of these measurement categories (particles, fibers and NVR) were tabulated and the average measurement and S/N ratios for each set of cleaning parameters were calculated. For these measurements, the most desirable values were lowest average and highest S/N. The average values for each measurement and their corresponding S/N ratios for the test phases are graphically represented in Figures 5 through 7 The processing parameters which appeared to have the greatest and least influence on each measurement will be the basis for the discussion which follows

First Test Phase

The first test phase consisted of two tests, the first of which consisted of all the processing parameters at their lowest settings and was anticipated to be the least robust With all the processing parameters at their highest settings, the second test was predicted to the most robust. These are identified as Tests 1 and 2 on Figures 5, 6 and 7, respectively

NVR results from these first two tests were the opposite of what was expected Based upon a report provided by the Navy [2] and the fact that as temperature increases, the solubility of surfactants utilized in the cleaning agents decreases, it was decided to reverse the rinse temperature parameters while keeping everything else the same. For example, the highest rinse setting of 140 °F was matched with the remaining parameters of Test #1, thereby classifying the higher rinse temperature as the least robust This was designated as Test #3 and it can be seen in Figure 5 the average NVR was high the S/N was low Test #4 was then established as a further test on the effect of rinse temperature where a low rinse temperature setting of 70 °F (76-84 °F, actual) gave comparable NVR and S/N results to Test #1. These results indicated NVR was affected by the ability to effectively rinse the object being cleaned. Additionally, if the surfactants were not completely removed during the rinse process, they could add to the NVR results This may also explain why two of the four test specimen sets which were not contaminated but included in the cleaning process contained NVR values of 1.0 mg for Test #1 and 3.2

mg for Test #2. The higher NVR for Test #2 (high rinse temperature) further confirmed the belief that surfactant residue was being picked up as part of the NVR and rinse temperature directly affected the ability to remove the surfactants.

Both fiber and particle counts for Test #s 1 and 2 were high (Figures 6 and 7, respectively). Investigation of several potential sources revealed the vacuum oven to be the cause. The oven had just been reconstructed and needed additional cleaning. For all subsequent tests, the drying process was performed in an oven which met the requirements of five particles maximum in the range of 100-175 microns and no particles greater than 175 microns. However, Tests #3 and #4 did not give adequate particulate matter removal with the use of qualified ovens.

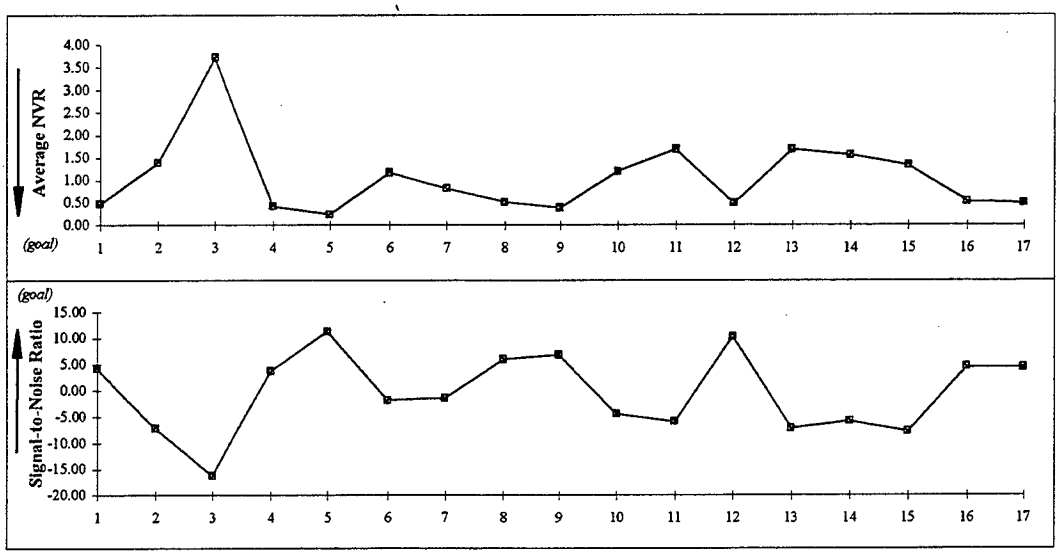

Figure 5. L_{18} Array NVR Test Results

The first four tests revealed there was no correlation between the amount or location of contaminant applied and the amount remaining following cleaning. There were no differences between the ability to clean nickel alloy 718 and titanium alloy test specimens. Based upon these results, the amount of contamination applied to each specimen was no longer measured. However, the use of both alloys in testing continued in order to obtain a good statistical number of data points for each process run though they were not evaluated separately.

Second Test Phase

Since the NVR goal of 1 mg per square foot was attained with the lowest parameter settings, a decision was made to discontinue the original test plan of completing the full Taguchi L_{18} array test matrix. Since the removal of particulate matter had developed as the major issue, thirteen tests were added to the revised test plan (Test #s 5-17 in Figures 5-7). These tests consisted of varying the rinse techniques and ultimately increasing the cleanroom cleanliness levels in an effort to increase the effectiveness of particle and fiber removal. Other parameters were further evaluated to gain a better understanding of the cleaning process.

For NVR, a difference between average values below 1 mg was considered insignificant as was a difference of 2 or less for S/N ratio. Testing conclusively showed rinse temperature as the most important control factor in cleaning effectiveness (low average NVR and high S/N ratio). A rinse temperature of 120 °F or lower was consistently more effective in removing surfactants from the cleaning agents than the

140 °F rinse. A previously stated, this was due to the fact that as temperature increases, surfactant solubility decreases; solubility is the key factor in adherent removal from substrate surfaces.

Another parameter of importance in obtaining low NVR and a high S/N ratio was rinse time and thoroughness of the manually directed hand spray rinse. Several automated rinse cycle times with various combinations of the hand spray rinse were evaluated. It was found that an automated spray rinse cycle of 2.5 minutes at 120 °F followed with a thorough hand spray rinse of at least 5 minutes produced one of the most effective rinses. Utilizing a rinse technique of rinsing until no foaming was observed when flushing orifices and cavities also proved to be effective. Though this technique was not specifically timed, for more complex items, a minimum rinse time of 5 minutes would be required to achieve the desired effect.

Both cleaning solution temperatures of 120 °F and 140 °F produced effectively cleaned test specimens when combined with the more robust rinse temperatures and times. Test #4 was the only one conducted with the high cleaning solution temperature and lower rinse temperature while Test #s 16 and 17 were performed with the lower cleaning solution and rinse temperatures (Figure 5).

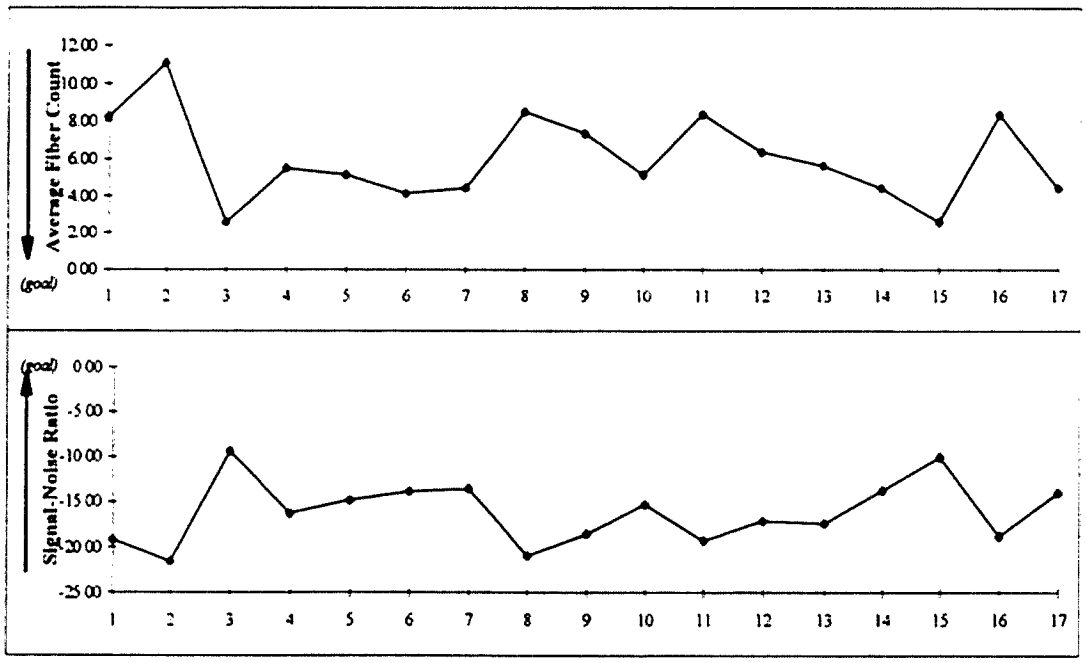

Figure 6. L_{18} Array Fiber Count Test Results

Ultrasonic power was tested at two levels, the lowest possible setting of 33% of the full power available, and at 100%. The tests selected for comparison were those which used the lower rinse temperature and longer rinse time. Test #4 was run at 100% while Test #s 16 and 17 were run at 33%. The were no significant differences between the two levels.

Three ultrasonic cleaning cycle times of 3, 6 and 10 minutes were evaluated. Test #1 had a 3 minute cycle, Test #s 16 and 17 used a 6 minute cycle and Test # 4 has a 10 minute cycle. These tests were chosen for comparison as they also had the lower rinse temperatures and longer rinse cycle times. It was determined that each cycle time provided similar NVR averages and S/N ratios (Figure 5).

Presoak time was the soak time prior to the ultrasonic cleaning cycle. The three times evaluated were no presoak cycle, 5 minute cycle for the first cleaning step only and a 10 minute presoak for each of three cleaning steps. As in the ultrasonic cleaning cycle time evaluation, those tests with lower rinse

temperatures and longer rinse times were used for evaluation. Test #1 had no soak cycle, Test #s 16 and 17 each had a 5 minute time for the first step, and Test #4 had a 10 minute presoak time. No significant differences were noted between the three.

The recirculation cycle following ultrasonic cleaning was added as a means for particulate removal from both the surface being cleaned and the cleaning solution itself. Two different recirculation times of 5 and 20 minutes (Test #s 5 and 4, respectively) were evaluated in the tests with longer rinse times and lower rinse temperatures. Both times were effective.

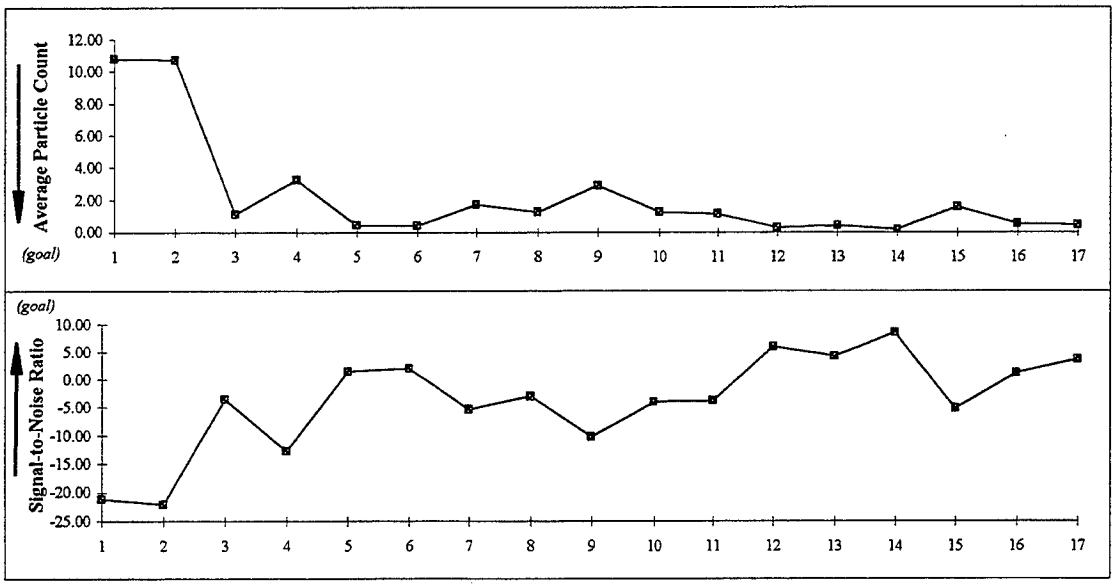

Figure 7. L_{18} Array Particle Count Test Results

Three different cleaning step processes were evaluated. This included a process of all three cleaning solutions (Figure 2) or Process Option #1, a process which included the aqueous cleaner Turco 3878 NC-LF followed with the nonionic surfactant Turco 4215 Additive (Process Option #2), and lastly, a process which consisted the mild alkaline cleaner Turco 4215 NC-LT once again followed with the nonionic surfactant Turco 4215 Additive (Process Option #3). The tests selected for these processes consisted of the lower rinse temperatures and longer rinse times. Process Options 1, 2 and 3 were used for Tests #s 4, 16 and 17, and 1, respectively. Each cleaning process provided equivalent cleaning effectiveness as exhibited by similar NVR averages and S/N values.

Two tank positions were evaluated, a central position (upper basket) and a bottom peripheral position (lower basket) as identified in Figure 4. The lower basket position was used in Test #s 1 and 2. Test #3 consisted of the upper basket position and also had the 140 °F rinse temperature. With the significant difference in average NVR values and S/N ratios between these two positions, the central location appeared to be the more robust. Based upon this observation, all subsequent tests included both positions for evaluation. However, when the data was reviewed for all tests with a lower rinse temperature, there were no significant differences between the two positions.

Previous testing of ultrasonic systems showed particle removal would not be difficult with the proposed aqueous cleaning process. Particles had been successfully removed even when cleaning in environmentally uncontrolled areas. For this test program, the acceptable particulate cleanliness levels was none greater than 400 microns. However, this level was not met during the first two test phases. The

cleanroom was evaluated and confirmed to be in compliance with the current specification requirements for a Class 100,000 cleanroom

One of the control factors introduced and evaluated as a possible influence on particle removal was the type of hand spray rinse nozzle used. Hand rinsing with no nozzle, the original nozzle and a 3-hole needle point nozzle was evaluated at a hand rinse time of less than five minutes and a time of greater than or equal to 5 minutes. For a time of greater than or equal to five minutes, there was a slight reduction in average particles for the 3-hole needle point nozzle versus the original nozzle (Test #s 12, 13, 16 and 17 vs. Test # 10), however, this trend was not present at less than five minutes (Test #s 14 and 15 vs. Test #s 8 and 9). It was concluded either the original nozzle or the 3-hole needle point nozzle were equally effective provided a rinse of five minutes or greater was used. The use of the spray wand without a nozzle may have been as effective as the nozzles had it been tested at five minutes or greater in addition to less than five minutes (Test #s 6 and 7).

Another factor evaluated as having a potential effect on particulate removal was daily wipe down of the cleanroom. The original schedule of wiping down the room once each week included Test #s 3 through 11. In an effort to enhance particulate removal, a daily wipe down with a minimum one hour wait to let the room settle, was instituted for Test #s 12 through 17. Statistical analyses showed Test #s 4 (weekly wipe down) and 15 (daily wipe down) to be anomalous data points and were therefore discarded. It was noted daily wipe down of the cleanroom had a significant effect on reducing the average number of particles and increasing the S/N ratio, though the number of particles greater than 400 microns was still unacceptable.

Other potential contributory factors were as follows: the introduction of a static charge by the gaseous nitrogen (GN2) used to blow dry following cleaning resulting in ineffective removal of particulates and the room itself. A decision was made to discontinue the use of GN2 during future testing. It was also discovered the cleanroom was not properly sealed and the outside of the cleanroom ceiling had accumulated dust and construction debris over the years. The outside of the cleanroom ceiling was thoroughly cleaned and the penetrations were sealed. The effect of these modifications on particulate removal was seen in the last phase of testing.

Fibers were a problem during previous testing of ultrasonic cleaning systems and continued to be so. All the evaluations performed for particles were also performed for fibers (Figure 6). None of the data obtained could be statistically eliminated, therefore, fibers were noted as a potential problem area.

The baseline established to compare the new aqueous precision cleaning process was the current vapor degreasing method. The same test specimens used during this test program were contaminated, precleaned, precision cleaned and then verified. Using the same special analytical method for evaluating the NVR and particulate matter for this test program, these test specimens were evaluated for cleanliness levels. The average NVR was 2.1 mg. per square foot, the average particle count was 4.4, and the average fiber count was 11.1. As can be seen by the results given in Figures 5 through 7, the aqueous precision clean process was more effective in removing the NVR, particles and fibers than the current vapor degreasing method.

Third Test Phase

This phase of testing was performed following the cleanroom modifications previously described. Based upon the results from the first two phases of testing, the following parameters were determined to affect the robustness of the cleaning process: A) ultrasonic power level and B) spray rinse temperature. Immersion rinse temperature was added as the third parameter C) for this phase of testing. These parameters were evaluated as control factors utilizing an L_4 orthogonal array (Table II).

The ultrasonic power level was again tested at 33% and full (100%) power. No significant differences were found between the two as in earlier testing.

Spray rinse temperature was evaluated at both 70 °F and 120 °F. The results showed little variation from the original testing in that a rinse temperature of less than or equal to 120 °F consistently provided acceptable NVR results.

	Control Factors		
Trial	A	B	C
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

Table II. L_4 Orthogonal Array

As rinse temperature was determined to be a critical process parameter, evaluation of immersion temperature was investigated as part of the third test phase. The results showed that an immersion temperature of 70 °F was somewhat more effective than one at 120 °F. However, since this parameter was not more thoroughly investigated as were the others in the initial test phases, the results were determined to be inconclusive.

CONCLUSIONS AND RECOMMENDATIONS

The ultrasonic aqueous precision clean facility was designed to provide a robust cleaning operation. Through the Taguchi testing performed in this study, the system was proven to be very robust. This was evidenced by an average NVR of 0.47 mg per square foot obtained during the first test using the lowest settings which was well below the requirement of 1 mg per square foot. The S/N ratio was high, indicating the probability of achieving the average NVR value was very high.

Based upon the test results, it was determined that the only critical factor in achieving the NVR goal of 1 mg per square foot was an effective rinsing process, which included temperature, time and technique. These control factors were those which affected the ability to effectively rinse off the cleaning agents, more specifically, the surfactants within the cleaning agents. Effective rinsing technique consisted of a thorough final manually directed hand spray rinse to remove the detergents used in the cleaning process. A spray rinse cycle of 2.5 minutes and a final hand spray rinse of 5 minutes was implemented. The technique of rinsing until no foaming was observed when flushing crevices or cavities was employed.

The testing performed conclusively showed rinse temperature as the single most important control factor in cleaning effectiveness. With the high temperature rinse test of 140 °F resulting in a significantly higher average NVR value and lower S/N ratio than the 120 °F or below rinse tests, a rinse temperature of 120 $\pm$ 10 °F was incorporated into the process. This was applied to the immersion temperature requirement as well.

Of the two cleaning solution temperatures evaluated, 110 °F and 140 °F, both produced effectively cleaned test specimens when evaluated with the more robust rinse temperatures and times. To be cost effective, the less costly process temperature of 110 °F was utilized.

The ultrasonic power was tested at two levels, the lowest possible setting of 33% of the full power available and at 100%. When the more robust rinse times and temperatures were used, there were no significant differences between the two power levels. Hardware processing at 33% ultrasonic power level was incorporated into the cleaning process.

The presoak step was a soak cycle which preceded the ultrasonic cleaning cycle Three times were evaluated no presoak cycle, 5 minute cycle and 10 minute cycle Since no significant differences were found between no presoak cycle and the presoak cycles with the more robust rinse temperatures and times, a presoak cycle was not a specific requirement for the procedure.

Recirculation cycle following ultrasonic cleaning was introduced as mechanism to remove particulate matter from the cleaned surface and from the cleaning solution. No significant difference was noted between the 5 and 20 minute times evaluated. Therefore, a 5 minute recirculation time was incorporated into the cleaning process

Three different cleaning processes were evaluated. This included all three cleaning solutions, a process with the aqueous cleaner Turco 3878 NC-LF followed by the nonionic surfactant Turco 4215 Additive, and lastly, the mild alkaline cleaner Turco 4215 NC-LT followed with Turco 4215 Additive. When tested with the more robust rinse temperatures and rinse times, there were no differences in cleaning effectiveness as evidenced by the similar NVR averages and S/N values. All three cleaning process options were made available for cleaning hardware

The preferred tank position, though not as critical, was determined to be centrally located in the vicinity of where the spray rinse nozzles were aimed The noise factors of type, amount and location of soil to be removed, and the alloy being cleaned, did not affect the cleaning ability of the system due to its robustness.

All of the modifications to improve fiber and particle count results were successful. With aqueous particulate verification in place, production hardware has consistently passed respective program requirements. With the experience accumulated with production hardware, the gaseous nitrogen blow dry process was not included as a process requirement. Daily wipe down of floor surfaces and as a minimum, weekly room wipe downs were incorporated to be consistent with current in-house cleanroom practice.

As compared to the baseline solvent precision cleaning method, the aqueous precision clean process was found to be more effective in removing NVR, particles and fibers This process was developed to be as robust as possible for the cleaning operations required at Rocketdyne However, this process is operator dependent and cannot be changed due to the nature of the items to be cleaned These parts are low volume items which are unique from batch to batch This requires daily evaluation of process sequences, positioning, rinsing, handling and protection of hardware.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance of the Raging Waters CPI Team

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SUBSTITUTION OF SPRAY-IN-AIR AQUEOUS CLEANING FOR TCA DEGREASING OF SPACE SHUTTLE REUSABLE SOLID ROCKET MOTOR HARDWARE

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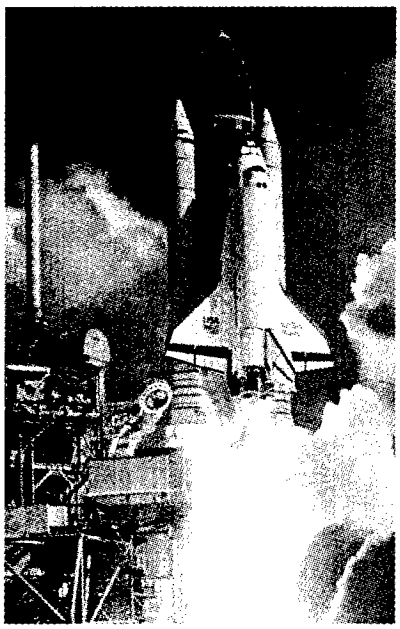
August 1996



ABSTRACT

Because the Clean Air Act eliminates the production of methyl chloroform for emissive uses after January 1, 1996, the bond surface preparation processes used for the Space Shuttle Reusable Solid Rocket Motor are being changed to eliminate methyl chloroform (TCA) degreasing. Spray-in-air aqueous cleaning, in conjunction with automated cosmetic grit blast, will be used to prepare metal hardware for subsequent bonding operations.

The cleaner that has been selected is Brulin 1990 GD®. An extensive development and qualification effort is being conducted for this change. Testing completed to date with laboratory, mid-scale, and full-scale equipment shows that bond strengths are as good or better than those prepared with TCA vapor degreasing. Full-scale motor and igniter component cleaning tests and witness panel tensile and peel tests have yielded data and practical lessons that verify the equivalence of aqueous cleaning and TCA processing.

INTRODUCTION

In a typical solid rocket motor, rubber insulation is bonded directly to metal surfaces. The insulation protects the metal from the intense heat produced during motor operation. The safe operation of a solid rocket motor depends upon the integrity of these bonded assemblies; therefore, precision cleaning effectiveness is paramount.

Four cleaning processes, i.e., spray under immersion, immersion with mechanical agitation, immersion with ultrasonics, and spray in air (SIA), were evaluated. Because of the level of cleaning required and the size of the full-scale components to be cleaned, SIA was selected as the most robust and cost effective option. The selected cleaner, Brulin 1990 GD, is an alkaline, low foaming aqueous cleaner and is not corrosive to D6AC steel and 7075 aluminum parts. It cleans our most tenacious preservative, Conoco HD-2® grease, and maintains cleaning capability even after significant soil loading.

Small cylindrically shaped flight components were cleaned in a mid-scale (40-in.-diameter turntable) SIA machine. This machine has a rotating turntable and fixed nozzle systems to clean both outside diameter

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and inside diameter surfaces. Components completely covered with a thin layer of HD-2 corrosion preventative grease were effectively cleaned using a predefined wash density. Additionally, nozzle aiming, nozzle standoff distance, wash pressures and temperature were evaluated for a 10 percent cleaner solution. Rinsing and drying processes were developed for various geometries. Sets of witness panels (normally accompanying production hardware through processing) and tapered double cantilever beams (TDCBs) were cleaned at various parameter levels in order to compare bond strength results with TCA cleaning tests.

Test matrices were defined and executed which optimized process parameters and provided a comfortable margin to ensure that parts would be acceptably cleaned under the worst of conditions. The wash parameters chosen were:

- 10% cleaner concentration used at 150°F
- Wash flow rate: 2.5 gpm/nozzle
- Wash pressure: 70 psi
- Wash time: 3 minutes
- Wash density: 0.070 gal/in.^{2}
- Rinse density: 0.035 gal/in.^{2}

This paper presents details from completed test plans which expanded on these basic guidelines to provide verification that the SIA aqueous cleaning system will produce effective and robust cleaning processes and product bond strengths as good or better than traditional TCA degreasing processing methods for full-scale solid rocket motor components.

TEST ARTICLE DESCRIPTION

A Proceco Typhoon®, 40-in. turntable, stainless steel, three-stage SIA aqueous cleaning system was used to clean cylindrical parts with geometries representative of the smallest RSRM hardware. This test was intended to define any scale related wash parameters, verify findings of earlier laboratory-scale tests, and expand our understanding of the rinse and drying processes. Cleaning effectiveness was determined by visual and blacklight inspection as well as being verified by bond tensile and fracture toughness test data derived from coupon samples that were cleaned with the hardware.

HD-2 grease was cleaned from the following components using various wash, rinse, dry parameters, and concentrations of Brulin 1990:

- 8 x 12 witness panels, aluminum and steel
- TDCB beams, aluminum and steel
- One scrap igniter chamber
- One modified NASA (MNASA) nozzle housing

Wash and rinse solution samples were taken for analyses. DEXTER® EA913NA structural adhesive was used to bond TDCBs for fracture toughness data and to bond buttons to witness panels for tensile data.

FINDINGS

Many of the design concepts for the full-scale SIA system were evaluated with this machine. Rinse and dry processes were developed, and significant experience was gained with both the equipment and wash and rinse solutions. Experience has been gained with three-stage Proceco cleaning equipment and wash/rinse solution chemistry changes with use and grease loading.

The formation of precipitates from calcium in HD-2 grease and it's reaction with Brulin 1990 was more apparent and troublesome than was seen on earlier tests. Heater operation and resultant temperature cycling are contributing factors. Wash and rinse densities defined in earlier tests were effective and independent of scale-up. The full work height available (48 in.) and part diameter were used to calculate total surface area. The nozzle size, number of side nozzles, and gallons per minute per nozzle at test pressure were used to determine the run time required to meet the wash and rinse densities. It was shown that times and drying parameters are machine design/part geometry dependent. Reduced temperatures and cleaner concentrations made nozzle aiming more critical and reduced the cleaning effectiveness at tooling interfaces. Cleaning is not as effective at the rotating table level in the wash chamber because of interference with the spray pattern. Flat surfaces perpendicular to the spray nozzles are easily cleaned at minimum parameters. Difficult geometry, such as blind threaded holes and surfaces parallel to the spray were cleaned effectively only with higher pressures or longer wash times. In addition, some geometry on the MNASA nozzle housing was cleaned effectively only when nozzle aiming and standoff were set up specifically for its geometry. Wash time was used as a variable to maintain a constant wash density with various wash pressures.

Second stage rinse (recirculated and filtered) time was set up to duplicate the 0.035 gal/in.^{2} rinse density established in earlier SIA tests. The density was effective even at a high number of cleaning cycles. The multistage SIA machine allowed increased understanding of significant variables related to drying. Water that is allowed to pond on D6AC parts will cause light flash rusting as it evaporates. Smooth vertical surfaces flash dried very quickly when hot. The third stage rinse (fresh deionized water) cools the parts if the rinse is longer than about 1 minute (machine design limitation). Rinse runoff samples were taken every 30 sec of the final fresh water rinse to evaluate conductivity response to rinse time. These measurements of conductivity of the runoff flow are plotted in Figure 1 and suggest that 2 minutes is a minimum final rinse requirement for this machine (at a given flow rate). Dry time was strongly dependent upon part geometry and temperature. Pooled water can be easily vacuumed-off which greatly reduces dry time and oxidation potential. The 200°F heated air-blowoff worked, but was only a little better than opening the door and letting the parts flash dry.

Bond Results

The TDCB samples were evaluated for cleanliness using black light and a contamination scanning instrument (ConScan), assembled and bonded, and tested. The fracture energy data show little sensitivity to wash soil loading or rinse conductivity and is presented in Table 1 and 2. Comparing these data to RSRM historical data validates the equivalence of the new cleaning process compared to TCA vapor degreasing.

Igniter Bondline and Full-Scale Cleaning Testing

The testing evaluated bondlines which are unique to the RSRM igniter chamber, adapter, and initiator described in Figure 2. This includes vulcanized rubber insulation, filled epoxy adhesives-to-metal bondlines, and the initiator liner (liquified form of rubber insulation)-to-metal bondline. Four epoxy bondlines were evaluated: adhesive-to-metal bondline for the chamber insert (CI), adhesive-to-metal bondline for the

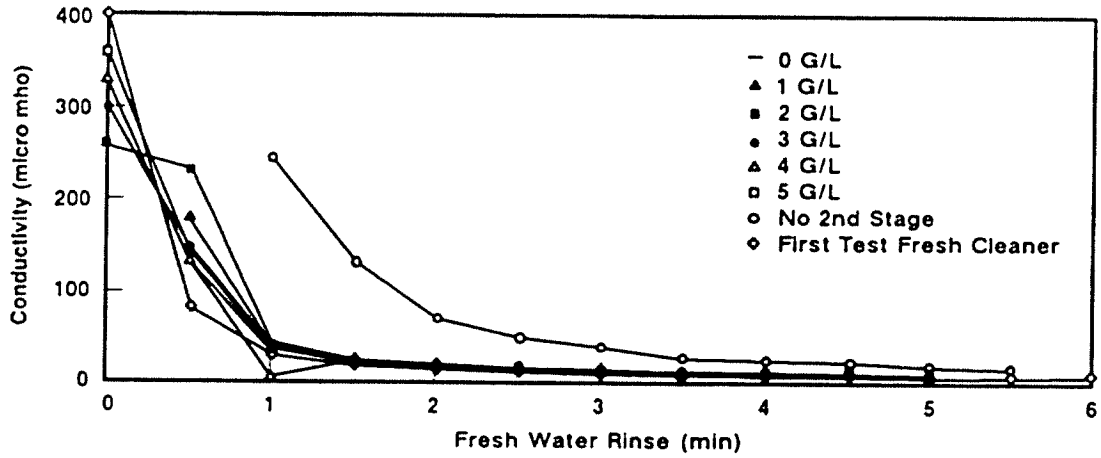

Figure 1. Rinse Conductivity

Table 1. EA913 Fracture Energy for Aluminum TDCBs

SOIL LOAD	HD-2 Grease	SIA Clean Only			SIA Clean Followed by Grit Blast		
		$G1_c$*	cV	Adhesive (%)	$G1_c$*	cV	Adhesive (%)
	0 g/l	10.85	1 5	37	15 49	6 6	13
	1 g/l	9.85	4 9	37	14 91	8.0	13
	2 g/l	16.15	5.5	0	14 04	5.2	12
	3 g/l	9.0	22.2	47	13.91	5 4	18
	4 g/l	9.7	3 8	48	13.80	5 1	33
	5 g/l	10 7	38.3	37	14 94	5 8	15
	5 g/l wash then 5 min fresh rinse only	9 13	38 4	58	8.16	33.9	63

* Normal RSRM average for this substrate, adhesive, and adherend is 7.6 in -lb/in ^{2}—5 5 cV

$G1_c$ = fracture toughness (in -lb/in ^{2})
cV = coefficiant of variation

Table 2. EA913 Fracture Energy Versus Conductivity for Aluminum TDCBs

FW RINSE	Time	1 micro mho			5 micro mho		
		$G1_c$*	cV	Adhesive (%)	$G1_c$*	cV	Adhesive (%)
	0	7 14	14 7	12	7 08	28.2	23
	30 sec	15 19	15 8	75	14 43	4 6	75
	2 min	14 18	6 4	83	12.17	1 8	77
	4 min	13 99	1 4	80	14 91	0 7	77
	6 min	16.09	3.0	73	14 42	1 1	82

* Normal RSRM average for this substrate, adhesive, and adherend is 7 6 in -lb/in ^{2}—5 5 cV

$G1_c$ = fracture toughness (in -lb/in ^{2})
cV = coefficiant of variation

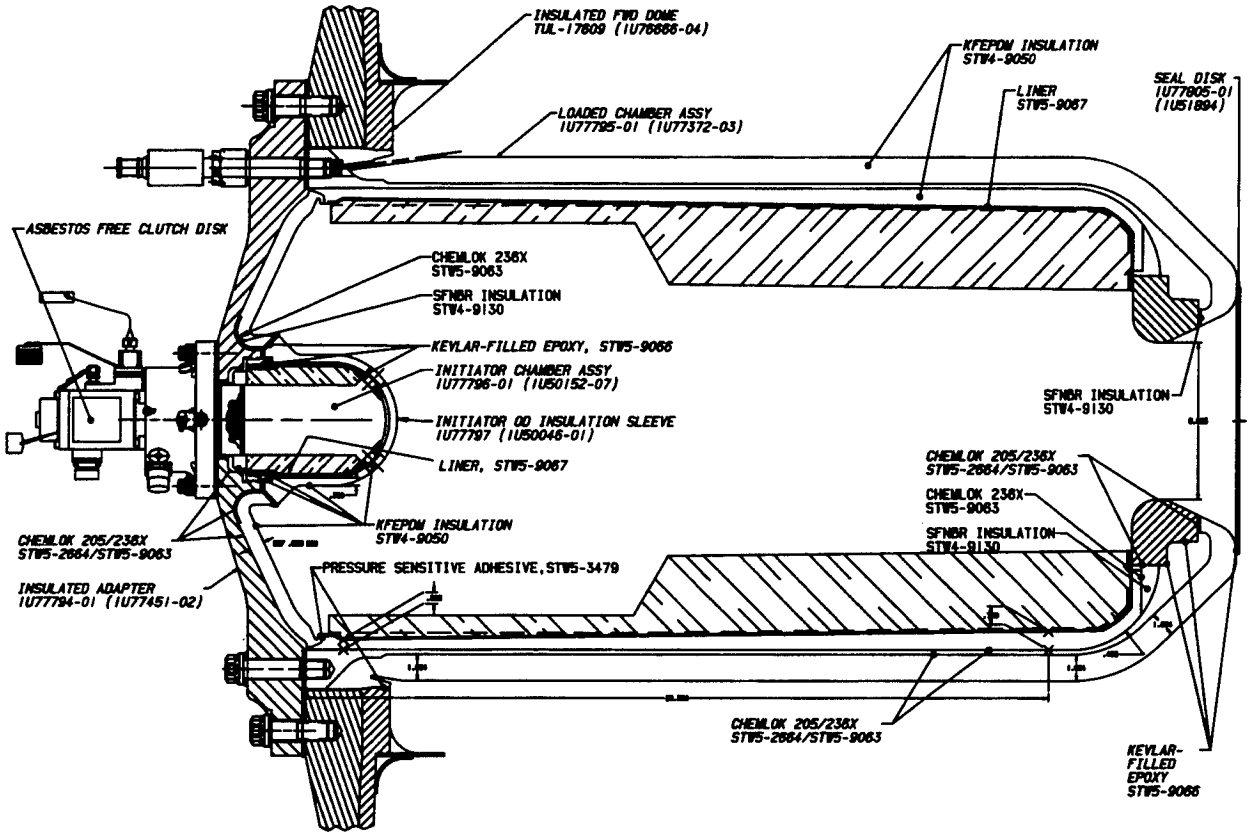

Figure 2. Igniter Description

initiator insert (II), adhesive–to–metal bondline for the initiator external nitrile butadiene rubber (NBR) insulation (IE), liner–to–metal bondline for the initiator (IL), and NBR vulcanized to metal.

Bond Tests

Adhesive tensile button test specimens were prepared and evaluated for each bondline. Specimen process included SIA cleaning, grit blast and ConScan inspection, reflecting the new production bond surface preparation process. A second set of adhesive tensile button specimens were prepared using the baseline TCA process. Tensile testing was done both at zero time and also after 16 weeks of accelerated aging. Table 3 contains tensile strength results for each epoxy bondline. Comparison of results for TCA and and SIA provides verification that the new process is adequate to produce flight hardware.

Adhesive TDCB test specimens were also prepared and tested for the CI, II, and IE bondlines. Adhesive TDCB specimens were SIA cleaned, grit blasted, bonded, and tested after zero– and 16–week accelerated aging. A second set of TDCBs were similarly prepared using the baseline TCA process. Fracture energy results presented in Table 4 are similar for the SIA and the TCA specimens.

Witness panel specimens were prepared to compare insulation bond specimens prepared for bonding using TCA and SIA cleaning processes. These are shown in Table 5 and 6. The process control alert ranges are displayed in the right–hand column. Again, these data show that bondline preparation using the new SIA process is as good or better than current processes using TCA vapor degrease methods.

Table 3. Median Tensile Strength for 0- and 16-Week Aging

	0-Week		16-Week	
	TCA (psi)	SIA (psi)	TCA (psi)	SIA (psi)
CI	663	671	637	656
II	663	680	661	670
IE	779	713	774	753
IL	151	155	112	114

Table 4. Median Fracture Energy for 0- and 16-Week Aging

	0-Week		16-Week	
	TCA (in.-lb/in^2)	SIA (in.-lb/in^2)	TCA (in.-lb/in^2)	SIA (in.-lb/in^2)
CI	3.71	3.70	3.40	3.39
II	4.26	4.19	3.99	3.47
IE	5.14	5.70	4.80	5.86

Table 5. NBR/Steel Vulcanized Bondline Testing

Witness Panel Mechanical Properties		Baseline ASNBR		16-Week Aging		PCA Range (flight)
		TCA	SIA	TCA	SIA	
Tensile	Average (psi)	901	858	942	896	701-933
	STDEV	50	59	42	42	
	cV (%)	5.6	6.9	4.4	4.6	
	Cohesive Failure (%)	97-100	98-100	96-97	95-98	
Peel	Average (pli)	202	202	220	222	185-219
	STDEV	4	3	5	7	
	cV (%)	1.9	1.6	2.4	3.1	
	Cohesive Failure (%)	100	100	100	100	

Table 6. EPDM/Steel Vulcanized Bondline Testing

Witness Panel Mechanical Properties		Baseline EPDM		16-Week Aging		PCA Range (flight)
		TCA	SIA	TCA	SIA	
Tensile	Average (psi)	905	931	983	1,050	638-1,096
	STDEV	101	112	120	116	
	cV (%)	10.9	12.2	12.2	11.1	
	Cohesive Failure (%)	100	100	100	100	
Peel	Average (pli)	97	98	104	103.6	70.7-145
	STDEV	6.4	5.3	8.3	7.7	
	cV (%)	6.57	5.44	8.01	7.43	
	Cohesive Failure (%)	100	100	100	100	

Full-Scale Cleaning Tests

Tests were conducted using a full-scale igniter chamber, adapter, and initiator. A full-scale chamber and adapter were processed through a high-pressure waterblast (36,000 psi) refurbishment process then through the ODC-free bond surface preparation process up through ConScan inspection. The chamber was installed in the SIA parts washer with the flange down using a chamber handling/holding fixture. Three threaded holes on the flange were used to mate the handing fixture to the chamber. The SIA cleaning process removed HD-2 grease from all acreage regions but small amounts remained in the threaded holes. Residual water was removed from the part surfaces using a vacuum system to speed drying and prevent oxidation of the metal due to pooled water. The use of higher wash pressures reduced the grease remaining in the threaded holes, but the use of directed nozzles to completely clean the area was deemed not necessary. Cleaning results for the adapter were similar to the chamber. A larger percentage of the surface was masked by the tooling, and the orientation of the part on the table reduced the effectiveness of the wash spray impingement. These concerns were easily dealt with by lengthening the wash time, and rotating the component part way through the wash to expose those areas of the surfaces masked by the tooling attach points. This only illustrates that cleaning effectiveness in a SIA system is dependent upon the geometry of the parts being cleaned. Results indicated that the proposed ODC process for the igniter chamber, adapter, and initiator provided an acceptable level of cleanliness for bonding.

CONCLUSION

Replacement of TCA vapor degreasing with SIA aqueous process using 10 percent Brulin 1990 GD has been tested for product adhesive bondline integrity. Full-scale demonstrations verify that the new process is equal to or better than TCA degreasing. Future activities will implement this process throughout the RSRM motor production.

Development of Statistical Process Control Methodology for an Environmentally Compliant Surface Cleaning Process in a Bonding Laboratory

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ABSTRACT

Bonding labs at both MSFC and the northern Utah production plant prepare bond test specimens which simulate or witness the production of NASA's Reusable Solid Rocket Motor (RSRM). The current process for preparing the bonding surfaces employs 1,1,1 trichloroethane vapor degreasing, which simulates the current RSRM process. Government regulations (e.g., the 1990 Amendments to the Clean Air Act) have mandated a production phase-out of a number of ozone depleting compounds (ODC) including 1,1,1 trichloroethane. In order to comply with these regulations, the RSRM Program is qualifying a spray-in-air (SIA) precision cleaning process using Brulin 1990, an aqueous blend of surfactants. Accordingly, surface preparation prior to bonding process simulation test specimens must reflect the new production cleaning process.

The Bonding Lab Statistical Process Control (SPC) program monitors the progress of the lab and its capabilities, as well as certifies the bonding technicians, by periodically preparing D6AC steel tensile adhesion panels with EA-913NA epoxy adhesive using a standardized process. SPC methods are then used to ensure the process is statistically in control, thus producing reliable data for bonding studies, and identify any problems which might develop. Since the specimen cleaning process is being changed, new SPC limits must be established.

This report summarizes side-by-side testing of D6AC steel tensile adhesion witness panels and tapered double cantilevered beams (TDCBs) using both the current baseline vapor degreasing process and a lab-scale spray-in-air process. A Proceco 26" Typhoon dishwasher cleaned both tensile adhesion witness panels and TDCBs in a process which simulates the new production process. The tests were performed six times during 1995, subsequent statistical analysis of the data established new upper control limits (UCL) and lower control limits (LCL). The data also demonstrated that the new process was equivalent to the vapor degreasing process.

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* This Work performed under NAS8-38100 with NASA/MSFC

INTRODUCTION

This program provided a means of conducting a short-term SPC program in which D6AC steel tensile adhesion witness panels and TDCBs were prepared side-by-side using both the current baseline vapor degreasing process and the proposed ODC-safe spray-in-air process. Data was then gathered to enable the HSO Bond Lab to transition its SPC Program away from using 1,1,1 trichloroethane vapor degreasing to the spray-in-air method of washing the bond surfaces with an approved cleaner (Brulin 1990 GD) and rinsing in deionized water. This was accomplished by cleaning one tensile adhesion witness panel and three sets of TDCBs and then bonding with EA-913NA epoxy adhesive. Subsequently, four additional test runs were performed using only the SIA process.

TEST ARTICLE ASSEMBLY

Two tensile adhesion panels (see Figure 1) and six tapered double cantilever beam (TDCB) sets (see Figure 2) were processed for each of six test runs. Four runs were conducted with EA-913NA Lot 82, three with Lot 83, and three with Lot 87.

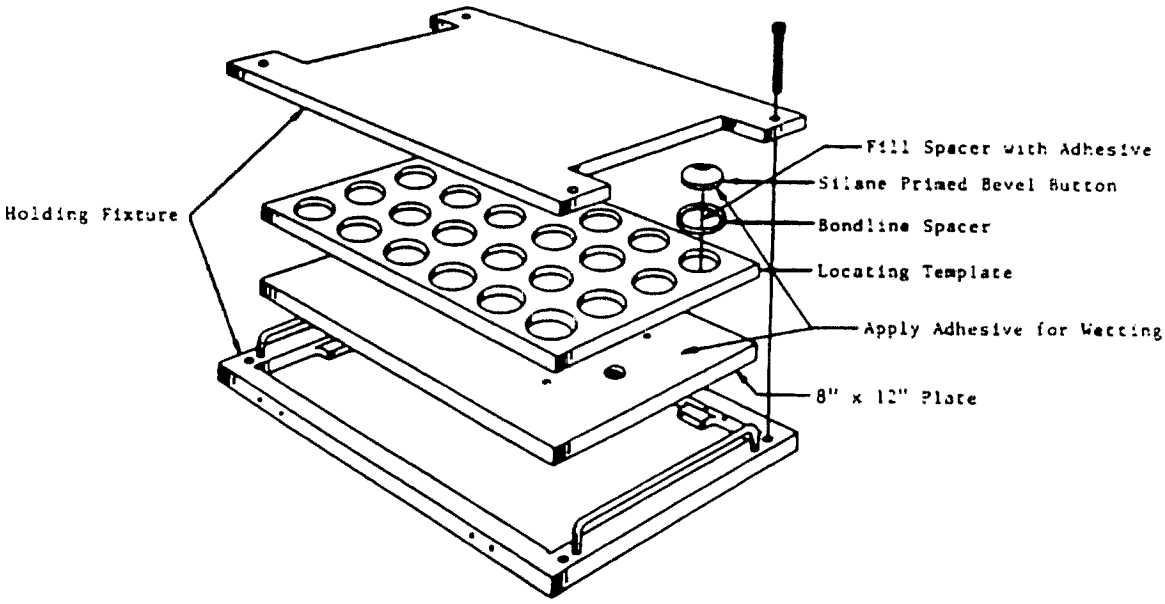

Figure 1. Tensile Adhesion Panel

The current (1,1,1 trichloroethane vapor degreaser) process was conducted as follows:

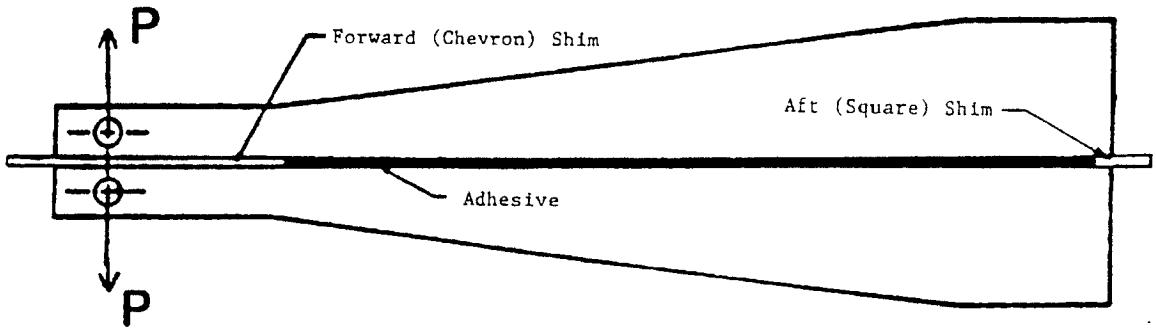

Figure 2. Tapered Double Cantilever Beam (TDCB) Specimen

1) Rough grit blast bonding surfaces using ZirClean® blast media at a pressure of 80 psi, a stand-off distance of 2 to 4 inches, and an impingement angle of 90°; Blow off grit dust using missile-grade air at 80 psi;

2) Vapor degrease hardware in Dow SM 1,1,1 trichloroethane for a minimum of 15 minutes; Allow to cool;

3) Final grit blast bonding surfaces using virgin ZirClean® blast media at a pressure of 80 psi, a stand-off distance of 2 to 4 inches, and an impingement angle of 20°; Blow off grit dust using missile-grade air at 80 psi;

4) Measure and record OSEE readings;

5) Transport to bonding lab in sealed nitrogen- or missile-grade air-purged ZipLok® bags.

6) Apply thin uniform coat of UF-3296 silane primer to bonding surfaces within 30 minutes of final grit blast operation;

7) Allow to dry at least 1 hour prior to bonding.

The proposed (Brulin 1990GD spray-in-air) process was conducted as follows:

1) Rough grit blast bonding surfaces using ZirClean® blast media at a pressure of 80 psi, a stand-off distance of 2 to 4 inches, and an

impingement angle of 90°; Blow off grit dust using missile-grade air at 80 psi;

2) Wash hardware in spray-in-air washer using deionized water with 10% concentration of Brulin 1990GD, wash temperature of 150 to 175°F, wash pressure of 130 psi, wash density of 0.070 gal/in^2, (5 minutes 23 seconds with the existing holding fixture); hold for 3 minutes;

3) Rinse hardware in spray-in-air washer using deionized water, rinse temperature of 150 to 175°F, rinse density of 0.035 gal/in^2, for 17 minutes 30 seconds; hold for 2 minutes to ensure complete drainage;

4) Blow off hardware with clean air at a temperature of 200°F for 5 minutes;

5) Final grit blast bonding surfaces using virgin ZirClean® blast media at a pressure of 80 psi, a stand-off distance of 2 to 4 inches, and an impingement angle of 20°; Blow off grit dust using missile-grade air at 80 psi;

6) Measure and record OSEE readings;

7) Transport to bonding lab in sealed nitrogen- or missile-grade air-purged ZipLok® bags.

8) Apply thin uniform coat of UF-3296 silane primer to bonding surfaces within 30 minutes of final grit blast operation;

9) Allow to dry at least 1 hour prior to bonding.

RESULTS

Results of this testing are presented in Tables 1 and 2 and in Figures 3 through 6. Figure 3 compares the SIA and VD processes (the first 12 runs in Table 1) and also indicates the current minimum allowable median tensile adhesion strength (4930 psi), and Figure 4 compares the SIA and VD processes and denotes the current upper and lower specification limits for critical energy release rate (11.0 - 24.2 in-lb/in^2). Clearly, both surface preparation methods produced data which exceeded these specification requirements; in fact, a number of the TDCB results were above the upper limit of this specification, but this has been commonplace with recent lots of EA-913NA. Because of this material change, the specification upper limit may be adjusted up to 32 in-lb/in^2. The different lots of EA-913NA appeared to behave differently, though both met or exceeded specification requirements, so they are plotted and tabulated separately.

Table 1. Tensile Adhesion Test Results

Test	Adhesive Lot No.	Tensile Adhesion Strength (psi) Range	Median	Avg	C.V.(%)	Avg. Failure Mode % Adhesive-to-Panel
Vapor Degreased 1	0082	7731-8173	7965	7912	1.7	0
Vapor Degreased 2	0082	7972-8428	8271	8225	2.0	0
Vapor Degreased 3	0082	8012-8455	8252	8243	1.7	0
Vapor Degreased 4	0082	7239-8680	8267	8078	6.7	0
Average			8183			
Vapor Degreased 5	0083	8107-8780	8606	8545	2.3	0
Vapor Degreased 6	0083	8344-8672	8538	8530	1.1	0
Average			8572			
Brulin 1990GD 1	0082	6742-8169	7824	7753	4.7	0
Brulin 1990GD 2	0082	6869-8275	7816	7760	6.3	0
Brulin 1990GD 3	0082	8099-8478	8347	8334	1.2	0
Brulin 1990GD 4	0082	6699-8574	8053	7972	6.3	0
Average			8010			
Brulin 1990GD 5	0083	8400-8721	8613	8589	1.4	0
Brulin 1990GD 6	0083	8054-8712	8386	8410	2.0	0
Average			8499			
January SPC	0083	5892-8600	7216	7398	14.9	2
May SPC I	0087	8336-8711	8603	8587	1.2	0
May SPC II	0087	6668-8667	8017	7820	9.1	5
June SPC I	0087	8365-8841	8597	8628	1.5	0
Average			8109			

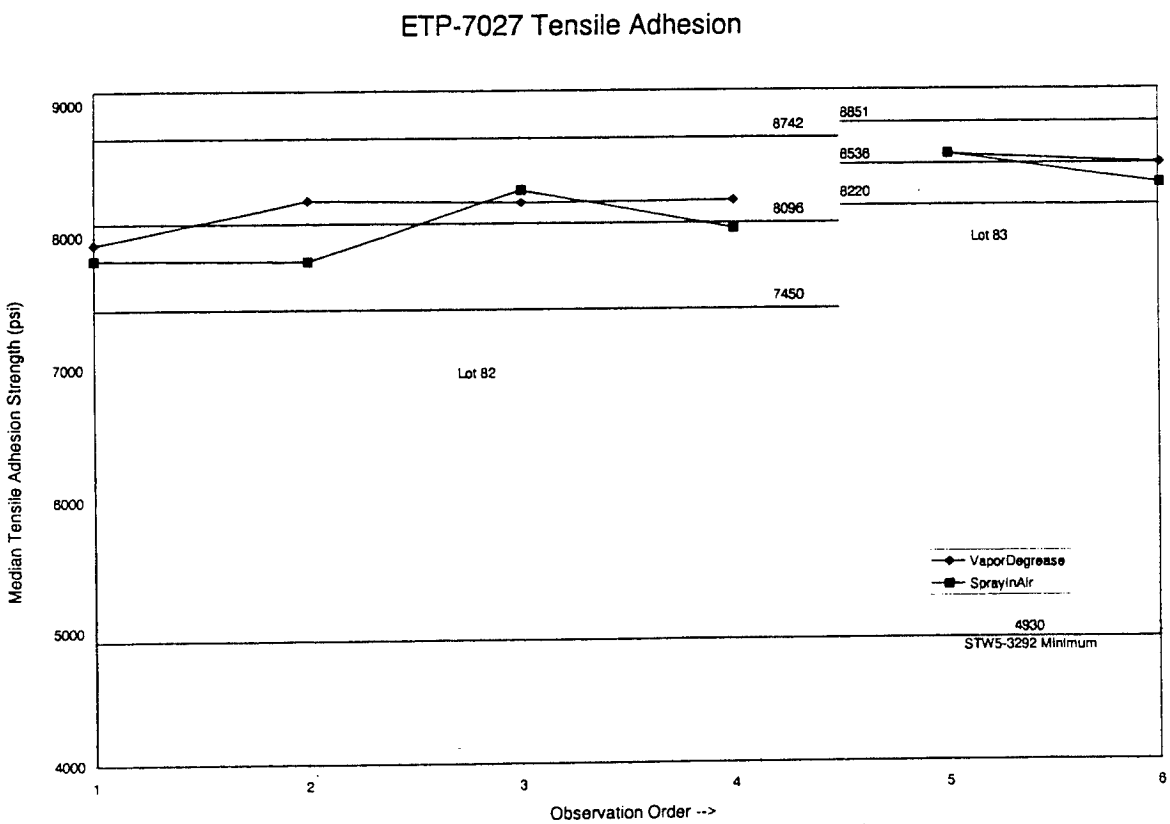

Figure 3. Results of ETP-7027 Tensile Adhesion Testing

Table 2: Fracture Toughness Test Results

Test	Adhesive Lot No.	Critical Energy Release Rate (in lb/in²) Range	Median	Avg	C.V.(%)	Avg. Failure Mode % Adhesive-at-Beam
Vapor Degreased 1	0082	27.32-28.05	27.72	27.70	1.3	0
Vapor Degreased 2	0082	24.63-25.08	24.73	24.81	1.0	0
Vapor Degreased 3	0082	26.03-26.53	26.25	26.27	1.0	0
Vapor Degreased 4	0082	23.72	23.72	23.72	-.-	0
Average				25.63		
Vapor Degreased 5	0083	18.70-21.68	20.19	20.19	10.4	0
Vapor Degreased 6	0083	20.72-21.68	20.91	21.10	2.4	0
Average				20.65		
Brulin 1990GD 1	0082	26.32-29.58	26.64	27.51	6.5	0
Brulin 1990GD 2	0082	26.82-28.99	28.69	28.17	4.2	0
Brulin 1990GD 3	0082	24.25-24.87	24.56	24.56	1.8	0
Brulin 1990GD 4	0082	21.07-24.30	22.69	22.69	10.1	0
Average				25.73		
Brulin 1990GD 5	0083	18.73-18.85	18.79	18.79	0.5	0
Brulin 1990GD 6	0083	--.-- - --.--	--.--	--.--	-.-	-
Average				18.79		
January SPC	0083	19.66	19.66	19.66	-.-	0
May SPC I	0087	23.79-24.64	24.20	24.21	1.8	0
May SPC II	0087	----	-----	-----	-.-	-
June SPC I	0087	23.86-25.37	24.95	24.73	3.2	0
Average				22.87		

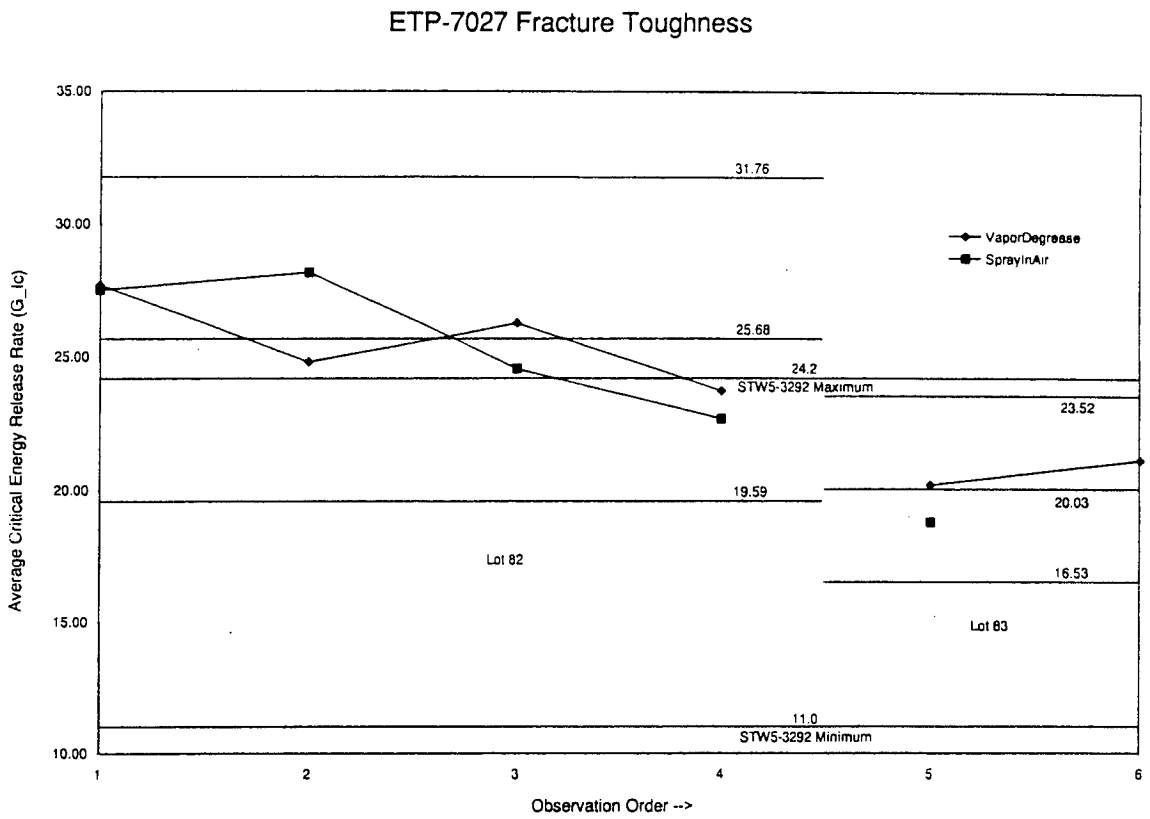

Figure 4. Results of ETP-7027 TDCB Testing

Based on these comparison tests, monthly SPC runs have employed SIA precision cleaning (the last four runs in Tables 1 and 2). Figures 5 and 6 present all the SIA-cleaned specimens from Tables 1 and 2. All values were used to calculate statistical means and upper and lower control limits ($\pm 3\sigma$). This SPC mean is higher than the previous one for precision cleaning by 1,1,1 trichloroethane vapor degreasing days, probably due to improvements in the manufacture of the EA-913NA adhesive. However, the relatively wide range of the control limits may be indicative an increase in the number of process variables associated with the spray-in-air cleaning process, e.g., wash and rinse pressure deviations, deionized rinse water purity, etc. This possibility will need to be carefully monitored.

CONCLUSIONS

The SPC Program is very important to the Thiokol/HSO Bond Lab, serving a number of roles including lab calibration, technician certification, and reality check, and should be continued, with each bonding technician preparing one panel and three TDCB specimens per month. Spray-in-air washing with Brulin 1990GD has replaced 1,1,1 trichloroethane vapor degreasing as the standard bonding surface cleaning method for the HSO Bond Lab SPC Program, and will serve as the standard method for preparing control specimens.

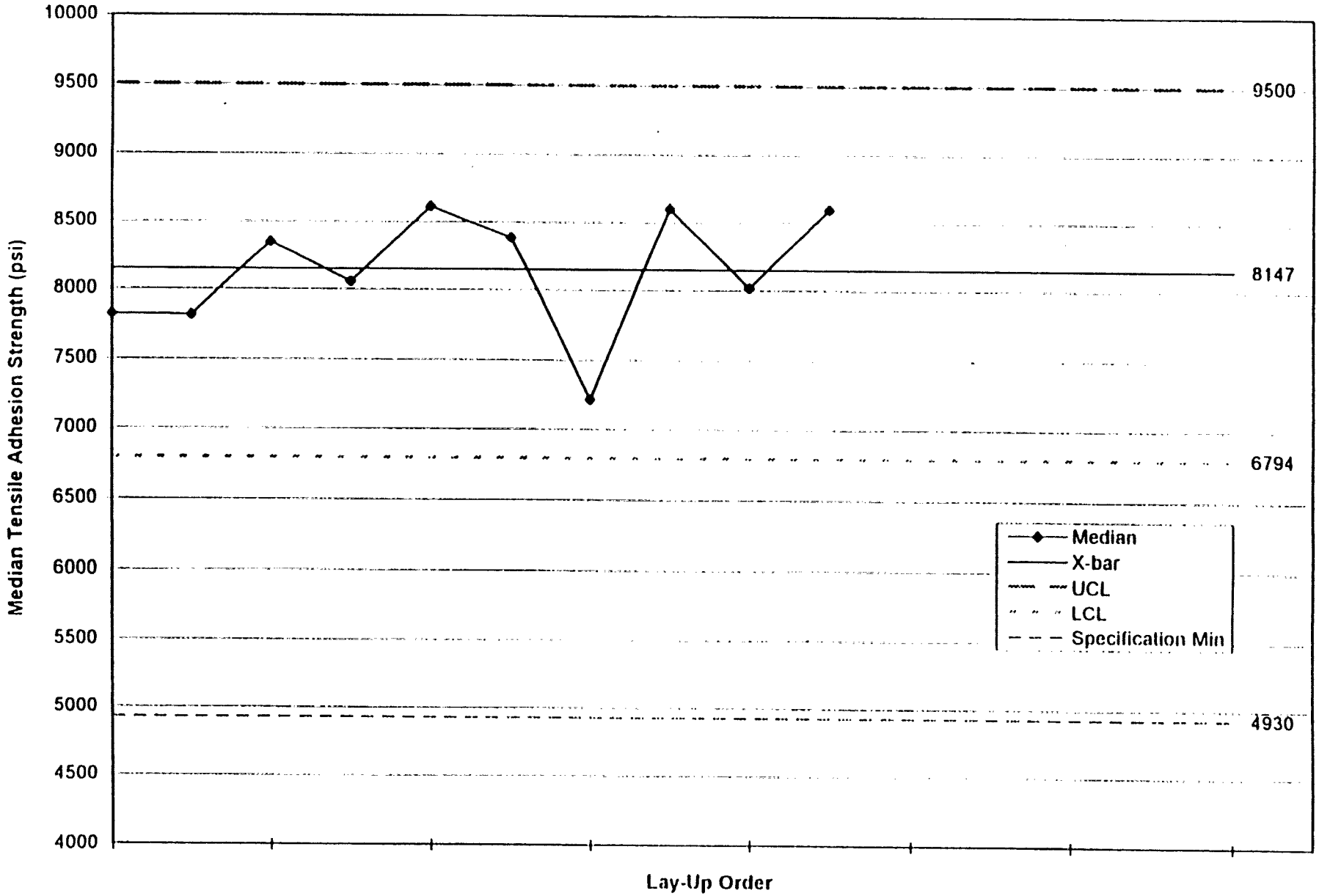

Figure 5. Median Tensile Adhesion Strength for All SIA Runs

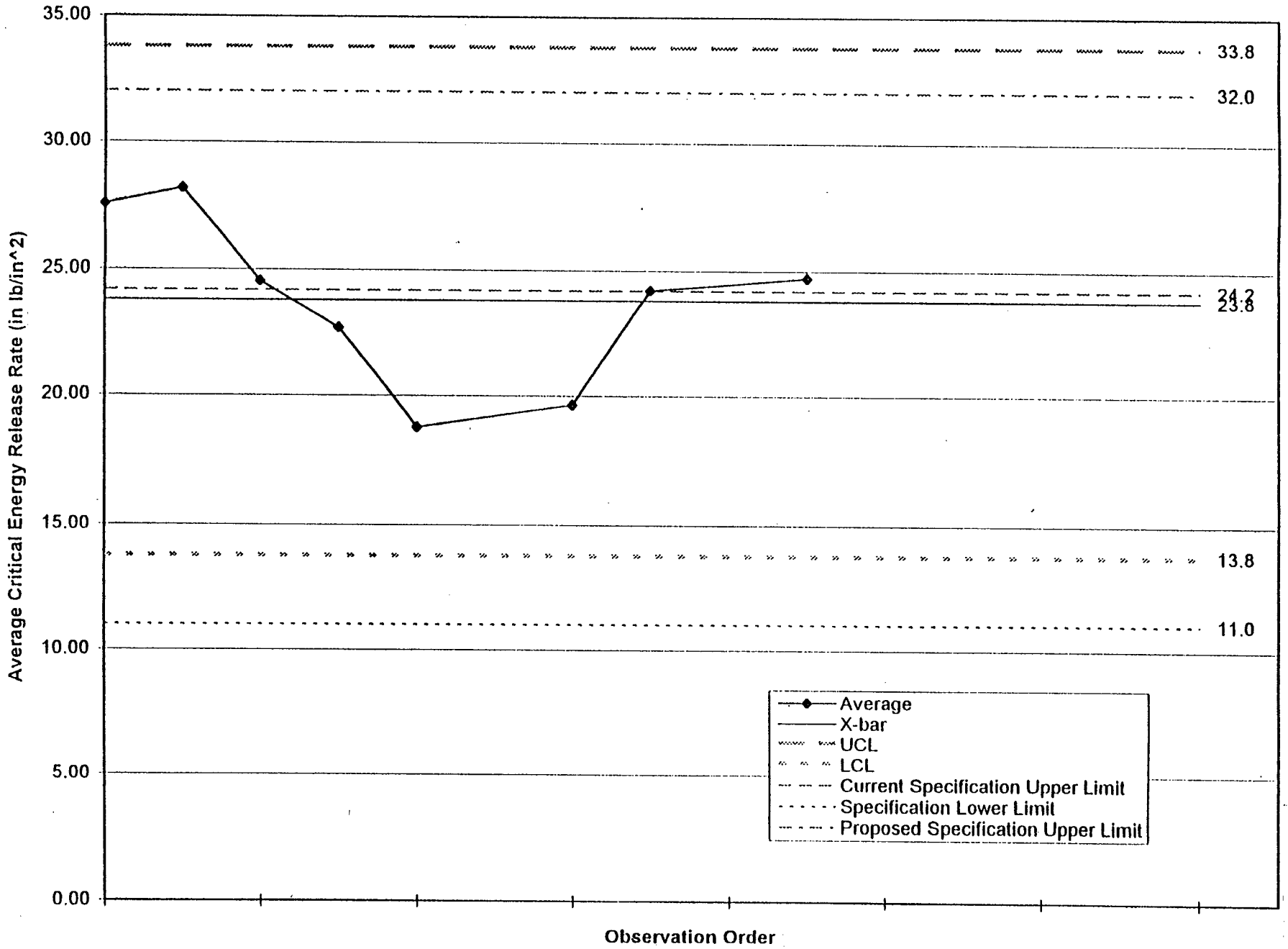

Figure 6. Fracture Toughness Results for All SIA Runs

REPLACEMENT TECHNOLOGIES FOR PRECISION CLEANING OF AEROSPACE HARDWARE FOR PROPELLANT SERVICE*

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ABSTRACT

The NASA White Sands Test Facility (WSTF) is developing cleaning and verification processes to replace currently used chlorofluorocarbon-113- (CFC-113-) based processes. The processes being evaluated include both aqueous- and solvent-based techniques. Replacement technologies are being investigated for aerospace hardware and for gauges and instrumentation. This paper includes the findings of investigations of aqueous cleaning and verification of aerospace hardware using known contaminants, such as hydraulic fluid and commonly used oils. The results correlate nonvolatile residue with CFC 113. The studies also include enhancements to aqueous sampling for organic and particulate contamination.

Although aqueous alternatives have been identified for several processes, a need still exists for nonaqueous solvent cleaning, such as the cleaning and cleanliness verification of gauges used for oxygen service. The cleaning effectiveness of tetrachloroethylene (PCE), trichloroethylene (TCE), ethanol, hydrochlorofluorocarbon 225 (HCFC 225), HCFC 141b, HFE 7100®[1], and Vertrel MCA®[2] was evaluated using aerospace gauges and precision instruments and then compared to the cleaning effectiveness of CFC 113. Solvents considered for use in oxygen systems were also tested for oxygen compatibility using high-pressure oxygen autogenous ignition and liquid oxygen mechanical impact testing.

SCOPE OF CLEANING OPERATIONS

Cleaning operations at WSTF encompass support for materials, components, and propulsion test systems and a large depot activity. As part of these operations, components are cleaned for a variety of services including oxygen, hydrogen, hydrazines, and nitrogen tetroxide. Cleanliness levels to 50A are required for high-pressure oxygen service.

Three approaches have been used as part of the CFC 113 conservation process begun in 1988: control of CFC 113 stocks, use of aqueous cleanliness verification technologies, and investigation of alternative solvents.

CONTROL OF CFC 113 STOCKS

Conservation was implemented by first establishing centralized control of CFC 113 stocks. The use and issue of CFC 113 in squirt bottles for field cleaning was eliminated, and access to the stock of CFC 113 was strictly controlled. Field cleaning operations using CFC 113 have been curtailed where possible.

Figure 1 shows the results of the conservation efforts. During 1984-85, two vapor degreasers with inefficient solvent recoveries were replaced by a single, more efficient unit. During 1986-87, CFC 113 rinses were eliminated from the cleaning operations, and field operations using CFC 113 were eliminated. During 1990-91,

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[1] HFE 7100 is a registered trademark of 3M Specialty Chemicals.
[2] Vertrel MCA is a registered trademark of DuPont Nemours.

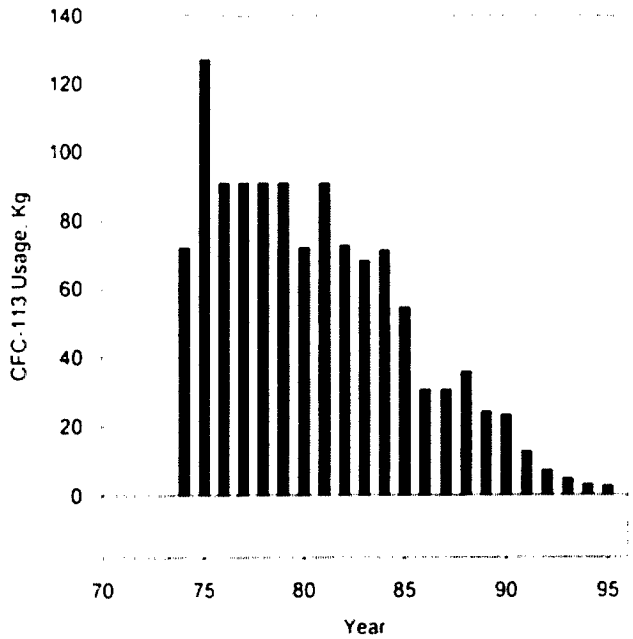

Figure 1. CFC 113 Use in WSTF Cleaning Operations by Year

CFC 113 was eliminated from pre-cleaning operations and was used only for cleanliness verification of critical applications. In 1992, access to the CFC 113 stock was limited by sealing or locking all valves to the supply. In 1993, the use of CFC 113 was monitored on a weekly basis; all CFC 113 was recycled through the vapor degreaser, and full-time operation of the vapor degreaser cooling coils was initiated. Numerous other conservation efforts were also initiated through education and engineering supervision of cleaning operations.

Further savings in CFC 113 consumption were realized by assessing cleaning processes and determining where CFC 113 could be eliminated without decreasing process effectiveness. The pre-clean process, consisting of both preliminary and final CFC 113 rinses, was eliminated before final cleaning and verification. The cleaning process now consists of an aqueous degreaser step if required, followed by cleaning in basic solution, water rinse, acid cleaning, and a double countercurrent rinse with ultrapure water. The parts are then dried in a nitrogen-purged, HEPA-filtered oven before cleanliness verification and packaging. Only in critical applications such as oxygen service or for flight hardware, or as required by specification, is a final CFC 113 rinse and cleanliness verification sampling performed. The use of ultrapure water in all final rinses is one key to effective aqueous cleaning processes. Process control is maintained by spot checking for residual contaminants. Components are sampled with a 100-mL portion of CFC 113, and the nonvolatile residue (NVR) is determined. A representative control chart is given in Figure 2 for the pre-clean process previously described.

AQUEOUS TECHNOLOGIES

The application of aqueous cleanliness verification is based on a procedure developed at Kennedy Space Center (KSC) (Allen et al 1992). In this procedure, parts are sampled in 50 °C (122 °F) ultrapure water using either a 25 kHz, 1000 W ultrasonic bath or a 20 kHz, 600 W ultrasonic probe. The organic content of this water is then determined using a high-temperature, catalytic-combustion, total organic carbon (TOC) analyzer. A pilot study was carried out using coupons contaminated with commonly encountered hydrocarbons. Figure 3 shows the compiled results of testing with hydraulic, vacuum pump, and air hydraulic oils. The mass of contaminant hydrocarbon, determined gravimetrically, is plotted vs the mass of hydrocarbon as determined by ultrasonic aqueous sample and TOC determination. A linear regression on the data gives a 63-percent recovery of the hydrocarbons tested. Also plotted are the water blanks taken before the contaminants were added.

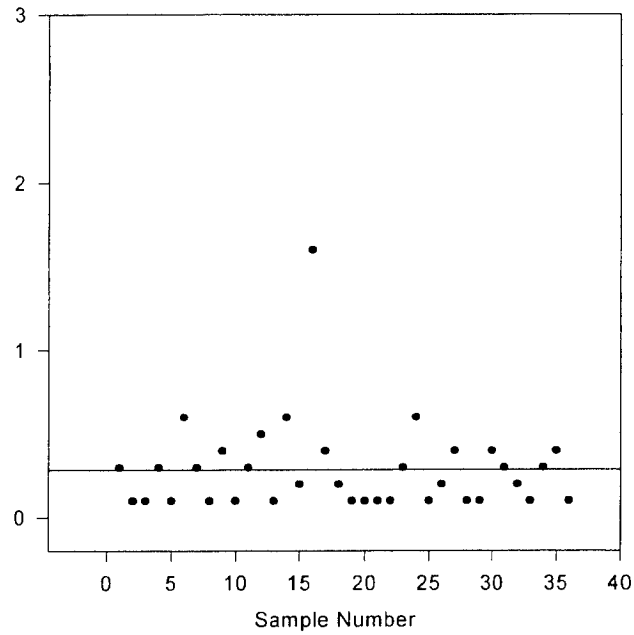

Figure 2. Process Control Chart for Pre-clean Process

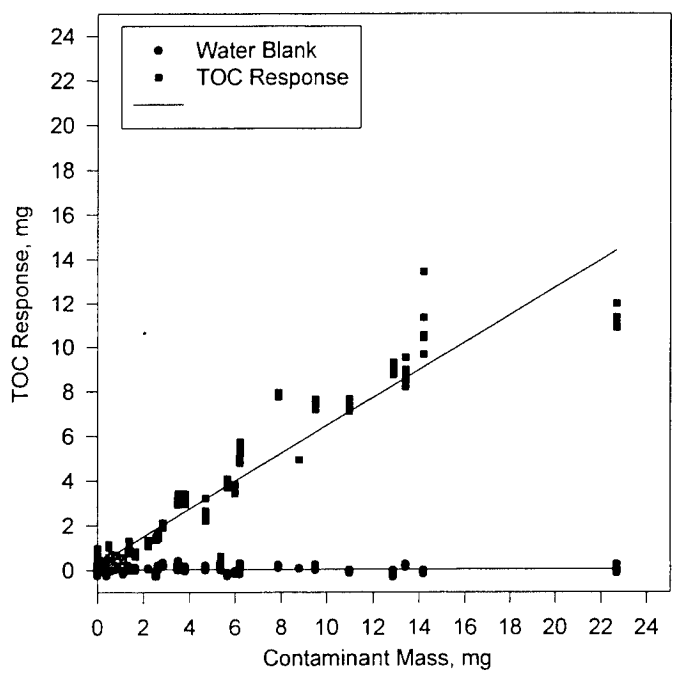

Figure 3. Combined TOC Response vs Contaminant Level

A similar study using actual hardware, primarily small fittings, was conducted by contaminating a batch of parts, randomly splitting the batch, and performing parallel sampling using CFC 113 and the aqueous ultrasonic sampling. The results indicate a correlation between the CFC 113 and the aqueous ultrasonic sampling (Figure 4).

In testing to assess the effectiveness of aqueous ultrasonic sampling for particulates, actual hardware was used. Batches or components, primarily small fittings, were taken through the standard cleaning process to a level of visually clean. Before inspection, each batch was randomly divided in half and transferred to a Class 100 clean room. One-half of the batch was placed in a clean beaker and enough 55 °C ultrapure water was added to cover the

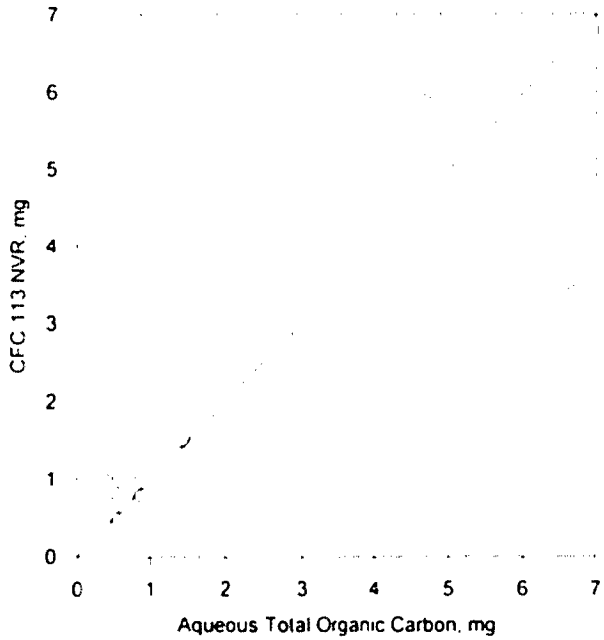

Figure 4. Combined TOC Response vs Contaminant Level

samples. The tip of an ultrasonic probe with a protective glass sleeve was immersed in the water to a depth of at least 2 cm. Approximately 550 W was delivered to the water-immersed components in 0.3 s intervals with a 50 percent duty cycle for 30 s, giving a total exposure time of 15 s. The water was then decanted into a filter funnel. The particles on the filter were then counted as a function of size.

The second half of the batch was placed in the CFC 113 sampling funnel and rinsed with approximately 100 mL of CFC 113 that was collected in a filter funnel. No rinsing with CFC 113 was performed before the sampling. The particles on the filter were then counted as a function of size.

Figure 5 shows the trend of higher recovery by aqueous ultrasonic sampling. Out of 66 points in the plot, only 6 are significantly above the 1-to-1 correspondence line. Even if the two methods of sampling were absolutely equivalent, a certain amount of scatter off the 1-to-1 correspondence line would be expected because of the lack of random distribution of particles throughout the batch being sampled and the limited number of parts in the batch. Currently, WSTF is performing studies comparing aqueous ultrasonic probe sampling for both total organic carbon and particulates.

ALTERNATIVE SOLVENTS

While many evaluations of aqueous processes as alternatives have been carried out, a need still exists for nonaqueous solvents. A recent investigation by the Navy has identified the cleaning and verification of high-pressure gauges and precision instrumentation as one area for which no aqueous alternative exists and for which an alternative must be identified (Antin 1994). As part of an effort sponsored by KSC and Naval Sea Systems Command, several alternative solvents were examined. Solvent properties considered in the cleaning of gauges and instrumentation include:

- The ability to remove contaminants
- The ability of the solvent to be removed from the cleaned part
- The solvent's flammability characteristics, which are crucial for solvents to be used in oxygen systems
- The solvent toxicity
- The ability of the solvent to be used as a verification fluid

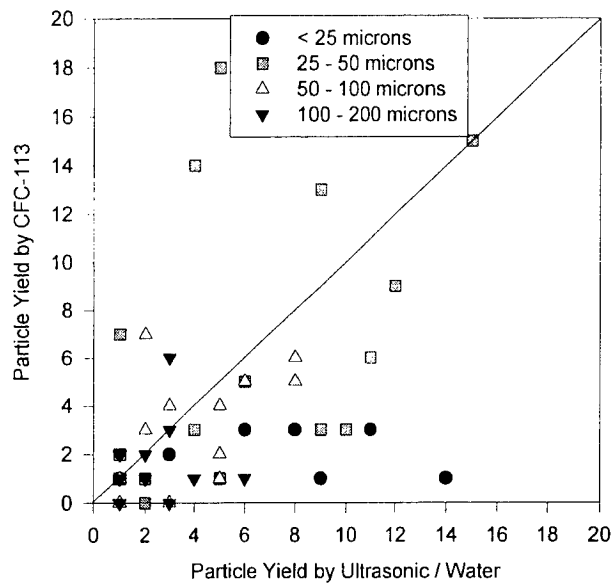

Figure 5. Effectiveness of Particulate Verification for Aqueous Method

The solvents that have been investigated to date represent a wide range of chemistries and include a chlorinated hydrocarbon, an alcohol, a perchlorinated alkene, an ether, two hydrochlorofluorocarbons, a hydrofluorocarbon, and a hydrofluoroether. In addition, CFC 113 was submitted for comparative purposes. The solvents studied and their physical properties are listed in Table 1. Tert-butylmethylether and n-Hexane were evaluated in early testing but were not considered for further testing because of toxicity concerns.

Table 1. Solvents Studied and their Physical Properties

Solvent	Boiling Point (°C)	Threshold Limit Value (ppm)	Flammability
CFC 113	48	1000[a]	No
HCFC 225	53	50[b]	No
Trichloroethylene	87	50[a]	Yes
HCFC 141b	32	500	*
HFE 7100	60	600	No
Vertrel MCA	39	200	**
Tetrachloroethylene	121	25[a]	No
Ethanol	78	1000[a]	Yes

[a] *Guide to Occupational Exposure Values*, American Conference of Governmental Industrial Hygienists, 1994.

[b] TLV data provided by manufacturer.

* Flammability limits have been established, but HCFC 141b does not have a flash point.

** Flammability of Vertrel MCA as a mixture has not been determined, and it has no flash point.

The solvents were evaluated using a variety of gauges and instrumentation types, which included closed- and open-ended high- and low-pressure Bourdon tube-type gauges. This type of gauge was selected because it presents the greatest challenge to a cleaning solvent. The solvents were evaluated according to their ability to remove a variety of commonly encountered contaminants including Krytox 240AC, the hydraulic fluids Mil-H-5606 and Mil-H-83282, and the gauge calibration fluids Spinesstic 22 and Sebacate. The gauges were contaminated with a known amount of contaminant before cleaning.

In general, the gauge was cleaned using five solvent volumes. Closed-end tubes were filled with solvent and then evacuated and purged to remove the solvent using a cleaning panel designed so that the maximum pressure used to fill the gauge was 35 psi (238 kPa). Open-ended gauges were rinsed with five 100-mL volumes of the solvent. In both cases, the final volume of solvent was collected, and an NVR was determined. The solvent removal was expressed as a percentage of contaminant removed.

The efficiency of these solvents in removing selected contaminants from Bourdon tubes in either closed or open configurations is given in Table 2. Nearly complete contaminant removal was shown by HCFC 225 and CFC 113 in both open- and closed-tube configurations. All solvents showed acceptable contaminant removal for the open-tube configuration. As expected, the greatest range came from the closed-tube configuration. The performance of HFE 7100 is of note since a lower contaminant removal efficiency was expected based on vapor degreasing operations. The greater-than-expected performance is because of the physical action of the gauge-cleaning process which adds to the inherent contaminant-removal ability of the neat solvent. This may be of importance to NASA operations in which solvents are used to flush components where mechanical action is present and the HFE 7100 would be expected to perform well.

Table 2. Average Solvent Cleaning Efficiencies

Solvent	CE Gauges	OE Gauges	Average
Tetrachloroethylene	74	97	87
Ethanol	82	86	85
Trichloroethylene	84	98	92
HCFC 225 60/40	100	98	99
HCFC 141b	96	98	97
3M HFE	93	91	92
CFC 113	99	95	97
Vertrel MCA	98	98	98

Flammability is an issue with nonhalogenated organic solvents used for cleaning parts; alcohols, ketones, and ethers can be extremely flammable. In the case of cleaning parts for oxygen, oxidizer, and air service, if the solvent is not completely removed from the part or is absorbed into softgoods, the part may ignite during operation. Flammability is not only a concern for organic solvents, but also for some chlorinated and fluorinated solvents that contain hydrogen.

The autogenous ignition temperature (AIT) was determined for the test solvents according to the procedures described in ASTM G-72 (91). The AIT for each solvent was determined at 50 and 2000 psig. The results are given in Table 3.

Table 3. AIT Results for Solvents Tested

Solvent	AIT	
	@ 50 psig (°C)	@ 2000 psig (°C)
HCFC 225	No ignition	No ignition
Trichloroethylene	108	77
Tetrachloroethylene	136	161
HCFC 141b	No ignition[a]	No ignition[a]
HFE 7100	No ignition	No ignition
Vertrel MCA	No ignition	167

[a] Nonvolatile residue of solvent less than 17 ppm.

An AIT was observed for PCE, TCE, and Vertrel MCA, while HCFC 225 and HFE 7100 did not ignite under the test conditions. The ignition behavior of HCFC 141b was dependent on the amount of NVR carried by the solvent, whereas at NVR below 17 ppm no ignitions were observed; however, at higher NVR an autogenous ignition temperature was measured (Table 4). The AIT recorded for TCE is low compared to other compounds typically considered oxygen compatible. A slow temperature rise for PCE and TCE was observed during the 50 psig test, indicating that both compounds burned slowly or gave off little heat at that pressure.

Table 4. HCFC 141b Oxygen Compatibility Test Compared to NVR

NVR (ppm)	AIT @ 50 psia & @ 2000 psia	Mechanical Impact 98 J or 72 ft-lb	
28	Exotherm[a]	Ignition	6/38[b]
20	NR[c]	Passed	1/60
17	NR	Passed	0/20
3	NR	Passed	NR

[a] Two mild exotherms were observed at 261 and 321 °C.
[b] 6/38 ingitions: 3 @ 72 ft-lb, 1@ 65 ft-lb, 1 @ 60 ft-lb, and 1 @ 55 ft-lb.
[c] A mild exotherm was observed at 2000 psia at 47 °C.
NR = No reaction

The solvents were also tested for ignition by mechanical impact at ambient pressure in liquid oxygen according to the procedures described in ASTM D-2512. HCFC 141b and Vertrel MCA were the only solvents of those tested that reacted in mechanical impact. For HCFC 141b, the mechanical impact sensitivity was again a function of the amount of NVR contained in the solvent; so long as the NVR level was kept below 17 ppm, the solvent did not react in mechanical impact. The Vertrel MCA was also reactive in mechanical impact at energy levels from 72 to 20 ft-lb. However, the reactivity seems to be a function of the nitromethane stabilizer that was present in a concentration of 0.3 to 0.9 percent. When the Vertrel MCA was tested without the nitromethane added, it did not react at an energy of 72 ft-lb.

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ROCKET MOTOR MANUFACTURE AND USE: REPLACEMENT AND PREDICATIONS TECHNOLOGIES

Recovery and Reuse of Rocket Propellants

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Abstract

This report describes ongoing process development efforts by the U.S. Army Missile Command (MICOM) to support environmentally safe rocket motor demilitarization demonstrations. This MICOM developed technology is used to recover valuable oxidizer and fuel ingredients from tactical and strategic class 1.1 and 1.3 solid propellants for recycle/reuse. The closed-loop demilitarization method employs liquid ammonia as the processing solvent for ingredient extraction and recovery. A pilot plant facility was designed and constructed in Magna, Utah to demonstrate this Army technology using Multiple Launch Rocket System (MLRS) and Chaparral tactical solid rocket motors. In July 1996, the pilot plant successfully completed full scale MLRS propellant testing in a batch process mode at rates approaching 90 kg (200 lb.) per hour. The facility is currently being relocated to a permanent site at Redstone Arsenal, AL. Once the transition is completed, processing demonstrations using class 1.1 Chaparral rocket motors will be performed.

Discussed in this report are process and design considerations defining the operation of the pilot plant facility. Critical equipment and system components for each unit operation are identified. Process descriptions of the integrated class 1.1/1.3 rocket motor demilitarization system involving propellant removal, ingredient extraction, binder separation, oxidizer recovery, and solvent regeneration are provided. Test results demonstrating the ability of energetic products recovered by this process to be recycled into other products, and future work plans to be performed in support of this program also are included.

Introduction

The demilitarization of obsolete, over-aged, and treaty-limited solid rocket motors is a substantial and pressing problem. Safe, environmentally sound, and economical methods are required to dispose of large numbers of rocket motors that exist throughout the world. A special challenge associated with this problem is the large stockpile (approximately one-third of the United States inventory by weight) of class 1.1 rocket motors. With major funding provided by the Office of the Undersecretary of Defense (OUSDA), the Joint Ordnance Commander's Group (JOCG), Demilitarization and Disposal Subgroup, has identified alternative technologies to replace the less acceptable open burning/open detonation (OB/OD) disposal method. These alternative technologies are being investigated by the appropriate Unites States military services for development and pilot plant demonstration. Researchers at MICOM have developed the near-critical fluid extraction technology described herein for recovering and reusing valuable strategic ingredients from class 1.1 and 1.3 solid propellants.

The overall objectives of this program are to provide design criteria for a full-scale plant to demilitarize class 1.3 and 1.1 solid rocket motors using liquid ammonia processing solvent and to recover propellant ingredients with commercial and military market values. A major goal of this Army resource recovery and reuse (R^3) program is to design, construct, and demonstrate a pilot plant test facility for demilitarizing all major types of solid rocket motors in the U.S. and foreign defense inventories (Figure 1). The ammonia-based process is designed to extract and separate rocket motor ingredients within a closed-loop system. The pilot-scale demonstrations consist of propellant removal, processing, and hardware component recovery using tactical Army MLRS and Chaparral rocket motors.

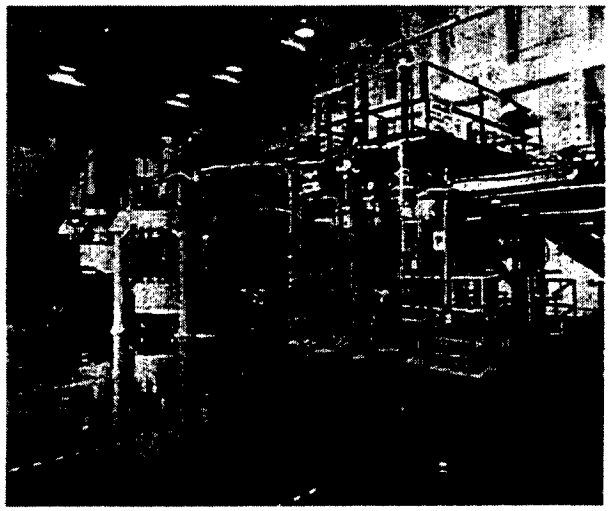

Figure 1. Pilot Plant Facility

The unique aspect of this Army program is that its foundation is the recovery, recycle, and reuse of high value ingredients and components. In addition, the program proposes alternate uses for lower value by-products thereby minimizing the generation of hazardous waste and its inherent disposal problem.

Unlike traditional disposal methods where neither product nor an associated value are recovered, this program is investigating the potential market uses and inherent product value of reclaimed and recycled ingredients. This program is conducting small-scale demonstration tests of products which incorporate reclaimed ingredients. It is anticipated that the market demand for these materials will increase as a result of these tests. Market demand and product values from the subsequent sale of recovered products will be used in the economic analysis for a full-scale production facility as an offset against capital facility and recurring operating costs. At its current operating capacity, the existing pilot plant can meet the throughput requirements for processing Army tactical rocket motors.

Process Description

A closed loop ammonia-based process is used to extract and separate rocket motor ingredients. For both the 1.3 and 1.1 propellant hazard classes, the critical fluid method uses a four-step, continuous process. The four basic steps are: (1) propellant removal by cutting or erosion into small pieces; followed by, (2) solvation of the oxidizers by the liquefied gas solvent; (3) separation and recovery of the rubber/aluminum fuel binder components and the solid oxidizer(s) (e.g., AP, HMX, and RDX) by evaporation of the liquefied gas solvent; and (4) recompression/liquefaction of the gas solvent for reuse. The critical fluid process is closed with no release of solvent to the environment. There is no air, ground, or water pollution produced and government permits are minimized.

Step 1: Propellant Removal

Propellant removal from the rocket motor can be accomplished using: (a) high speed, dry propellant machining or (b) high pressure, liquid ammonia jet washout.

Dry Machining

The machining of live solid rocket motor propellant is performed remotely. Operators control and monitor the machining and chip collection systems from a protected control room. A tactical motor is placed in a horizontal rotation fixture and rotated. The operators then position a cutting tool, which is attached to a horizontal machining arm, and the propellant chipping process is ready to begin. The machining arm is fed along the motor centerline to bring the cutting tool in contact with the propellant grain in a controlled manner to produce consistent chips and

minimize heating of the tool and propellant. A catch pan is provided to collect any chips which may fall out of the open end of the rocket motor.

A vacuum-driven chip collection system collects the chips through the center of the cutter and support tube during the machining process. The attached vacuum hose transports the chips to a gas-solids separator which deposits the chips into an approved, plastic-lined drum. All propellant chips are separated from the air stream in this manner while the air stream continues into a redundant filtering system which removes any harmful constituents. A draft fan finally discharges the filtered air into the atmosphere.

The propellant chips can be directly placed in the pan filter for processing. In this process, liquid ammonia is added to the pan filter allowing for the extraction of propellant ingredients. For the purposes of this paper, the extraction process described below refers to propellant removed using the liquid ammonia washout procedure.

Liquid Ammonia Washout

Washout of the rocket motor using liquid ammonia also is performed remotely. After the rocket motor has been positioned, an isolation pinch valve between the motor and leach vessel is opened. The motor begins to rotate at approximately 5 rpm. Low pressure ammonia is introduced at the top of the motor and at the chute between the motor and the leach vessel. The lance is equipped with four spinning jet nozzles and begins rotating at approximately 1,000 rpm. Figures 2 and 3 depict the setup of the washout process. The lance, following its preprogrammed path, begins traversing up the motor at approximately one inch per minute. Propellant is eroded (washed out) using high pressure (15,000 - 30,000 psi), liquid, anhydrous ammonia directed through the rotating jets at the propellant surface. The low pressure ammonia (spent wash) flushes the interior surfaces and promotes flow through the chute into the leach vessel.

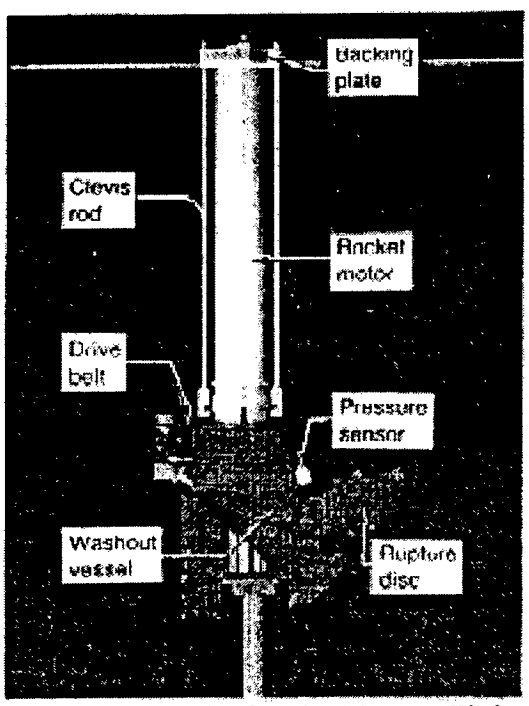

Figure 2. Schematic of Rocket Motor on Washout Assembly

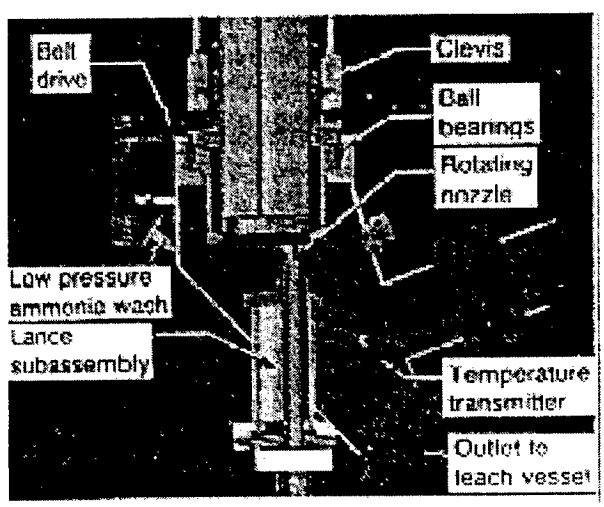

Figure 3. Detailed Schematic of Washout Assembly

Once the washout is completed, the lance stops rotating and the high pressure flow is stopped. The low pressure (spent wash) flow continues for two minutes before being terminated. The low pressure wash procedure removes any remaining loose propellant from the washout equipment. The lance is extracted from the motor after motor rotation is stopped, and the isolation valve is closed. The washout chute and motor are vented to the atmosphere and flushed with nitrogen to remove ammonia gas.

Step 2: Ingredient Extraction and Transfer

Leach Vessel (For Extracting Soluble Propellant Ingredients from the Insoluble Cross-linked Rubber Binder Components)

After the leach vessel (Figure 4) has been leak checked and purged with ammonia, it is given an initial charge of liquid ammonia or spent wash to submerge the agitator blades. Once the blades are submerged, the agitator turns on and the washout process (described above) begins. The leach vessel receives the propellant/ammonia slurry from the washout station through an 8-in.-diameter port located in the top section. The washout operation proceeds until all the propellant has been removed from the rocket motor. When the washout is complete, the isolation valve closes, and the leaching sequence begins. When the leach sequence is completed, the vessel contents are ready to be transferred to the pan filter.

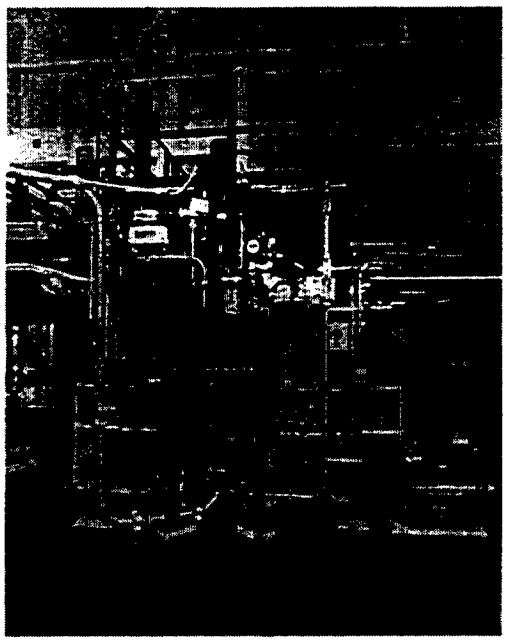

Figure 4. Leach Vessel

Pan Filter

Slurry Transfer: After the pan filter (Figure 5) has been leak checked and purged, it is ready to receive slurry from the leach vessel. Transfer of slurry from the leacher to the pan filter is accomplished by controlling the differential pressure between the two vessels. The control system ensures that the pressure in the pan filter vessel is 20 psi less than the leach vessel and that the crumb discharge valve of the pan filter is closed. When those conditions have been satisfied, the computer opens the leach vessel discharge valve to initiate transfer. Flow rates are monitored to determine when the transfer has been completed. Upon completion of slurry transfer, the leach vessel discharge valve is closed.

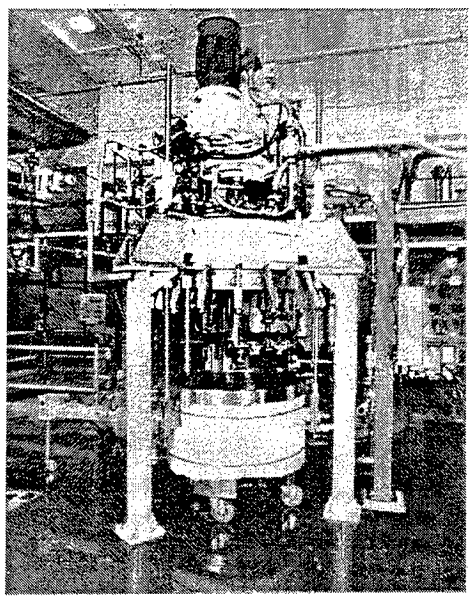

Figure 5. Pan Filter

For the class 1.3 MLRS process, the constituents of the slurry transferred to the pan filter are ammonia with: (a) aluminum-filled binder (crumb) and (b) dissolved AP. The pan filter separates the slurry into two streams. The AP/ammonia solution is transferred to the pan dryer, and the crumb remains on the filter media.

For the class 1.1 Chaparral process, the constituents of the slurry transferred from the leach vessel to the pan filter are ammonia with: (a) dissolved HMX; (b) dissolved BTTN; (c) dissolved NG degradation products (ammonium nitrate, ammonium nitrite, ammonia salts of organic acids); and (d) undissolved binder with trace heavy metals. The pan filter separates the slurry into two streams: the filtrate and the crumb.

Agitation: After the pan filter has received the slurry, the agitator in the pan filter begins rotation. The action of the agitator minimizes agglomeration and packing of the crumb. The agitator has axial translation as well as rotational capabilities. This allows the agitator paddles to be moved through the vessel top to bottom. Agitation is maintained throughout filtering, drying, and discharging operations.

Step 3: Separation of Insoluble Rubber Binder from Liquid Filtrate Containing Dissolved Oxidizer(s)

Filtration

The filtering operation begins by opening the filtrate outlet valve on the bottom of the pan filter. The filtrate can be sent to either the pan dryer or the spent wash tank through a diverter valve. The filtrate from the initial charge is sent to the pan dryer. Subsequent washings are sent to the spent wash tank. When filtrate flow to the dryer has stopped, the filtrate outlet valve is closed. The crumb remaining on the filter is washed with clean ammonia via the leach vessel. This removes trace amounts of AP or HMX remaining in the crumb. Multiple washes may be required to remove residual AP or HMX. The filtrate from washing is referred to as spent wash and is sent to the spent wash tank.

Crumb Drying (Recovery of the Rubber/Aluminum Fuel Binder)

After the crumb has been thoroughly washed, the crumb drying operation begins. Heat is applied to the crumb by flowing heat transfer fluid to the jacket on the pan filter. As the temperature in the vessel begins to rise, residual ammonia is driven from the crumb. The ammonia that is driven off is recycled by the ammonia recovery system. At a predetermined value of temperature or pressure, heating of the vessel is discontinued. The vessel is flushed with nitrogen before discharging the crumb to the crumb receiver.

Crumb Discharge (Final Recovery of the Rubber/Aluminum Binder)

The crumb is discharged through a port on the side of the pan filter and collected in the crumb receiver. The agitator provides the motive force to discharge the crumb.

Spent Wash Tank (Holds Dilute Ammonia used for Washing Residual Amounts of Oxidizers from the Rubber Binder)

The spent wash tank is the same size as the leach tank and is capable of holding approximately 200 gallons of solution. It receives spent wash from the pan filter or fresh ammonia from the ammonia supply tank. Spent wash is transferred to the washout station by using nitrogen to increase the differential pressure between the spent wash tank and the washout equipment. The total ammonia transferred is controlled using a flow meter and a control valve.

Filtrate Transfer (Transfers Dissolved Oxidizers in Preparation for Oxidizer Recovery)

Transfer of filtrate from the pan filter to the pan dryer is accomplished by differential pressure between the two vessels. The control system will check that the initial pressure differential between the pan filter and the pan dryer is less than 20 psi and that the solids discharge valve of the pan dryer is closed. When those conditions have been satisfied, the filtrate discharge valve on the pan filter vessel opens, and the diverter valve is positioned to send filtrate to the pan dryers. The filtrate flow rates are monitored to determine when the transfer is complete. When complete, the filtrate discharge valve on the pan filter is closed.

Pan Dryer Agitator/Scraper

After the pan dryer (Figure 6) has received the filtrate, the agitator in the pan dryer begins rotation. Agitator rotation is maintained throughout filtering, drying, and discharging operations. The action of the agitator minimizes agglomeration and packing of the material as the ammonia evaporates. Agitator rotation also improves heat transfer within the liquid filtrate during the ammonia evaporation cycle.

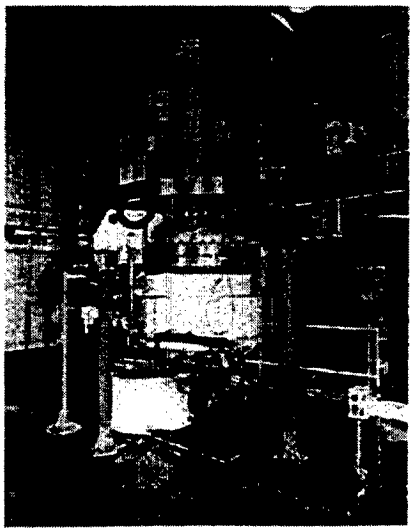

Figure 6. Pan Dryer

Drying (Recovers Dissolved Oxidizers in Dry Form by Evaporating the Liquid Ammonia Solvent)

The drying operation begins by applying heat to the ammonia filtrate solution by circulating a heated glycol solution through the exterior walls of the vessels and through channels in the agitator/scraper. The ammonia is evaporated at a constant pressure until the vessel temperature reaches a maximum of 120° F. The ammonia is recycled by the ammonia gas recovery system. At the predetermined temperature, the heat source is shut off, and the pressure is reduced to ambient. The vessel is purged with nitrogen, and the vessel and product are allowed to cool before discharging the material to the receiver.

AP Discharge (Finalizes Class 1.3 Oxidizer Recovery)

The AP is discharged through a port on the side of the pan dryer and collected in the AP receiver. The agitator provides the motive force to discharge the dried AP.

HMX Discharge (Finalizes Class 1.1 Oxidizer Recovery)

After drying, the residue containing HMX is slurried with a solvent. This slurry is sent to a bag filter where wet HMX is recovered. In a full scale production operation, the solvent (containing BTTN and NG degradation products) would be recovered for conversion and reuse in a commercial product.

Step 4: Ammonia Gas Recovery (Re-liquefies Ammonia Processing Solvent for Recycling within Closed-Loop System)

The design of the ammonia recovery system has evolved based on vapor loading, compression ratios, and available power for the compressor. Ammonia vapor from the AP/energetics dryer and the crumb filter/dryer passes through two filters (redundant system) to the ammonia compressor. The compressed vapor is then condensed in a water-cooled condenser. If ammonia vapor is generated at a rate greater than the compressor can handle, excess vapor accumulates in a surge tank.

The liquefied ammonia flows into the liquid ammonia storage/supply tank. This tank feeds the high pressure ammonia pump, the leacher, and make-up to the spent wash tank. Ammonia is lost from this closed-loop recovery system because of purging and venting. The level in the liquid ammonia storage/supply tank is periodically replenished from an outside source.

Hazards Analysis

The liquid ammonia demilitarization pilot plant design has been thoroughly reviewed for potential hazards.[1, 2] Recommendations have been made and implemented to eliminate or control these hazards. With the implementation of these recommendations, the design adequately addresses and controls the identified hazards. A thorough evaluation of procedures, contingencies, process interlock effectiveness, operator training, and operator interaction with equipment has been made to ensure safe operations. These operations have been tested and validated by the successful batch processing of 200 pound quantities of class 1.3 MLRS propellant. The hazards analysis for batch processing full scale class 1.1 Chaparral propellant is nearing completion.

Economic Considerations

Due to the flexibility of proposed production designs, a full scale plant could use either multiple small vessels or one large processing vessel. Operating and capital costs will ultimately determine the specific approach taken. The demonstrated pilot plant also could be used for the full scale demilitarization of most Army rocket motors.

From the class 1.3 process, the primary recoverable ingredient with potential value is AP. From the class 1.1 process, HMX/RDX would be the high value ingredient recovered. Crumb (Al/rubber binder) from the class 1.3

process may be marketable as a fuel additive for cement kilns and mining explosives to achieve additional process cost offsets.

Preliminary economic models being developed for analysis with pilot plant operational data already support this technology as being economically viable. Assuming near-market values for high purity recovered HMX/RDX, the pilot plant potentially can be economically competitive with OB/OD. Due to differences in virgin ingredient manufacturing costs, the class 1.3 (AP recovery) process itself is not as economically favorable as the class 1.1 (HMX/RDX recovery) process. However, considering that the stockpile is a mixture of class 1.1 and class 1.3 rocket motors, the overall benefits of this technology are both real and substantial.

Reuse of Recovered Ingredients

Ingredient recycling investigations at MICOM were conducted to evaluate potential recycle/reuse applications of reclaimed HMX and RDX in commercial and military products. The primary recycle/reuse efforts that have been conducted include the following: (1) a jointly coordinated Austin Powder Company and U.S. Bureau of Mines evaluation and demonstration to recycle/reuse reclaimed RDX in commercial cast booster mining charges; (2) a Holston Defense Corporation bench scale demonstration to confirm that reclaimed HMX and RDX can meet the literal military specifications MIL-H-45444B and MIL-H-398C, respectively, and (3) a Thiokol Corporation (Longhorn facility) effort to perform military specification crystallization, particle sizing, and incorporation into a military end item explosive formulation for recovered HMX and RDX.

The results from these efforts indicate that the recovered RDX can be successfully used in commercial mining products (Figure 7). It was also shown that recovered HMX and RDX can meet military specification requirements when recrystallized in accordance with their manufacturing processes. The results from the Longhorn effort also proved that recovered RDX could be successfully recycled into a M112 demolition block (Figure 8). In addition, recovered HMX was performance evaluated against virgin HMX with excellent results.

Figure 7. Commercial Mining Booster Charge Using Recycled RDX

Figure 8. Army M112 Demolition Block Using Recycled RDX

Future Work

In July 1996, the pilot plant successfully completed full scale, demilitarization demonstrations using 200 pound batches of Class 1.3 MLRS propellant. Through a joint effort between MICOM and the Redstone Technical Test Center (RTTC), the pilot plant currently is being relocated to a permanent site at Redstone Arsenal, AL. Once the transition is completed, processing demonstrations using Class 1.1 rocket motors, such as Chaparral and Hellfire, will be performed. Upon successful completion of these demonstrations the facility could be converted into a low level production plant for the demilitarization of Army tactical rocket motors.

Conclusion

The mechanical processes used to demilitarize class 1.1 and 1.3 solid rocket motors have been successfully demonstrated in a 200 lbs./hour pilot plant facility. Valuable ingredients, such as HMX/RDX, AP, and aluminum/rubber binder are recovered for recycling and reuse at acceptable rates and purities. The closed-loop process is conducted with minimal impact to the environment. The pilot plant emphasizes commercial equipment and has a modular engineering design. The design, when scaled to a full scale production unit, has the potential to be cost-competitive with current OB/OD disposal methods. Design and equipment selection make the pilot plant attractive for continued demilitarization of small tactical motors upon completion of the current program scope.

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Replacement of Dichromate Catalyst Polysulfide Sealant

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Abstract

Several different catalysts may be used in two-part polysulfide sealant systems to cause polymerization of the prepolymer. The present sealant used on the Space Shuttle Solid Rocket Boosters (SRBs) contains a dichromate oxidizing agent. Due to health and environmental concerns related to the use of chromium compounds, a program has been undertaken to replace the current sealant with a system that dramatically reduces the total volume of chromated materials used. The resultant benefit is two-fold: reducing the hazardous waste generated during SRB hardware refurbishment and limiting potential worker exposure to chromium, which is listed as a carcinogen.

Through a qualification program downselection, a single sealant was selected for hardware overseal applications. A second, corrosion-inhibitive sealant was selected by a joint NASA-MSFC/USBI Corrosion Control Team for faying surface applications. The second sealant does contain free chromium from which corrosion-inhibitive properties are derived. However, use of this two sealant system reduces the total volume of chromated materials by approximately ninety percent. Future work will address replacing the sealant that comprises the remaining ten percent.

Introduction

The polysulfide sealant currently used on the Space Shuttle SRBs contains a dichromate oxidizing agent. Chromium compounds are recognized by the Occupational Safety and Health Administration and the Environmental Protection Agency as toxins and hazardous wastes. The National Institute for Occupational Safety and Health considers certain hexavalent chromium compounds to be carcinogens[1]. Occupational exposure to hexavalent chromium is known to cause lung cancer, bronchial asthma, nasal septum perforations, skin ulcers, and irritative dermatitis[2,3]. Additionally, chromium containing solids from manufacturing and wastewater treatment are classified as hazardous wastes and must be handled as such[4].

Environmental impact became a primary driver in the replacement of the two-part dichromate catalyst polysulfide sealant at USBI in the early 1990s. Reduction of chromates is an objective driven not only by government regulating

agencies, but has been identified as a goal by United Technologies Corporation, USBI's parent company. Additional incentive to eliminate dependence on the current sealant material was provided in 1994 when USBI was notified by the sealant manufacturer that it was considering discontinuing production of the sealant[5]. To date, continued high demand for the dichromate catalyst polysulfide sealant has indefinitely postponed the deadline to cease manufacture of the product. Nonetheless, the discontinuation of the current sealant remains a probable eventuality for economic, health, and environmental reasons. Thus, a program to identify and qualify a suitable replacement for the dichromate polysulfide sealant has been pursued.

Approach

Sealant is used, in its most general sense, to isolate hardware from a hostile environment. At USBI, the dichromate catalyst polysulfide sealant is used in two primary application categories: (1) as an overseal and fillet material, which is removed and reapplied after each flight, and (2) as a faying surface and fastener barrier seal in permanent installations, which potentially remain intact throughout the life of the hardware. The relative volumes of sealant material used in these two application categories is roughly 9:1, respectively.

Due the use-cycle of the SRB hardware (launch, splashdown, retrieval, refurbishment, and reuse), the overseal and fillet application category requires that the sealant perform primarily as a salt water barrier. The faying surface and fastener installation category also requires salt water barrier protection; however, an additional requirement of corrosion prevention capability was levied on the sealant used in these permanent installations. Chromated sealants are proven to impart corrosion-inhibitive characteristics to aluminum in a salt water environment[6,7]. Thus, in the interest of providing maximum corrosion protection to the hardware, it was determined by a joint NASA-MSFC/USBI Corrosion Control Team that a corrosion-inhibitive chromated sealant would be used for permanent installations and that a phased reduction of, as opposed to a total ban on, chromated sealants is warranted.

Qualification Test Plan

With this philosophy in mind, a generic sealant qualification test plan was developed to qualify environmentally preferable products with physical, thermal, and volatile properties acceptable for SRB performance[8]. The test program includes physical and mechanical properties, environmental exposure, and thermal verification testing. Specific sealant candidates are not identified in the qualification test plan.

The qualification tests required for an SRB replacement sealant are presented in Table 1. The test plan describes the scope of each test, specifies the reference documents and test procedures (using industry standard test specifications wherever possible), delineates the number and configuration of the test specimens, and defines the pass/fail criterion, if applicable, for each test category. It should be noted that the scope statement of each test identifies the sealant application category (fillet and overseal, or faying and fastener installation) to which each qualification test applies. This approach ensures that testing is restricted to that which represents and validates the SRB end-use application configuration.

Table 1. Summary of SRB Replacement Sealant Qualification Tests.

Test Set	Test Category	Test Method
Physical/Mechanical Testing	Flatwise Tensile Testing at Room Temperature	ASTM C 297[9]
	Flatwise Tensile Testing at 300°F	ASTM C 297
	Flatwise Tensile Testing with Thermal Protection System (TPS) Materials	ASTM C 297
	Compatibility with Hand Wipe Cleaner	ASTM D 471-79[10]*
	Flammability	NHB 8060.1, section 4.1, test 1[11]
	Torque-Tension	MSFC-STD-486B[12]
Environmental Exposure Test	Kennedy Space Center (KSC) Environmental Exposure	Pressurized salt water chamber exposure, followed by 6 month beach exposure.
	Corrosion Test	ASTM B 117[13]
Thermal Verification	Radiant Testing	Simulated flight heating environment exposure.**
	Convective Testing	Simulated flight heating environment exposure.**

* includes only parameters utilized and reported in USBI-ANAL-277-94[14]
** reference BPC-ANAL-67-87[15]

Materials Selection

An initial criteria for candidacy was established to provide the basis for materials selection of those sealants to be used in SRB fillet and overseal applications. Initial candidacy requirements were the following:

1. Temperature resistance ≥ 275°F.
2. Comparable or superior mechanical properties to baseline sealant.
3. Resistance to salt water immersion.
4. Ability to cure at room temperature.

Fifty-six suppliers were surveyed, resulting in the identification of seven candidate sealants that were represented by their suppliers as meeting the initial candidacy requirements. Final downselection to the prime fillet and overseal replacement candidates was based on the selection criteria shown in Table 2. Failure to meet any one requirement could be considered cause for candidate rejection.

Table 2. Final Downselect Criterion for Prime Fillet and Overseal Replacement Sealant Candidates.

Sealant Characteristic	Criterion
Application Characteristics	Comparable or better than baseline sealant.
Flammability	Comparable or better than baseline sealant.
Mechanical Properties	Acceptable for SRB performance: comparable or better than baseline sealant if unspecified.
Volatile Content	Less than seven percent.
Compatibility with TPS Materials	Exhibits compatibility with overlying TPS materials: bond strength between sealant and TPS equal to or better than baseline sealant/TPS system.

Engineering tests were performed to eliminate initial candidates and/or determine superiority of candidates in a particular sealant characteristic category. Review of the data in combination with application of the above final selection criteria resulted in identification of a single prime sealant replacement candidate for overseal and fillet applications. Like the baseline sealant, the replacement candidate is a two-part polysulfide sealant. Unlike the baseline sealant, it has a manganese dioxide curing catalyst and greatly reduced health and environmental impacts, i.e., no volatile organic compound (VOC) emissions and no chromium content.

A second sealant candidate was selected for faying surface and fastener applications due to the additional corrosion prevention requirement levied on sealant used for permanent installations. Since the primary consideration for sealant in this application is corrosion prevention, the joint NASA-MSFC/USBI Corrosion Control Team was tasked to identify a sealant candidate for faying surface and fastener installations. The team selected a two-part, manganese-cured polysulfide sealant containing an additional quantity of soluble metallic chromates which provide an effective barrier against the common causes of corrosion of aluminum or dissimilar metals. This sealant candidate meets the requirements of MIL-S-81733C, Military Specification, Sealing and Coating Compound, Corrosion Inhibitive.

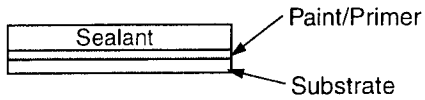
The selection of the two manganese dioxide catalyst polysulfide sealants for replacement of the current dichromate catalyst polysulfide sealant offers the following benefits:

1. The overseal and fillet candidate has comparable application parameters to the current sealant.
2. The faying surface and fastener candidate has a longer pot life which facilitates permanent installations of large structures and numerous fasteners.
3. Manganese dioxide curing system provides improved catalyst characteristics[10]:
   - Catalyst system is quite stable.
   - Catalyst system does not require a volatile carrier for cure.
   - Manganese dioxide systems are less sensitive to catalyst-to-base ratio than dichromate systems.

Testing

Qualification testing determined that the proposed two sealant system is a viable alternative to the current SRB sealant. Comparative summaries of test results are presented in Tables 3-7. For the purpose of the test result summaries, the current SRB sealant is designated as "Baseline", the overseal and fillet sealant candidate as "Overseal" and the faying surface and fastener installation sealant candidate as "Faying". All comparative values are based on average test values. Relative rankings are listed from best-to-worst, with number 1 indicating the best performance.

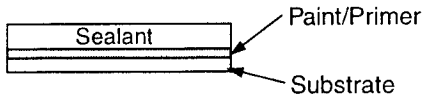
Table 3. Comparative Results of Flatwise Tensile Tests: Sealant at Room Temperature.



Sealant Type	Substrate	% of Requirement	Relative Ranking
Baseline	painted Al	288	2
Overseal	painted Al	418	1
Faying	painted Al	253	3

Sealant Type	Substrate	% of Requirement	Relative Ranking
Baseline	painted steel	510	2
Overseal	painted steel	783	1
Faying	painted steel	348	3

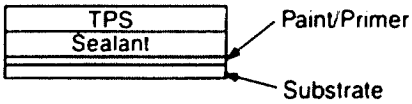
Table 4. Comparative Results of Flatwise Tensile Tests: Sealant at 300°F.



Sealant Type	Substrate	Relative Ranking
Baseline	painted Al	3
Overseal	painted Al	2
Faying	painted Al	1

Sealant Type	Substrate	Relative Ranking
Baseline	painted steel	3
Overseal	painted steel	2
Faying	painted steel	1

Table 5. Comparative Results of Flatwise Tensile Tests: Sealant-to-TPS at Room Temperature.



TPS	Sealant	% of Requirement	Relative Ranking
MCC-1	Overseal	433	1
	Baseline	311	2
BTA	Overseal	315	1
	Baseline	200	2
K5NA	Overseal	355	2
	Baseline	358	1
Insta-Foam	Overseal	320	1
	Baseline	190	2

Notes: MCC-1 denotes Marshall Convergent Coating
BTA denotes Booster Trowelable Ablative

Table 6. Compatibility with Hand Wipe Cleaner.

Sealant Type	% Volume Change	% Weight Change	% Hardness Change
Baseline	-2.6	-3.1	8
Overseal	3.3	-1.3	1
Faying	-3	-1.1	0

Note: The negative values in the table represent a decrease, or drop, in the final value compared to the initial value.

Table 7. Flammability Test Results.

Sealant Type	Burn Length (inches)
Baseline	12 (total burn)
Overseal	7
Faying	12 (total burn)

Discussion

Tables 3-5 demonstrate that the flatwise tensile strengths of the replacement sealant materials at room temperature, at 300°F, and in combination with the various TPS materials used on the SRB, respectively, exceed the qualification requirements. In most cases, the flatwise tensile strengths of the overseal candidate also exceed those of the baseline sealant. Sealant-to-TPS flatwise tensile testing (reference Table 5) is not required for the faying surface sealant candidate since the faying surface sealant will not contact the TPS materials in the end-use configuration. Table 6 shows that measurable values of percent volume change, percent weight change, and percent hardness change are nearly identical when samples of the various sealants are exposed to the hand wipe solvent that is currently used for surface preparation on sealants for the SRB. The solvent causes essentially no measurable volume or weight change on

any of the sealants tested; percentage changes in the 2-3% range are within the level of reproducibility of this test method. Flammability test results, given in Table 7, indicate that the replacement sealants perform comparably or, in the case of the overseal sealant, better than the baseline sealant.

Torque-tension testing is designed to determine the room temperature torque-tension relationship for threaded fasteners installed wet with faying surface sealant. The tests result in plots of induced load versus torque. These curves will be provided to the design and analytics engineering organizations as reference information to support design implementation and stress analyses.

KSC Environmental Exposure testing is designed to evaluate the effect of a simulated splashdown and exposure to six months of beach climate (reference Table 1). The environmental exposure is complete and showed no hardware degradation. Slight fungi/algae attachment was noted; however, these washed off easily after hardware removal from the water. The Corrosion Test specified in the generic qualification test plan is being waived for this program because the faying surface sealant candidate is listed on the qualified products list of MIL-S-81733. The corrosion testing required of materials qualified to MIL-S-81733 is more stringent than that required in the qualification test plan.

Thermal Verification testing exposes test panels representative of hardware configurations to simulated design flight heating environments to assess the performance of the sealant. Faying surfaces and fillet application are not considered thermal issues; only bolt head overseal is addressed. Pass/fail criterion unique to the SRB hardware was developed by USBI Thermal Analysis personnel. Testing was successfully performed in the NASA Marshall Space Flight Center Improved Hot Gas Facility.

In addition to the aforementioned qualification testing, process sensitivity testing is underway. Lessons learned through this testing will be evaluated for incorporation into process requirements and procedures during replacement sealant implementation. For example, studies were performed with regard to surface preparation and sealant adhesion. It was shown that for sealant applied over aluminum surfaces coated with the urethane topcoat paint system currently used on SRB hardware, adhesion is improved by sanding or through the use of a commercially available adhesion promoter. Obviously, the trade-off between improved sealant adhesion must be weighed against the cost of an additional operation during hardware refurbishment. However, this example serves to demonstrate the need for process sensitivity testing, in addition to the defined qualification testing, that should be performed prior to implementing a new material system and its associated processes.

Conclusions

Chromium compound reduction is being pursued throughout industry for economic, health, and environmental reasons. A qualification program at USBI has identified and proven the viability of a two sealant replacement system for the current dichromate catalyst polysulfide sealant. Implementation of this sealant replacement system will reduce the total volume of chromated sealant used by roughly 90%, reducing the hazardous waste generated during SRB hardware refurbishment and limiting potential worker exposure to chromium.

A phased approach to reduction of chromated sealants has been chosen due to material performance requirements. To facilitate this phased reduction, a generic qualification test plan that categorizes tests according to end-use applications was devised. Defining the performance requirements of the

materials, selecting material candidates based on these requirements, and employing tests that accurately represent and validate the end-use are key to this approach. A generic test document simplifies the next phase of the program when future candidates are considered. A similar methodology may prove useful to others who cannot transition directly from their current system to a non-chromated system due to known critical performance constraints.

Additional process sensitivity studies are in progress to facilitate implementation of the new sealant system at USBI. Future work will address replacement of the chromated corrosion-inhibitive sealant with a non-chromated, environmentally-friendly corrosion-inhibitive sealant.

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Updated Assessment on the Environmental Impacts of Rocket Effluents

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ABSTRACT

Three independent studies regarding the environmental impacts of testing and launching rockets were published in the 1991 - 1992 time frame. Each of these studies concluded that these impacts are quite minor, but that there are several aspects which suffer from a lack of reliable data. Since these studies were published, there has been additional work in field measurements, exhaust cloud modeling, ozone depletion predicted by atmospheric models, and in alternate propellant development. There have also been changes in the recommendations of the AF Armstrong Laboratory (AL) regarding the concentrations of HCl to which the public should be exposed. The implementation of the most conservative of these recommendations had an impact on the launch probability of AF launch vehicles at Vandenberg Air Force Base (VAFB).

This paper discusses the conclusions of the three earlier studies in light of the most recent data. Ozone depletion calculations using various models have been published. These will be reviewed and compared, along with the few actual measurements which have been made. Both the transient local ozone depletion data, along with the longer term regional and global ozone depletion estimates are described. Recent calculations show that NO_2 produced from afterburning and atmospheric oxidation of liquid rocket exhaust clouds may be of comparable toxicity to HCl plus NO_2 from solid rockets. Neither type of rocket motor is predicted to pose a significant health risk. Current Air Force activities to improve launch probabilities include the modification of the plume dispersion program used to predict ground concentrations of exhaust species, and additional field measurements to verify the model predictions.

BACKGROUND

The environmental impacts of chemical propulsion continue to be an area of research and concern from time to time. Three independent reviews[1,2,3] were published in the 1991 - 92 time frame which summarized the data available at that time regarding the atmospheric effects of launching rockets. Additional studies were published previous to that time,[4,5] and have included the impacts of launching and testing rockets on both the atmosphere and on the biota in the vicinity of the launch or test site. The AIAA sponsored a workshop on the atmospheric effects of chemical rocket propulsion in Sacramento in June, 1991. Representatives from the propulsion industry, NASA, DoD, the EPA, environmental groups, the Library of Congress, and the atmospheric science community all helped in putting together a position paper. The paper was published in October, 1991 after approval by all parties concerned. The conclusions of the study regarding the magnitude of the effects were:

1. Using a launch model of 9 Shuttles and 6 Titans per year, on a global basis, stratospheric ozone depletion was calculated to range from 0.0065% to 0.024%. Depletion is expected to be somewhat higher in the northern mid-latitudes, where most of the launches occur. In the near vicinity of the plumes, ozone depletion may be high (>80 %), but recovery occurs rapidly. Global ozone depletion due to heterogeneous reactions that may take place on the surfaces of alumina, soot, or ice is expected to be small if the chemistry associated with rocket particulates is the same as that of natural stratospheric particulates.

2. The global contribution to anthropogenic sources of acid rain by chemical rockets is estimated to be less than 0.01%. Current data suggest that local effects are confined to areas less than 2,500 feet from the launch site.

3. The contribution of chemical rockets to global warming is minute.

4. The extensive experience base in rocket testing and flights suggests that concerns with toxicity of rocket ingredients or effluents are manageable by proper operational controls.

The AIAA report recognized that there were many areas which had not received adequate research. For example, the global, regional, and local stratospheric ozone effects cited are almost all calculated effects based on atmospheric models. There was very little experimental data available on either measurement of the exhaust species themselves, or their effects. The AIAA recommended that research be conducted on both stratospheric ozone effects and on local tropospheric air and ground effects.

Shortly after the publication of the AIAA report, the World Meteorological Organization issued its 1991 assessment on the state of knowledge of stratospheric ozone depletion.[2] The WMO report includes a chapter on the effects of rockets on stratospheric ozone. This chapter was included because of a request by the Russians to do so. It was the conclusion of this study that the impact of chemical rockets, particularly the Space Shuttle, on global stratospheric ozone is, at most, a third order effect, and not of great concern. It also included a discussion on local ozone effects, concluding that while there may be significant ozone depletion in the air around the rocket plume, the atmosphere recovers rapidly. An upper limit of local ozone destruction following a Shuttle launch was obtained by satellite data showing no ozone depletion within the detection limits of the Total Ozone Mapping Spectrometer (TOMS).

The third of the major studies conducted[3] was sponsored by the European Space Agency (ESA), and concerned the impacts of Ariane V launches on the stratosphere. The assessment was based on launching 10 Ariane V rockets per year, every year for 20 years. The conclusions in this study were very similar to those of the other 2 studies, and ESA did not recommend any changes in launch vehicles for environmental reasons.

As with the AIAA report, the ESA and the WMO reports recognize the limitations of the measured data obtained to date. Fortunately, there has been research in the areas of both stratospheric ozone and local tropospheric and ground effects recently. The ozone depletion data reported in the 1991-92 reviews were all calculations based on homogeneous chemistry. A rigorous global model on rocket exhaust impacts, with the inclusion of potential heterogeneous chemistries has been published very recently.[6] In addition, RISO (Rocket Impact on Stratospheric Ozone), a program to better understand the impact of a single rocket launch on the stratospheric ozone layer has been initiated. An outline of the RISO program was given at the 1995 JANNAF Propulsion and Subcommittee Joint Meetings in December, 1995.[7] Preliminary results from RISO as well as from a program to better define the tropospheric fate of rocket exhaust clouds were presented at a solid propellant lecture series at the 1996 AIAA Joint Propulsion Conference.[8]

DISCUSSION AND RESULTS

Update on the Stratospheric Impacts of Rockets

In the years since the AIAA, WMO, and ESA reports were issued, our understanding of atmospheric processes has improved, and additional refinements to the global models have been made. Additional modeling studies on the effects of rockets on stratospheric ozone have been published.[illegible] These studies have mainly focused on local stratospheric impacts of the exhaust cloud from a single launch, although Jackman et al.[illegible] considered global effects. There is some question as to the constituents of the exhaust cloud, particularly the distribution of chlorine between HCl (by far the major chlorine species at ground level), and Cl_2. Some models suggest that chlorine from rocket exhaust is distributed about equally between Cl_2 and HCl with afterburning under stratospheric conditions. Molecular chlorine will be photolyzed within minutes or hours, whereas HCl remains intact for days or weeks, but eventually releases its chlorine after reacting with a hydroxyl radical. On a regional or global basis, this is irrelevant, since in either case, the chlorine will eventually be released as free atomic chlorine. Some evidence that molecular chlorine can be formed in the afterburning region of a solid rocket motor has been obtained recently. Laboratory experiments have been conducted[13] in which a fuel consisting of hydrogen, carbon monoxide, and HCl, at the proportions predicted to exist at the exit plane of a rocket nozzle was burned in an atmosphere designed to simulate the stratosphere. Molecular chlorine was detected in these studies and shown to be at levels about what was predicted from the model calculations: 30 - 40 percent of the total chlorine. Attempts at measuring the proportion of active chlorine species present in the stratosphere rocket plume are being made as a part of the RISO program. Data reported thus far[8] show some indication of free chlorine, but have not been quantified.

On a local basis, an increase in the Cl_2/HCl ratio could lead to more significant ozone depletion within the plume. However, the work of Karol et al.[19] cited in the WMO report and in the AIAA report, predicts that even without free chlorine, the bulk of the ozone in the plume of a solid or liquid rocket may be depleted for a few hours due to the production of NO with afterburning. Karol used the U.S. Space Shuttle as a test case for a mostly solid propulsion system, and the Russian Energya for an all liquid system. There has been some debate on the quantity of NOx species produced in the afterburning region of rocket plumes, particularly at stratospheric altitudes,[20] with predicted NOx emission indices ranging from 0.06[12] to 33[19] g NOx/kg fuel, depending on the type of rocket and the model used. Obviously, the extent of NOx production will directly affect the relative contribution of chlorine species in solid rocket exhaust to the total ozone destruction resulting from the rocket. For the maximum stratospheric NOx production scenario, the overall impact on the total ozone column from the Space Shuttle was calculated by Karol to be at most an 8 percent decrease, which recovers after a few hours. Of the total ozone destroyed, about 25 percent was calculated to be due to HCl, and 75 percent to NOx.

Regardless of which, if any, model is most accurate, an upper limit on total column ozone destruction after a single launch can be established based on the work by McPeters et al.,[21] and Kruger et al.[10,15] using data from the TOMS. The TOMS instrument has passed over the southeast U.S. on several occasions within several hours after Space Shuttle launches and detected no ozone decrease. TOMS does not have an extremely high resolution footprint, but should be able to detect a column ozone decrease of about 10 percent over a 20x20 km area.

Larger decreases in the total local ozone column within a Space Shuttle exhaust cloud than Karol calculates have been predicted by Ross[22] who estimates up to 30 percent decreases in the total ozone column may be observed if wind conditions are such that the exhaust contrail is 'stacked' vertical by atmospheric winds. He predicts that the bulk of the ozone destruction will be due to free chlorine, produced from the photolysis of Cl_2, which, in turn, was produced during the afterburning from HCl. As a consequence of this prediction, and the limitations in the resolution of the TOMS instrument, the Aerospace Corp. has designed and built a new high resolution ozone imager (HIROIG), which has a much narrower field of view in order to focus on point sources of ozone depletion. This instrument has yet to be placed on a space platform, but has been used on the ground in an attempt to measure column ozone depletion following a Shuttle launch. The HIROIG instrument was deployed at the Kennedy Space Center for the July, 1994 launch, and collected data under nearly ideal conditions for ozone depletion measurements. The Shuttle was launched around noon on a clear day, with upper atmospheric winds blowing such that the contrail did stack back on itself, and the whole cloud drifted to a position nearly directly above the HIROIG. The final report on the HIROIG measurements has not yet been released, but preliminary indications are that no alarming ozone depletion was observed.

One of the goals of the RISO program is to measure the effect of a rocket launch on the total ozone column. Ground based lidar is being used to follow the exhaust cloud and to determine its vertical distribution. An array of mobile uv detectors is deployed on the ground to measure any changes in uv radiation as the exhaust cloud passes overhead. Testing to date[8] has shown the stratospheric portion of the exhaust cloud to shear rather rapidly into vertically thin segments (on the order of 100 m thick) which do not align. Even though ozone depletion within the plume may be large, the segments are so thin that there appears to be very little chance of significant vertical alignment, and consequently very little chance of measurable column ozone depletion. The ground based uv monitors have thus far borne out that conclusion.

The identification of the central role of heterogeneous processes in the formation of the Antarctic ozone hole has been well documented in recent years. Condensation of HCl and NO_2 onto polar stratospheric cloud (PSC) aerosols, and the subsequent release of active chlorine into a denitrified atmosphere are the most significant chemistries leading to the nearly complete depletion of stratospheric ozone at some altitudes during the Antarctic spring. It was recognized in the reviews discussed above that heterogeneous effects had not been included in the calculated effects of rockets on the stratospheric ozone. As mentioned, Jackman et al[6] have recently included the known stratospheric heterogeneous chemistries of sulphate aerosols and polar stratospheric clouds in their update on the effects of the Space Shuttle on stratospheric ozone. The result is that the predicted long term global stratospheric ozone decrease (0.014%) is roughly double that predicted for homogeneous chemistry only (0.0056%).

An additional question which arises regarding heterogeneous chemistry is: Can the same sort of chemistries which appear to be occurring on sulphate aerosols and PSCs also occur on the condensed phase species (Al_2O_3, H_2O, soot) produced by rockets? It is not currently known whether or not chemistries similar to those occurring on PSCs can occur on alumina from rockets, although there is some current research in the field. However, calculations by Carrier et al.[1] suggest that even with a high rate of reaction, the plume disperses too rapidly for significant ozone destruction by heterogeneous processes.

Another area of recent research has been the question of halocarbon (CFC) reactions on the alumina from solid rockets.[4] It has been suggested that alumina surfaces may act as catalytic sites for the decomposition of CFCs. If this is the case, then alumina could cause the CFCs to release their chlorine more rapidly than they otherwise would. This would result in the overall active chlorine burden in the stratosphere being increased in the short term, but decreased in the long term. Robinson's work indicates that CFCs in contact with alumina may indeed be decomposed. However, this study was performed using pure, single crystal alumina. The alumina from a rocket motor may be very different. In addition, if the alumina decomposes CFCs in the stratosphere, it should do the same in the troposphere, and would therefore prevent those CFCs from reaching the stratosphere and releasing their chlorine into the ozone destruction cycle. It is therefore not clear what the overall impact catalytic CFC decomposition on the surfaces of rocket exhausted alumina would have on stratospheric ozone.

While only a limited amount of experimental work specifically focused on the stratospheric impacts of chemical propulsion has been done, the evidence linking the Antarctic ozone hole in particular, and global stratospheric ozone depletion in general to the tropospheric emission of CFCs and other ozone depleting substances (ODSs) continues to grow. The link between active stratospheric chlorine species and the nearly complete removal of ozone from the Antarctic stratosphere at certain altitudes and seasons has been firmly established.[5] The efforts of the parties involved in the Montreal Protocol to eliminate the production and release of ODSs have begun to bear fruit. The rate of increase of the concentration of the most abundant CFCs has begun to slow, while the atmospheric concentration of trichloroethane has actually begun to drop. This is significant for chemical propulsion in that the same models and scientific understanding which led to the provisions of the Montreal Protocol were used to draw the conclusions in the papers cited above.

Local Launch Site Issues

Virtually all of the studies which have been done on the effects of rocket effluents around the launch site have focused on solid rockets, and in particular, the HCl and aluminum oxide emissions.[2,3] The one exception is that the impacts of a catastrophic failure of a liquid rocket using N_2O_4/Aerozine have been evaluated, since both of these ingredients are quite toxic. The studies which have been done show that plant and animal mortalities resulting from the HCl in the exhaust cloud of a Shuttle launch are limited to a region within about 1/2 mile of the launch pad. Leaf spotting from acidic deposition occurs up to several miles away, but the effects are temporary.

Because of the adverse health effects of HCl at concentrations greater than about 10 ppm, and the ceiling limit of 5 ppm under EPA and NIOSH, launch criteria have been established for ground level HCl concentrations. Prior to each launch at either VAFB or CCAS, local meteorological data and calculated rocket exhaust products are input into a plume dispersion model, REEDM, which calculates the maximum ground level concentrations of the exhaust species over the surrounding area. These data are used to assess the advisability of launching from a toxicological exposure basis. The Air Force has defined Toxic Hazard Corridor Tier levels, to which toxicological data can be applied to assess the potential danger to individuals near the launch site. The tier levels are defined as follows:[2]

Tier I: A zone for which certain sensitive individuals (asthmatics and those with pulmonary difficulties) may be at some risk from exposure.

Tier II: A zone that represents the concentration level above which there may be significant or irreversible effects from exposure.

Tier III: A zone that represents the concentration level which is immediately dangerous to life and heath.

The Air Force policy at VAFB has been to consider a Tier I condition predicted to impact the general populace or on base housing as a 'no go' for launch. The Tier I criteria have undergone 3 revisions in the past year, changing from 10 ppm time weighted average (TWA) for 30 minutes, to 1 ppm instantaneous (Oct. 27, 1994), to 1 ppm TWA for 1 hour (Dec. 30, 1994),[27] and finally to 2 ppm TWA for 1 hour or 10 ppm instantaneous (June 7, 1995).[28] The consequence of the Oct. 27, 1994 change to 1 ppm maximum peak concentration was a reduction in launch probability at VAFB of all launch vehicles using solid rocket motors. For example, the Titan vehicle launch probability was reduced to 27 percent based on the HCl restrictions alone. Realizing the hardship imposed on rocket launching by this very conservative restriction, a reassessment was made, resulting in the guidelines of 30 Dec. and 7 June. In an attempt to make the interim guidelines permanent, and to obtain a check of reasonableness for the recommended limits for both HCl from nominal launches, and for N_2O_4 in an accident scenario, the Air Force has requested that a committee from the National Academy of Science evaluate the toxicological data and give its recommendations on reasonable launch criteria. The committee's final report is expected in mid-1997.

It should be noted that the launch criteria are based on the ground concentrations of the exhaust species calculated using a computer model, REEDM, which has not been adequately validated by field measurements. Efforts are underway within the Air Force both to improve the REEDM model and to conduct field measurements to determine its accuracy. The status of these efforts was reported by Lundblad recently at the AIAA Solid Rocket Lecture Series.[8] Data presented during this presentation showed that the REEDM model consistently under predicts the exhaust cloud rise height by about a factor of 2. The subsequent downstream ground level concentrations of exhaust species are critically dependent on the rise height, since the higher the plume rises, the longer it has to disperse before impacting the ground. It appears therefore, that the model used to provide the data for launch decisions is overly conservative. Additional problems with the REEDM model are discussed in the companion paper which follows this one.

One area which appears to have been overlooked for the most part, is the tropospheric NOx emissions of rockets. NOx emissions have only been considered with regard to catastrophic abort scenarios for propulsion systems using N_2O_4/Aerozine propellants. Most of the calculations have used as input to the exhaust cloud dispersion models the species at the nozzle exit plane, which have not taken into account afterburning, and the possible production of NOx's. Those studies which have considered afterburning and NOx production have mainly focused on the stratospheric ozone effects of the major NOx constituent, NO. NOx effects have not been of serious concern in the launch site models because NO is fairly innocuous compared with HCl or NO_2. Calculations of afterburning chemistry at sea level show that fairly high levels (on the order of 2-3 percent of the total exhaust) of NOx are predicted when afterburning is completed, and that about the same amount is produced in both liquid and solid rockets.

A study to calculate the relative concentrations of HCl, NO, and NO_2 in the exhaust clouds of various rocket motors as the clouds diffuse and strike the ground has been conducted recently at Thiokol. As discussed above, there are regulations in place for maximum predicted HCl concentrations, and launches and tests have been delayed on this basis. Since NO_2 is more toxic than HCl, based on its lower permissible exposure limit (PEL), and on toxicological studies, it was felt that it was important to calculate their relative concentrations for different launch vehicles.

Table I shows the calculated exhaust products of many of the current U.S. launch vehicles. Two columns are shown for each vehicle, the first giving the nozzle exit plane species, and the second, the species predicted after the completion of the afterburning reactions in which oxygen from the air further oxidizes hydrogen and carbon monoxide. The values shown are in grams of product per 100 g of propellant. The total of all products are greater than 100 g for the afterburning cases because oxygen and nitrogen from the atmosphere are incorporated into some of the species. In the case of water, some is produced within the rocket chamber, as is reflected in the exit plane columns, some is produced when hydrogen and hydroxyl are oxidized, and some is present in the ambient air. The values given for water in the afterburning columns include as much water as would be present in air at 25°C and 46% relative humidity.

TABLE I
Exhaust Species from U.S. Space Launch Vehicles

Vehicle	Space Shuttle				Titan				Delta			
Motor, Propellant Type	RSRM, Solid PBAN/AP/Al		SSMEs, Liquid LO_2/LH_2		SRMU, Solid HTPB/AP/Al		LR87, Liquid N2O4/Aerozine		GEM, Solid HTPB/AP/Al		RS-27, Liquid LOx/RP1	
Species	Exit plane	With after-burning	Exit plane	With after-burning	Exit plane	With after-burning	Exit plane	With after-burning	Exit plane	With after-burning	Exit plane	With after-burning
Gl_2O_3	29.32	29.32			34.19	34.19			34.26	34.26		
CO	24.59	0.0			21.41	0.0	5.38	0.0	21.42	0.01	47.30	0.04
CO_2	2.76	41.25			2.05	35.42	16.81	24.49	2.05	35.49	22.92	93.90
Cl	1.30	0.06			1.65	0.02		0.0	1.60	0.13		
Cl_2	0.004	1.08			0.005	1.37		0.0	0.005	1.92		
H	0.102	0.0	0.155	0.018	0.14	0.0	0.046		0.14	0.0	0.18	0.0
H_2	1.99	0.0	3.60	0.157	2.00	0.0	0.25		2.05	0.0	1.20	0.0
H_2O	6.69	52.18*	92.38	119.39*	8.62	69.19*	34.75	87.67*	8.77	64.94*	25.80	55.49
HCl	19.41	19.55			18.31	18.52			18.55	18.03		
N_2	8.72	mixes with air			8.29	mixes with air	21.83	mixes with air	8.31	mixes with air	0.0	
NO	0.043	2.87		2.98	0.06	3.28	2.74	2.54	0.06	2.31	0.0	3.50
NO_2	0.0	0.001		0.002	0.0	0.01	0.007	0.01	0.0	0.008		0.008
O	0.021	0.0	0.158	0.46	0.038	0.0	0.997	0.0	0.04	0.0	0.218	0.01
OH	0.37	0.0	3.35	3.14	0.50	0.0	4.98	0.0	0.48	0.0	2.021	0.13
O_2	0.009	mixes with air	0.36	mixes with air	0.014	mixes with air	12.18	mixes with air	0.013	mixes with air	0.414	mixes with air

*Total water with afterburning includes atmospheric water. Assume 14,500 ppm water in ambient air (equivalent to 46% RH at 25°C).

From an environmental perspective, the most significant change in exhaust species with afterburning is the production of nitrogen oxides. The computer model predicts that all of the rocket motors shown produce between 2.3 and 3.5 g NOx per 100 g fuel during the afterburning process, with over 99 percent in the form of NO, with only a trace of NO_2. While NO is classified as a toxic chemical, it is less so than either HCl or NO_2. Its OSHA TWA PEL is 30 mg/m^3, with no ceiling limit listed. This is similar to the toxicity of carbon monoxide. The OSHA ceiling value for HCl is 7 mg/m^3 (5 ppm), and for NO_2 is 1.8 mg/m^3 (1 ppm).

Although NO is the species immediately produced in the afterburning of the rocket, measurements suggest that a significant fraction of the NO is converted to NO_2 within several minutes.[29] NO, NOx and ozone measurements were made by an instrumented aircraft which flew through the exhaust cloud of a Titan III launch in 1974. The passes were made at T+5 and T+34 minutes, and showed increasing levels of NO_2. At T+5 minutes, about 22 percent of the NOx was NO_2 while at T+34 minutes, this had increased to about 32 percent. Assuming that the model calculations are correct, and there is little NO_2 immediately after the launch, an excellent fit of the NO_2/NOx ratio vs. log(time) can be made. This is shown in Figure 1. The significance of these data is that within several minutes after the rocket launch, a significant portion of the NO has been converted to a species of much higher toxicity. The conversion of NO to NO_2 is well documented by atmospheric researchers. Data reported in Warneck[30] show 50 to 90 percent of the atmospheric NOx exists as NO_2, and that the lifetime of NO may be as short as 75 seconds.

While concern has been expressed over the past several years about the potential for public exposure to unacceptable levels of HCl from solid rocket motors containing AP, NO_2 has not been an issue even though it is potentially more toxic than HCl. This is largely because even with afterburning considered, NO_2 is only a very minor constituent of rocket exhaust. It is only when the conversion of NO to NO_2, and the relative rise heights of different exhaust clouds are included that NO_2 becomes significant. It is important to remember that for the regulatory limits, the real concern is not maximum exhaust cloud concentrations, but rather the maximum concentrations observed on the ground as the exhaust cloud disperses over the nearby landscape.

Calculations were performed for all of the launch vehicles listed in Table I using the EPA approved INPUFF computer model to predict the maximum concentrations of important exhaust species impacting the ground as a function of distance from the launch site for various meteorological conditions. Figure 2 shows a comparison between the maximum ground concentration of NOx from the Space Shuttle Main Engines (SSMEs) and the NOx plus HCl from a Space Shuttle Reusable Solid Rocket Motor (RSRM) as a function of distance from the launch site, as calculated by the INPUFF program. In the RSRM exhaust, the HCl to NOx ratio is about 6.7/1. Figure 3 shows the same comparison, except that only that fraction of the NOx calculated to be NO_2, based on the Titan data from Figure 1, is shown. In order to take into account the differences in the relative toxicities of NO_2 and HCl, their predicted concentrations were converted to a percentage of their PELs. Figure 4 shows this comparison, and indicates that for these two rockets, the peak toxicity of the plumes is similar, and the relative toxicity is dependent upon the location of the observer. .

It must be noted that the conversion of NO to NO_2 is likely to be dependent on the type of launch vehicle and on local meteorological conditions. Applying the rate of NO to NO_2 conversion from the Titan vehicle to other rocket motors is therefore only an approximation, but lacking other data, it is the best that can be done.

The principal reason that the NO_2 ground concentration from the SSMEs may be just as high as the HCl ground concentrations of the RSRM is the relative plume rise. Motors with very high thrust such as seen in the RSRM have a large heat release concentrated in a single plume, which results in a high plume rise and more dispersed species when they finally impact the ground. The concept is analogous to the construction of tall smokestacks at power plants. When the air pollutants are released at a high altitude, they are dispersed to harmless concentrations by the time they impact the ground, whereas if they were released at ground level, their concentrations would be significantly higher. Thus, even though the RSRM has a much higher mass flow rate and higher total quantity of emissions, the higher plume rise more than compensates for this, resulting in lower maximum concentrations on the ground.

A comparison between two different types of rocket motors is probably best made when the two motors have equivalent thrust, and hence similar payload capabilities. This could be done, but it does not reflect the reality

that the U.S. has a given set of qualified rockets, which is not likely to change in at least the next several years. In order to achieve, for example, an equivalent thrust from SSMEs as from RSRMs, clusters of lower thrust engines would be required. It is not clear how the plumes from these motors would interact. If they were configured such that the bulk of the afterburning and atmospheric mixing occurred in each separate plume prior to the plumes mixing significantly with one another, the plume rise would be similar to that seen with a single rocket engine, but the ground concentrations would be higher because of the greater total mass of exhaust. This worst case scenariois reflected in the upper curve shown in Figure 5. The ordinate values represent the NO_2 from the SSME clusters as a percentage of its PEL divided by the sum of the HCl and the NO_2 from the RSRM as a percentage of their PELs. The lower curve shows the same ratio, but for the motors as configured with no thrust normalization. In the worst case scenario, the peak value of the NO_2 from the SSME clusters actually reaches a higher percentage of its PEL than the HCl from the RSRM. In the nominal thrust case, the SSME cloud is more toxic within about 19 km of the test site, and the RSRM cloud is more toxic outside of that distance, while for the worst case scenario, the SSME cloud is more toxic out to about 25 km.

These findings for SSMEs and RSRMs are only relevant on a relative sense. None of the concentrations predicted by the INPUFF code exceed the PELs for any rocket exhaust species. However, decisions or recommendations of preferred rocket propulsion chemistry have been made in the past on the basis of predicted ground concentrations, and in fact, launches and static tests of solid rocket motors have been delayed at times. What these data suggest is that one of the proposed solutions for making rocket exhaust clouds less toxic, switching from solid to liquid booster rockets, may not improve the situation at all.

CONCLUSIONS

Since the release of the three major reviews of the effects of rockets on the environment in 1991-92, significant additional work has been done to better quantify those effects. Additional computer modeling has been conducted for both the stratospheric ozone impacts and the tropospheric effects. New field data from both atmospheric regions has also been reported. The basic conclusions of the major reviews, that rockets exhibit a very minor and manageable impact on the environment have not changed as a result of the new data.

Although it has been argued for years that solid rocket clouds containing HCl present no threat to the public health, there have always been concerned parties that have argued that less toxic exhaust clouds can be produced by switching to liquid propulsion. The data presented above show that this may not necessarily be the case, and that to the contrary, at many locations the toxicity of liquid rocket exhaust clouds may exceed that of solid rockets. Since neither exhaust cloud presents a real threat to safety, decisions on the choice of propulsion system should be made on the basis of cost, reliability, and safety, and not on the basis of local environmental impacts. In connection with this, launch site range safety should not focus entirely on HCl as it has done in the past, but should also consider NO_2 from all rockets in the test or launch decision.

ACKNOWLEDGMENTS

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Figure 1. Titan III Launch: Time evolution of NO_2 /NOx ratio in the exhaust cloud. Zero time point is calculated.

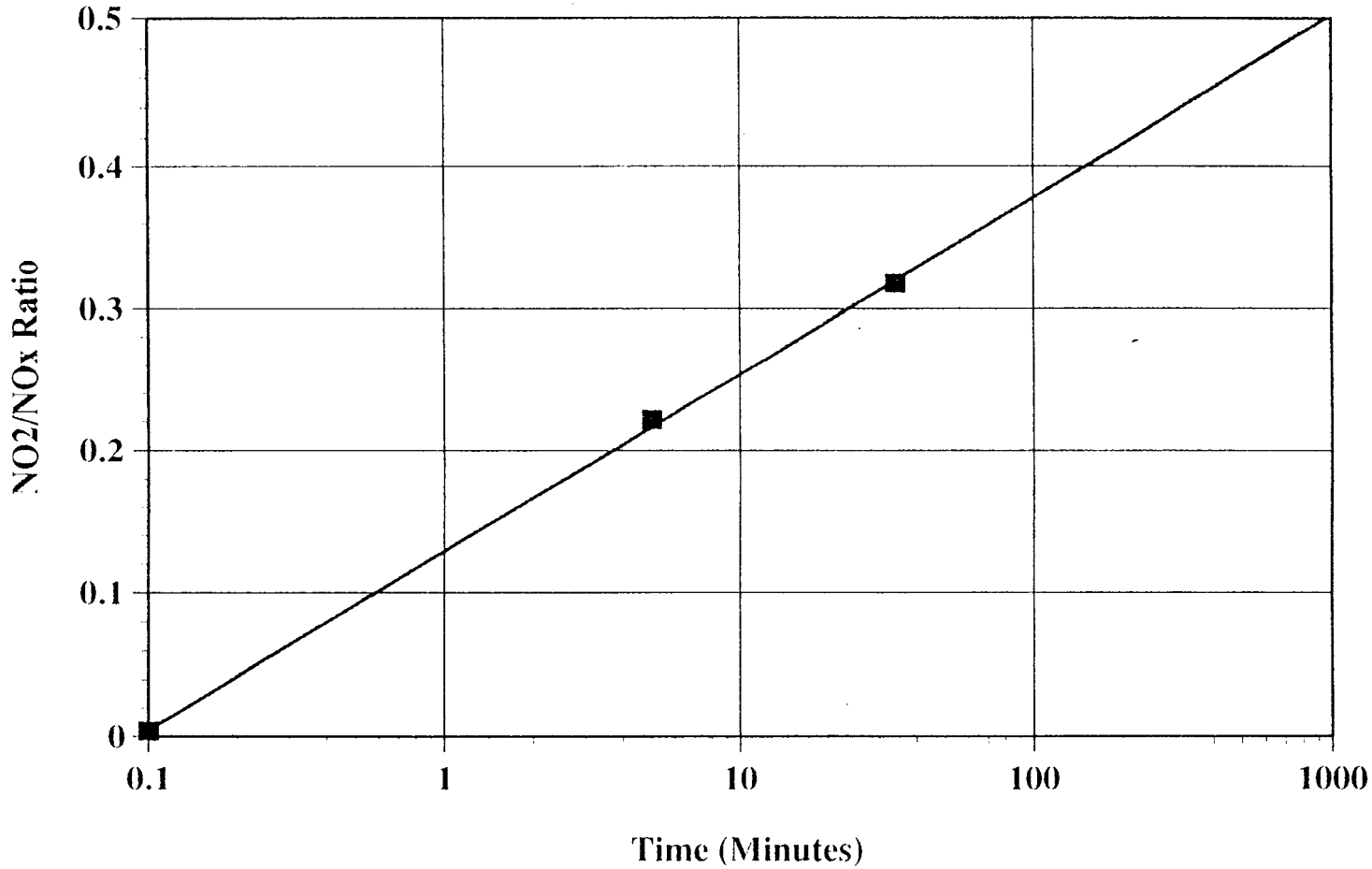


Figure 2. Comparison of NO_x from SSMEs to HCl and NO_x from RSRM.

Atmospheric Stability C, Wind = 8 m/s

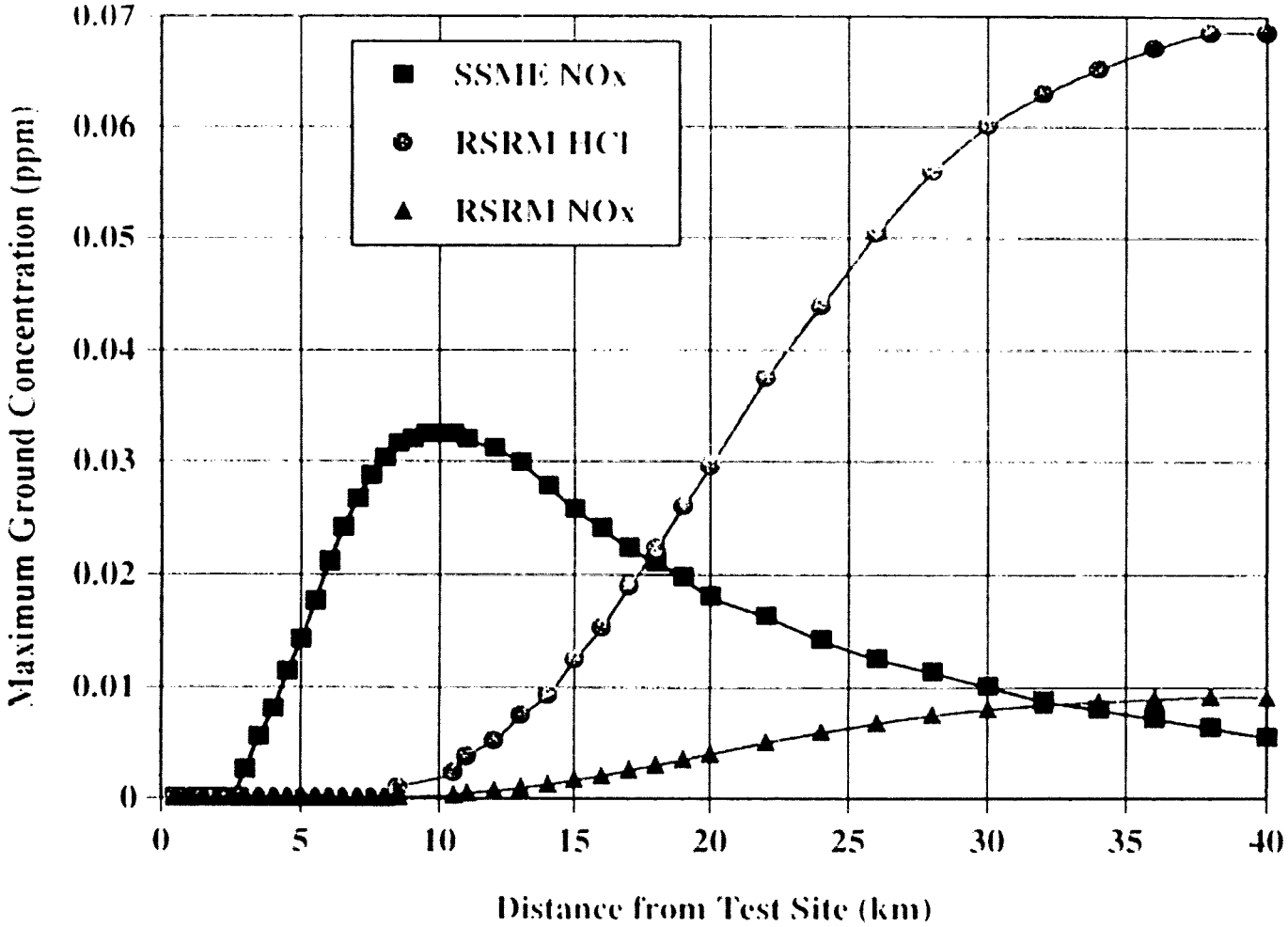


Figure 3. Comparison of NO_2 from SSMEs to HCl and NO_2 from RSRM.

Atmospheric Stability C, Wind = 8 m/s

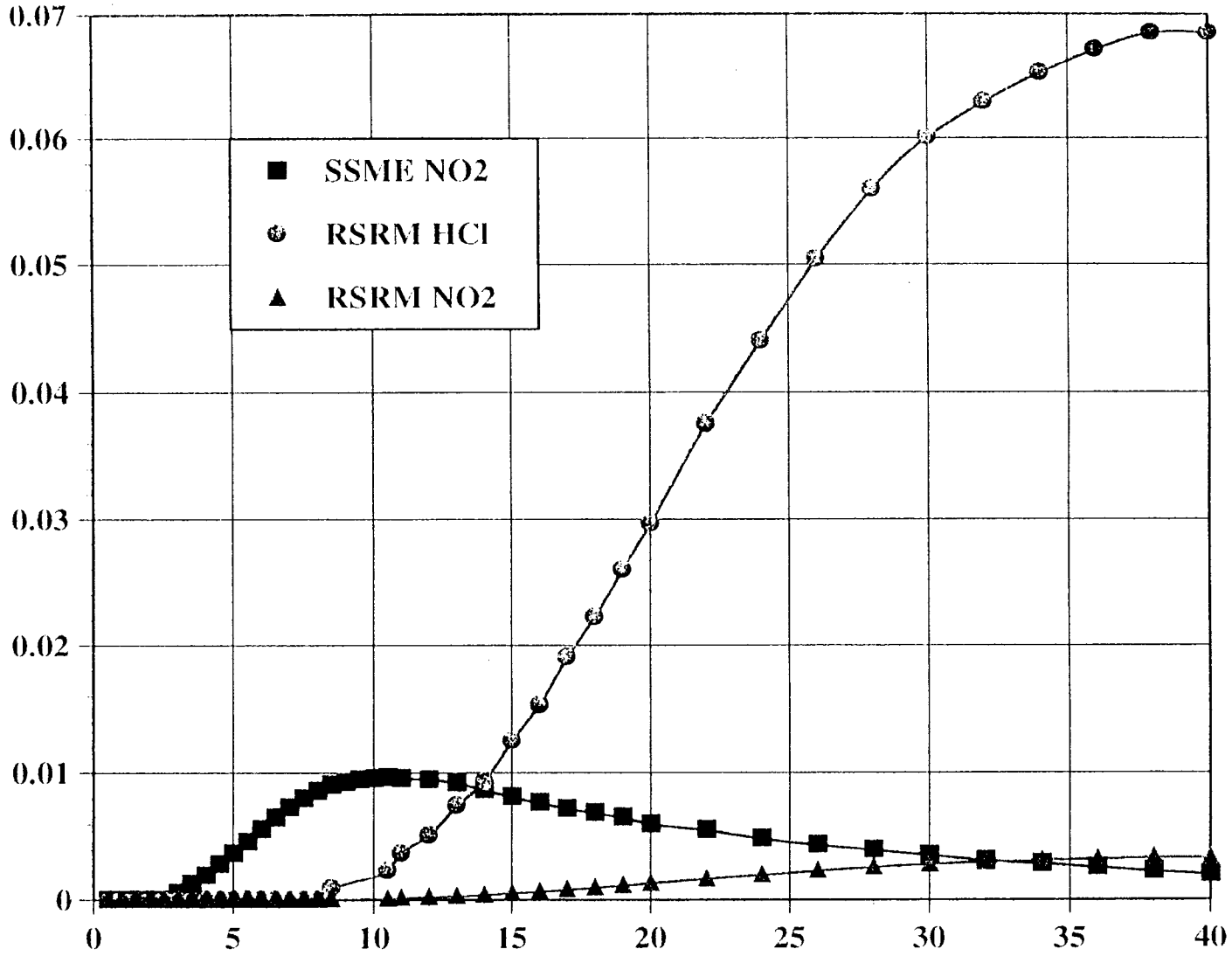


Figure 4. Comparison of NO_2 from SSMEs to HCl and NO_2 from RSRM.
Concentrations from Figure 3 divided by PEL of the given species
No thrust normalization. Atmospheric Stability C, Wind = 8 m/s

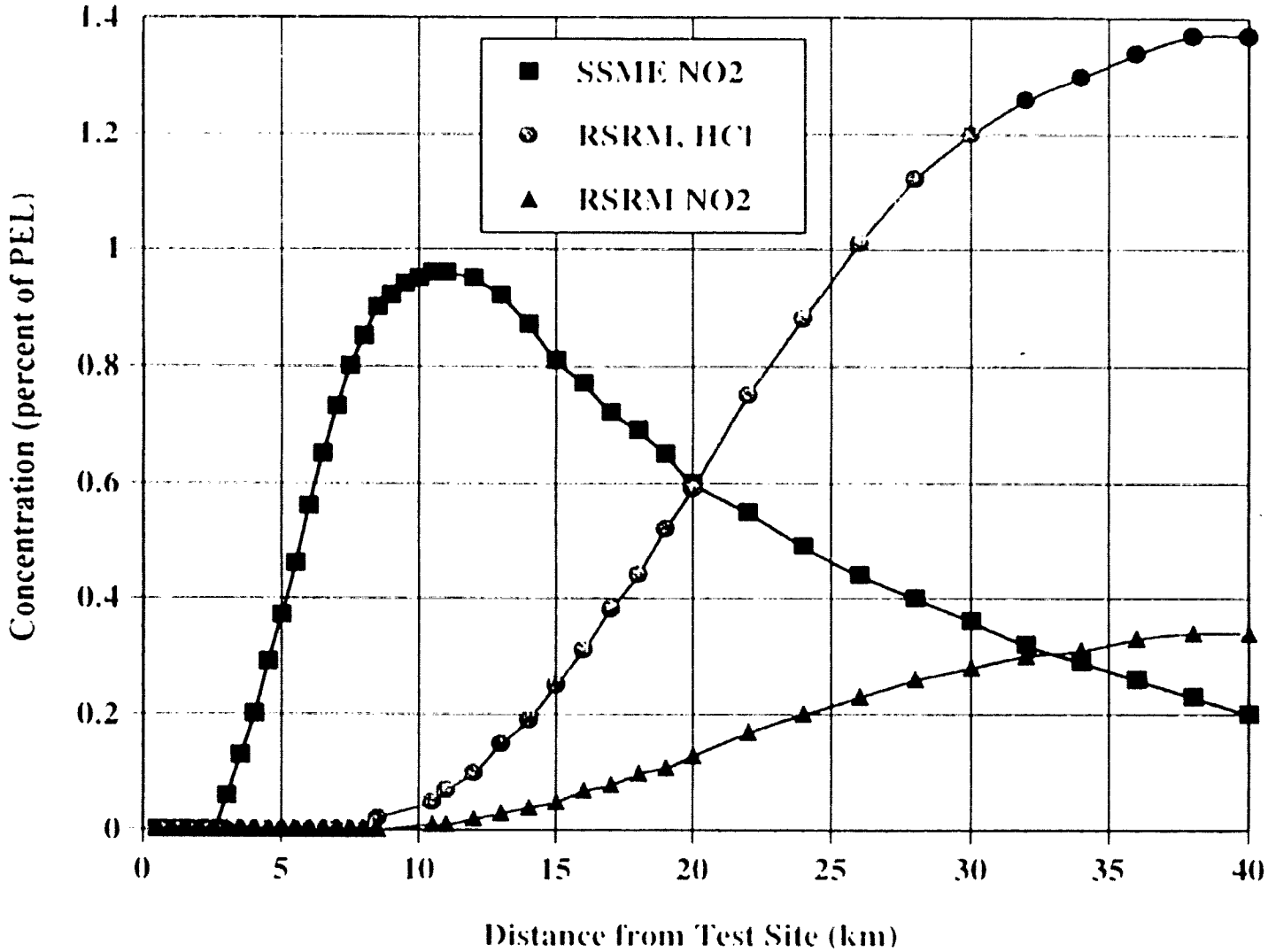
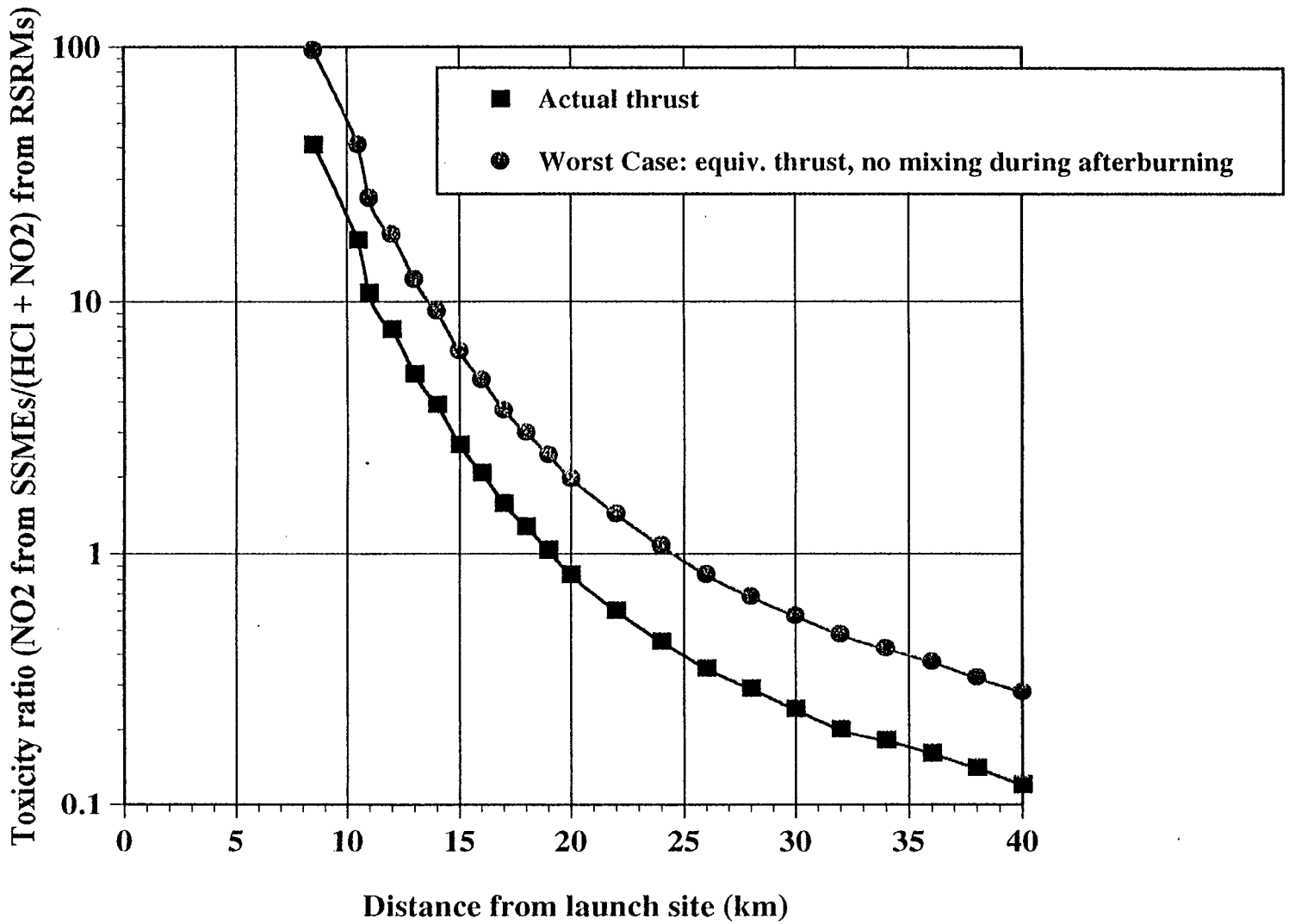


Figure 5. SSME vs. RSRM: Toxicity ratio: NO_2 from SSME as a percent of its PEL/(NO_2 + HCl) from RSRMs as a percent of their PELs versus distance from launch site. Top curve, worst case, equivalent thrust, separate SSME clusters with no SSME or RSRM plume mixing during afterburning. Bottom curve, nominal SSMEs vs. nominal RSRMs, assumes complete mixing of 2 RSRM plumes and 3 SSME plumes. Atmospheric Stability C, 8 m/s wind.



Solid Rocket Exhaust Cloud Modeling and Verification Measurements

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ABSTRACT

A considerable effort has been expended in the development and verification of computer models to determine the fate of exhaust clouds produced by the combustion of solid rocket propellants. One of the species of greatest interest has been HCl, since it is considered a hazardous air pollutant by the EPA. Three computer models, REEDM, INPUFF, and PCAD, have been used to predict the location and concentration of exhaust clouds of various rocket motors. Thiokol Corp. has recently commissioned El Dorado Engineering to compile and summarize their history of field measurements on solid rocket motor static tests and propellant open burns. Part of this effort was directed towards PCAD model validation. The data show the PCAD model to predict plume rise height, the location of maximum exhaust cloud ground concentration, and the value of the maximum concentration quite well - at least within a factor of two in most tests. In addition, SECOR International, Inc. has conducted side by side comparisons of INPUFF and REEDM, and finds REEDM to generally predict higher concentrations of exhaust species, apparently due to a lower calculated plume rise. Recent experimental measurements of Titan launches have also shown an under prediction of plume rise height by REEDM. Some of the concerns with the REEDM program as evaluated by El Dorado Engineering are noted, including incorrect source terms. Since launch decisions are made based on REEDM output, it is important that it be as accurate as possible.

BACKGROUND

As with any product that emits the products of chemical combustion to the atmosphere, rockets have been scrutinized for years for potential adverse environmental or health effects resulting from their testing, use, or manufacture. Solid rockets utilizing ammonium perchlorate, which produce HCl as a combustion product, have been of particular interest, since HCl has been identified as a hazardous air pollutant. Thiokol, as a leading manufacturer of solid rockets, has an obvious interest in understanding the potential environmental impacts of rocket exhaust, as well as in understanding the models used to determine the advisability of a launch or static test.

There have been a number of reviews of the environmental impacts of rocket motors published over the years.[1,2,3,4,5,6] While some of these have focused mainly on the stratosphere, several have attempted to assess the local tropospheric and terrestrial impacts at and around the test/launch site. Although the immediate short term impacts on the terrestrial flora and fauna have been carefully documented after each flight of the Space Shuttle (see, for example, reference 3), the ability to accurately predict *a priori* the location and concentration of the exhaust cloud has been a much more challenging problem. The necessity in doing so, however, is seen in the fact that the Air Force uses such predictions to determine whether or not to launch at a given time. Since the costs of launch delays can be in the millions of dollars, it is critical that the models used be as accurate as possible.

Several different computer models have been developed and used to try to predict the atmospheric fate of rocket motor exhaust constituents. Among these are REEDM, INPUFF, and PCAD. REEDM is the model used by the Air Force at both the western (VAFB) and eastern (CCAS) test ranges to predict the exhaust corridor and ground concentrations of species of concern. The results of the REEDM calculations are then used in deciding whether or not to proceed with the launch. Since launch delays are very costly and inconvenient, it is critically important that the models used to predict the downwind concentrations of exhaust constituents, as well as the allowable exposure criteria are as accurate and reasonable as possible. REEDM does not typically calculate the nature nor the percentages of the chemical species released from a rocket motor. These are calculated by other methods and entered as input into REEDM. INPUFF is an EPA approved model which was not developed specifically for rocket motors, but rather for general point source emissions such as industrial smokestacks. PCAD is a model developed by El Dorado Engineering which combines the NASA/Lewis thermochemical model for predicting the exhaust

species of rocket motors with plume rise equations and dispersion equations. The user can simply input the rocket propellant formulation and the motor parameters, along with the meteorological conditions, and PCAD calculates the location of the maximum ground concentration of the exhaust cloud, assuming a downwind path, and generates isopleths of constant concentration around the maximum.

A concern which always accompanies the use of a computer model is how well the results of the model reflect reality. Determining the accuracy of rocket exhaust cloud computer models is challenging and costly because several different phenomena must be accurately calculated at the same time. The results are dependent on the predicted exhaust constituents, ambient air mixing, afterburning, radiant heat loss, meteorology, and diffusion characteristics. Oftentimes, when validation measurements have been attempted, weather conditions changed such that the ground based instruments were not in the proper locations. Mobile instruments, which can be deployed in front of the exhaust cloud as it is being tracked improve the chances of obtaining meaningful measurements. The interpretation of measurements can also be complicated or misleading unless performed properly. Concentrations of exhaust species can only be measured at a finite number of locations. It is always possible that maximum concentrations are missed, or that the plume is not symmetrically dispersed. The problem may be even more complicated when a rocket producing a nonvisible exhaust cloud is used, since the cloud cannot be tracked optically.

RESULTS AND DISCUSSION

With all of these challenges in mind, El Dorado Engineering (EDE) has conducted successful sampling campaigns to measure the fate of the combustion products of solid rocket motor propellant. Under contract from Thiokol, the results of these studies have been compiled, and are reviewed here. In addition, EDE has conducted an analysis of the REEDM source terms and dispersion modeling, and has uncovered some significant discrepancies. Field measurements on both open air propellant burning, and combustion at high pressure within a rocket motor, exhausted through a nozzle have been evaluated. Specifically, the tests included:

- Static firings of two Pershing missile motors
- Open burning of propellant at the Hercules Bacchus/ Navy NIROP facilities
- Static firings of Space Shuttle booster rocket motors

The PCAD Model

The PCAD model consists of three primary components: products of combustion and heat of formation equations, plume rise equations, and dispersion equations. The products of combustion and heat balances are calculated from an adapted version of the traditional NASA/Lewis program[7] used to calculate the thrust of rocket propellants. The NASA/Lewis model was developed as a tool for the design of rocket motors, and is essentially a solution to a series of simultaneous chemical equilibrium equations that are iterated until the heat/temperature and chemical products balance. The routines utilized by PCAD are actually a modified version of the Edwards Thermo Equilibrium Program.[8] The products of these calculations are then coupled with plume rise equations which use meteorological conditions as well as the calculated heat released from the burning of the propellant as input data. The PCAD model's plume rise is calculated using Briggs plume rise equations in a form developed by the U.S. Army.[9] These plume rise results are in turn combined with traditional transport and dispersion equations and coupled with specialized rectilinear dispersion coefficients to estimate plume transport and concentrations at the maximum concentration location and at selected receptors. The dispersion portion of the PCAD model incorporates a Gaussian distribution equation, which includes an Alongwind Term to account for the enhanced dilution of the plume due to the fact that it is not a continuous release. The PCAD model is the only model known to EDE that predicts both products of combustion and dispersion. As a result of the validation testing discussed below, the PCAD model has been modified and updated. All data given is based on the current version of PCAD.

Pershing Testing

EDE was contracted to assist the U.S. Missile Command in the environmental assessment of the air emissions from the static firing of the Pershing missile motor disposal procedure for the INF treaty. In rendering this support, EDE provided four mini-modeling and sampling campaigns in Huntsville, Alabama, followed by final modeling and a very extensive test at Pueblo, CO. From these tests, EDE developed the technology for incorporating a tracer gas for field sampling, and developed procedures for deploying a mobile sampling team.

The concept of using tracer gases has been in existence for years. However, the application of tracer gas use for open burning and static firing of rocket propellant was entirely new, and EDE developed the technology to incorporate the tracer in the exhaust cloud. The use of tracer gases in the validation procedure is significant, because many of the theoretically predicted downwind concentrations of emission products were at or below the minimum detection limits of currently available analytical techniques. The detection level of sulfur hexafluoride (SF_6), the tracer gas of choice, is in the parts per trillion (ppt) range, which is several orders of magnitude below the detection limits of the combustion products of interest (HCl). Consequently,SF_6 was released into the exhaust plume of the rocket motor to permit reliable tracking and more positive definition of the plume path. Detection of SF_6 does not absolutely demonstrate the presence of the exhaust cloud, as the possibility remains that the two do not travel together for some reason. However, the detection of both HCl and SF_6 at several locations, and the fact that their relative concentrations were fairly constant, suggests that the tracer gas does travel with the exhaust cloud, and that the absence of an HCl detection in the presence of SF_6 detection means that the HCl concentration is simply below the detection limit.

The results of the Pershing motor tests are shown in Table I. The field data show good agreement with the PCAD model, with a maximum HCl concentration of 1.5 mg/m^3 detected at 5.6 miles downwind, while the PCAD model predicted 1.1 mg/m^3 at 3.6 miles downstream. The maximum measured quantity of SF_6 tracer was almost exactly at the PCAD-predicted distance to maximum concentration. It should also be noted that the SF_6 concentration was still very near its maximum value at 5.6 miles downwind, the location of the maximum HCl concentration. The predicted plume stabilization height of 1305 feet to the center of the plume also closely matched the actual measurement of 1530 feet to the plume top. The plume height was measured by flying a helicopter to the top of the visible plume and reading the altimeter.

Table I
Summary of Pershing Missile Motor Static Firing Predictions and Measurements

Parameter	PCAD Prediction	Field Measurement
Plume Stabilization Height	1305 feet	1530 to top of plume
Maximum HCl Concentration	1.06 mg/m^3	1.5 mg/m^3
Distance to Maximum Concentration	3.6 miles	5.6 miles to max HCl, 3.6 miles to max SF_6 (SF_6 concentration 86 ppt at 3.6 miles and 82 ppt at 5.6 miles)

Hercules Bacchus/Navy NIROP Testing

Hercules Bacchus/Navy NIROP testing, the main testing effort for the validation of the PCAD model, was performed as a series of open burning tests. EDE incorporated the previously developed technology for tracer gas and mobile sampling team use gained during the Pershing testing program.

The tests were quite successful. Because of budget constraints, it was mandatory to conduct testing on consecutive days. As EDE used towers for source sampling, tests could only be conducted on the days the wind blew towards the towers. Based on the local meteorological data, dates in July were selected as the most likely to

give consistently favorable winds. Of the possible ten days for testing, nine had suitable atmospheric conditions. EDE released rawinsonde weather balloons immediately prior to open burning, analyzed the meteorological results, ran the PCAD model which incorporated the meteorological data, and deployed the sampling team. In each case, measurement of the tracer gas indicated that the plume was caught. In only three cases was HCl above the background detected.

In addition to tracer gas release, source samples were obtained from the towers in the plume path. These source samples proved very valuable in analyzing the chemical combustion portion of the model. Of most importance, by examining the ratio of CO to CO_2 in the plume, the PCAD model was iterated to determine the air/fuel ratio, and subsequently, the amount of ambient air that takes part in the combustion process. This is critical in that this ratio is a first order driver in the plume rise height, which determines the location and concentration of the ground impact of the exhaust cloud. Based on these and further verification by the Army's bang box test series,[10] an air/fuel ratio of about 5:1 is now used in PCAD modeling of open burning.

PCAD predictions correspond well to the physical testing performed for the open burning operations at the NIROP facility. Table II gives the testing dates and the maximum SF_6 and HCl detection locations, compared to the PCAD predictions. In all cases,SF_6 was detected, indicating the presence of the plume. The location of maximum concentration was generally within a factor of two from the predicted location. The average magnitude of the difference between predicted and measured distance to maximum concentration was about 0.6 miles. A mean difference of only 0.1 miles indicates that there was not a consistent determinate error in the model predictions. In all cases in which HCl was detected, its concentration was at or above the predicted value. The results of the measurements of July 26 are somewhat suspect, since there was a background HCl concentration of 0.13 ppm measured, indicating another source of HCl in the vicinity. The maximum value measured on July 28 of 0.83 ppm close in to the burn pit suggests that at least part of the plume did not rise as expected, staying near the ground, and giving the unexpectedly high reading. Those HCl measurements which were taken at the expected concentration maximum were very close to the predicted value (0.12 and 0.17 ppm measured vs. 0.13 ppm predicted). The other day when HCl was detected, July 25, showed a measured reading of 0.5 ppm, about twice the value of 0.21 ppm which was predicted. These measurements indicate that the location and magnitude of the maximum concentration of an exhaust cloud from an open burn can be calculated reasonably well using the PCAD model, but that the user should anticipate that the nonideal behavior of the plume may lead to errors of a factor of 2 or so.

Shuttle Booster Rocket Testing

The final series of tests conducted by EDE focused on the Space Shuttle Solid Rocket Motors (SRM). This testing included taking samples on the hillside from plume impact, as well as helicopter and ground-level plume tracking. Plume height was also estimated from the helicopter tracking the plume. The plume models predict, and visual observations confirm, that the plume rise height is strongly dependent on the size of the rocket motor. Plumes from large rockets, with their high mass flow and consequent rapid heat release, tend to rise very high, while small rocket plumes stay much nearer the ground. Being the largest solid rocket motor in production in the world at just over 1 million pounds of propellant, the SRM produces exhaust clouds which rise as high as 15,000 feet. As a consequence, the deployment of samplers to capture the plume as it diffuses back to the ground is quite challenging. It was found that mobile samplers are necessary since the wind conditions change with time and distance from the launch site. For these tests, a helicopter was used to track the plume, and to aid in the deployment of mobile teams ahead of it.

A summary of the results of the Shuttle SRM testing is given in Table III. The PCAD model was generally quite good at predicting the plume stabilization height, with an average error of 10 - 30 percent. The predicted plume height was too high about as often as it was too low, indicating that, once again, there was no apparent systematic error. The asterisks on the predicted plume stabilization heights for the July, 92 and April, 93 tests indicate the possible source of the discrepancy between the predicted and measured plume heights was the lack of met data above 10,000 feet, so the predictions were extrapolations based on the lower altitude data.

Since tracer gases were not used in the SRM tests due to the huge amount that would be necessary in a plume this size, it is not possible to say whether or not the samplers were located at the maximum plume

Table II
Summary of Hercules/Navy Predictions and Measurements

Date	Parameter	PCAD Prediction	Field Measurement		
7/19/88	Maximum HCl Concentration	0.14 ppm	Non Detect		
	Distance to Maximum Concentration	0.80 miles	HCl: NA		SF_6: 1.8 miles
7/20/88	Maximum HCl Concentration	0.025 ppm	Non Detect		
	Distance to Maximum Concentration	1.9 miles	HCl: NA		SF_6: 1.0 miles
7/21/88	Maximum HCl Concentration	0.27 ppm	Non Detect		
	Distance to Maximum Concentration	0.73 miles	HCl: NA		SF_6: 1.0 miles
7/22/88	Maximum HCl Concentration	0.052 ppm	Non Detect		
	Distance to Maximum Concentration	1.4 miles	HCl: NA		SF_6: 1.7 miles
7/25/88	Maximum HCl Concentration	0.21 ppm	0.5 ppm		
	Distance to Maximum Concentration	1.1 miles	HCl: 1.5 miles		SF_6: 2.0 miles
7/26/88	Maximum HCl Concentration	0.062 ppm	0.3 ppm; background reading of 0.125 ppm		
	Distance to Maximum Concentration	1.3 miles	HCl: 1.0 and 1.5 miles		SF_6: 1.0 miles
7/28/88	Maximum HCl Concentration	0.13 ppm	0.83 ppm; 0.12 ppm at 1 mile and 0.17 ppm at 2 miles		
	Distance to Maximum Concentration	1.8 miles	HCl: 0.8 miles		SF_6: 1.9 miles
7/29/88	Maximum HCl Concentration	0.023 ppm	Non Detect		
		1.7 miles	HCl: NA		SF_6: 1.0 miles

Table III
Summary of Tracking and Sampling Emission Plumes from Static Firings of the Space Shuttle Booster

Date	8/88	8/89	1/90	1/91	7/91	11/91	7/92	4/93
Measured Plume Stabilization Height (feet)	8400	14,000	5,200 to bottom of plume	Bad weather	13,200	Bottom at 4,900	10,171	9,900
PCAD Predicted Plume Stabilization Height (feet)	11,470	12,900	9,305	5,746	11,928	5,224	17,214*	11,146*
PCAD Predicted Distance to Maximum Concentration (miles)	17.8	19.9	24.4	15.2	12.5	13.8	26.6	27.6
PCAD predicted HCl (mg/m^3)	0.378	0.274	0.609	2.28	0.314	2.97	0.123	0.415
PCAD predicted Al_2O_3(mg/m^3)	0.530	0.385	0.853	3.20	0.440	4.17	0.172	0.581
HCl sampled	Non Detect	Non Detect	Non Detect	NA: plume tracking only	Non Detect	NA: plume tracking only	Non Detect***	NA: plume tracking only
Al_2O_3 sampled	**	**	Detected at 1.3.5, 15, and 18 miles	NA: plume tracking only	Detected at 12.8 and 14.5 miles	NA: plume tracking only	Detected at 15.7 miles and in passive samplers at 13-16miles	NA: plume tracking only

*The predicted plume stabilization heights for these tests may have been high, as meteorological data was limited to 10,000 feet; further iterations with higher meteorological data would probably have led to a lower predicted plume stabilization height due to higher wind speeds.
**Methods for measuring alumina concentrations from fallout particulate was not well defined for these tests.
***Passive samplers for particulate showed chlorine content.

concentration. What can be said is that samplers did detect alumina particles, indicating the presence of the plume (assuming the particulates and HCl stayed together as they disperse through the atmosphere). It was not possible to determine the alumina concentration in the plume, since it was simply collected on cheesecloth. The location of the alumina detection once again agreed reasonably well (withing a factor of 2) with the PCAD predictions. The fact that the detection limits of the instruments used for HCl measurements were about 0.06 mg/m^3, the predicted maxima on those tests for which the instruments were used were anywhere from 0.12 to 0.61 mg/m^3, and there was no HCl detected in any cases suggests three possibilities. First, unlike small rockets motors or open burning, the PCAD model significantly over predicts the HCl concentration for plumes from large rocket motors. Second, the instruments were never in the right place to detect the maximum ground concentrations of HCl because a) the alumina detected was only from the edge of the plume where the HCl was below the detection limit, or b) the HCl did not track the visible portion of the plume for the 30 - 60 minutes required for the plume to disperse enough to impact the ground again. Finally, the instruments may have been in the right place, and the model may have accurately predicted the plume's degree of dispersion, but the HCl may have adsorbed on the surface of the alumina or been hydrated into an aqueous phase. Without further testing, it is not possible to absolutely determine which of these is most likely.

What is encouraging from these tests is that in no case, was a level of HCl detected which would be considered to be of any health concern. Contrary to natural expectations, large motors may actually be better at getting their plumes dispersed than smaller motors, despite the fact that they emit a much larger quantity of combustion products.

The PCAD model output enables one to get an idea of the predicted size of the plume footprint, and the likelihood of being within the 50 percent isopleth of the plume (any spot within this isopleth is predicted to see an HCl concentration at least half of the maximum). For the July, 1991 test, for which the predicted distance to maximum concentration was 12.5 miles, and alumina was measured at 12.8 and 14.5 miles, the 50 percent isopleth was approximately 4 miles x 14 miles, and the 10 percent isopleth about 9 x 20 miles. This large footprint of the 50 percent isopleth in which the concentration of the exhaust species should be quite similar, combined with the lack of HCl detection, suggests that the maximum HCl concentration from the Shuttle SRM is considerably less than the PCAD model predicts, and that the model is therefore quite conservative for large rocket motors.

As mentioned above, for the Shuttle SRM tests, canisters were buried in the hillside within a few hundred feet of the nozzle, and sampled the plume to measure the CO_2 to CO ratio at from 91 - 169/1. Whereas the measured CO_2 to CO ratio for the open burn suggested an air to fuel ratio of about 5/1 for self consistent model calculations, the value required for the SRM is lower, at about 3.5 to 1.

Comments on the REEDM and INPUFF Models

Under a subcontract from Thiokol, SECOR International, Inc. has performed model calculations of rocket static testing using the INPUFF model, and has compared the output of some of these calculations with REEDM.[11] INPUFF is a model approved by EPA for this application, which has been used by Thiokol for ambient air quality impact analyses associated with the static testing of various rocket motors. An analysis of the Shuttle SRM at the Thiokol, Utah test facility was performed to help satisfy impact analysis requirements associated with a PSD permit, as required by the USEPA. The REEDM/INPUFF analysis summarized here examined 5 different scenarios where the static testing of two different motors under three different meteorological conditions are performed. Information from ACTA was used to produce the 5 test cases, with common input assumptions used for the two models whenever possible. A qualitative assessment of the differences between the two models can be made by comparing the plume heights, and distance to and value of the maximum predicted HCl concentrations.

Table IV compares the two models for three Titan launches and two Peacekeeper launches. In two cases, the REEDM model gave peak concentrations of HCl considerably higher than did INPUFF (3.6 vs. 0.64 ppm and 1.22 vs. 0.64 ppm). In two cases, the models gave similar results, and in one case, INPUFF gave an HCl concentration about twice that of REEDM. The distances to the peak concentrations were within about 30 percent of each other in four of the five cases, but differed by a factor of seven in the last case shown in Table IV. For a given set of meteorological conditions, REEDM predicts an identical downwind distance to maximum HCl

Table IV
REEDM and INPUFF Model Comparison Study
Titan IV and Peacekeeper Static Tests
Vandenberg, AFB, California

Motor	Scenario	Peak Distance (km)	REEDM Peak (ppmv)	INPUFF Peak (ppmv)	Maximum
Titan IV	OP3733	11.0	3.58	0.645	REEDM peak
		1.2	3.57	0.645	INPUFF peak
Titan IV	OP4119	1.0	1.22	0.590*	REEDM peak
		20.5	1.01	0.639*	INPUFF peak
Titan IV	OP8260	3.0	1.55	0.600	REEDM peak
		4.8	0.891	3.02	INPUFF peak
Peacekeeper	OP4119	15.0	0.301	0.250	REEDM peak
		10.4	0.191	0.304	INPUFF peak
Peacekeeper	OP8260	3.0	0.619	0.350*	REEDM peak
		21.0	0.033	0.618*	INPUFF peak

*For these cases, the INPUFF run with unlimited mixing was used.

concentration, regardless of which motor was modeled. This seems to be contradicted by visual observations of static tests, where larger motors tend to give higher plumes.

An analysis of the data shows that the major reason for the large differences between the two models was in the plume height estimates. The plume height in the INPUFF model is computed using the Briggs neutral/unstable plume rise formula, and is considered to be the most widely used formula by the regulatory community. Plume heights were substantially higher in the INPUFF model than in the REEDM model. That the REEDM model consistently under predicts actual plume rise heights was shown in data presented at the recent AIAA Solid Rocket Lecture Series.[12] These data show that the plume rise height was generally 30 - 100 percent higher than predicted for 5 Titan launches. When the REEDM model was adjusted to use the same rise height predicted by INPUFF, the results of the two models were quite similar.

The analysis of the source terms of the REEDM model by EDE showed some rather obvious errors in the input terms. The Shuttle input, for example, uses the incorrect burn time (82 seconds instead of 123 seconds), the incorrect propellant weight (1.37 million pounds instead of 1.11 million pounds), has both an incorrect quantity and ratio of exhaust constituents, due at least in part to an incorrect accounting for air incorporation during afterburning. The REEDM manual states that the exhaust species are 'the fractions of the respective species in the exhaust cloud when afterburning is complete.' The propellant for the Titan IV and Shuttle SRM are very similar in formulation, and one would expect the HCl concentrations from the respective motors to be nearly identical, yet the Shuttle HCl concentration is given as 11.5 percent and the Titan IV as 19.8 percent of the total exhaust products. Not only are these numbers very different, but they are both too high. Incorporation of the minimum amount of air required for afterburning would result in the HCl concentration dropping to about 9 percent. In actuality, the CO_2/CO data cited above suggests that considerably more air is incorporated in the afterburning process, which would result in an even lower HCl concentration. Since the final HCl concentration is directly dependent on the initial HCl concentration, the use of artificially high HCl fractions in the input will result in artificially high HCl concentrations downwind.

CONCLUSIONS

A more complete and comprehensive analysis of the various models used in predicting exhaust product concentrations is ongoing. There are enough questions regarding the validity and accuracy of the REEDM model that a serious effort should be made to validate its predictions, since they are being used in making launch decisions which involve millions of dollars. To its credit, the Air Force is funding, albeit at a low level, studies to improve the REEDM model and to validate its predictions through field measurements. These studies should continue, and perhaps be accelerated, given the potential for cost savings.

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Advances in Clean Burning Hybrid Rocket Fuels

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Abstract

Hybrid rocket propulsion---based on a solid fuel and a liquid oxidizer--is attractive from an environmental as well as a performance standpoint. McDonnell Douglas Aerospace--Huntsville has developed a new hybrid fuel with numerous advantages including (1) low cost, commercially available, non-energetic ingredients that can be cleaned up without using hazardous solvents and disposed of in regular landfills; (2) a self extinguishing characteristic that keeps the fuel out of the flammable solid category and makes it safe to handle, ship, and store; (3) high efficiency combustion with a clean exhaust when burned in a rocket motor; (4) a higher regression rate, more uniform axial regression, and higher density than existing alternative, all organic hybrid rocket fuels; and (5) flexible operation during flight due to ability to throttle, shut down, and restart. This paper will discuss the new MDA fuel formulation, highlighting its environmental friendliness, its advantages, and test results obtained in motor firing tests.

Introduction

Although hybrid rocket propulsion has been known for many years, only one hybrid rocket has flown any significant distance, and hybrid propulsion has not been developed to the same extent as solid or liquid rocket propulsion. As hybrid propulsion is not a mature technology, improvements in understanding how to make optimum use of the concept are required prior to making it competitive with the solid and liquid propulsion alternatives that are currently used on operational launch systems. One supporting technology with opportunities for further development is that of fuel formulation. Fuel formulation is important as it drives performance characteristics such as ease of start up and shutdown, regression rate, relative regression rate as a function of axial position in the fuel grain, and combustion efficiency, as well as contributing to the density, the density specific impulse, and the overall performance and system efficiency.

Hybrid motors differ from classical solid motors in that there is no oxidizer in the solid fuel itself, and as a result combustion does not occur at the surface, but above it. Because the fuel does not actually burn at the surface, there is no "burning" rate. The surface regresses, or recedes, by heat transfer to the surface which decomposes the fuel either into small molecules which vaporize, and/or char which is eroded away in pieces by the gases rushing over the surface. Thus the regression rate is influenced by the rate at which the fuel ingredients thermally decompose and vaporize or are scrubbed off the surface. The more easily vaporized or scrubbed off the pyrolysis products are, the higher the regression rate.

A well recognized characteristic of hybrid motors is that the surface regression rate is a function of the oxidizer mass flux. Less well recognized is that it is also a function of temperature, and temperatures are higher in the aft end of the motor. Since at a constant mass flow rate of oxidizer, the oxidizer mass flux changes continuously throughout the motor operation, correctly interpreting data is neither easy nor simple. If the data is primarily fuel weight loss during firing, it is important to recognize that there are variations in fuel weight loss with respect to axial position within the fuel grain as well as a continuous variation in regression rate at any location over time.

As just about any oxidizable material can be used as fuel, the major emphasis to date has been on optimizing the delivery system for the oxidizer and designing to ensure that the combustion chamber does not produce acoustic pressure oscillations, rather than optimizing fuel formulation.

Fuel Formulation Considerations

State-of-the-Art

The characteristics desired in solid propellants are also desirable in hybrid rocket fuels. These include (1) thermal stability across a wide temperature range, (2) adequate strain capability to avoid cracking during thermal cycling while in storage and during ignition pressure transients, and (3) low vapor pressure. Thus while candle wax would burn satisfactorily, it would be excluded from serious consideration as a high performance hybrid rocket fuel due to its low softening temperature.

The good mechanical properties of a large portion of modern solid propellants arise through utilization of standard elastomeric binder systems which holds them together. A typical binder has a cured density of 0.92 g/cc. The binder system exhibits good thermal stability and good strain capability and does not off gas in vacuum.

One characteristic of a high performance fuel is high specific impulse, since mass flow times specific impulse yields thrust. Generally the lower the average molecular weight of the combustion products, the higher the resultant specific impulse. Using oxygen as the oxidizer, common combustion products from hydrocarbons are water, carbon monoxide, and carbon dioxide, with respective molecular weights of 18, 28, and 44. Thus the trend is that more hydrogen in the hydrocarbon means more water produced, generating a higher specific impulse.

Polyethylene, essentially a saturated linear hydrocarbon polymer containing repeating CH_2 units, produces high specific impulse as a fuel. However, the thermal decomposition reactions leading to the vaporization of polyethylene have high activation energies, and the regression rate is relatively slow. It also has a low density, ranging between about 0.93 and 0.94 g/cc depending on the grade. Thus it is not an optimum fuel for a high performance rocket. However, a chemically similar commercially available hydrocarbon with more branching works better. It decomposes more rapidly while still yielding a good specific impulse. Its density is also higher than that of either binder or polyethylene, at approximately 1.02 g/cc.

The consortium conducting the Hybrid Propulsion Demonstration Program (HPDP) at NASA MSFC is using a solid fuel based on a hydrocarbon filler in an elastomeric binder. The relatively low density of the hydrocarbon filler and the resultant flow considerations during processing limit filler content to about 60% by weight, leaving 40% binder. This contrasts strongly with a typical solid propellant containing only 12% binder. A high binder content limits the maximum density of the fuel, and tends to raise the cost as it is more expensive than most fillers. The sixty percent hydrocarbon filled fuel being used has a density of 1.0 g/cc. While this is significantly higher than that of kerosene or RP-1 which are roughly 0.81 g/cc, it is still much lower than 88% solids, metallized propellants which are around 1.8 g/cc.

Advanced Fuel Formulation

In 1993 MDA-HSV initiated an IRAD program to develop higher performance hybrid rocket fuel. The goal characteristics of the fuel ranked environmental friendliness high and included (1) clean burning with no solids (such as metallic oxide) and no acids (such as hydrogen chloride) as primary combustion products, (2) easy and safe to handle, process, clean up, ship, store, and dispose of, (3) higher in performance (increased density and increased regression rate), and (4) relatively inexpensive via use of commercially available materials produced in volume with established characteristics.

We noted that one way to maintain high specific impulse (I_{sp}) was to utilize fuels containing nitrogen, since they have high heats of formation. The best known of these, already established as liquid rocket fuels, are hydrazine and unsymmetrical dimethyl hydrazine (UDMH).

In searching for nitrogen compounds that are high melting point solids, are commercially available, are inexpensive, and are non-energetic, MDA-HSV identified two fairly high density amines. They are available in bulk at around $0.50 to $0.60/lb. The higher density additives were anticipated to lead to a higher density solid hybrid rocket fuel.

One amine has a high enthalpy of formation and maintains high I_{sp} in the formulation, while the other has a lower enthalpy of formation and lowers I_{sp}. Thus one formulation consideration would be to use as much of the former as possible and as little of the latter as possible.

These two fillers behave quite differently during heating to decomposition. While one decomposes to molecules that vaporize, the other forms significant amounts of char. Consequently, filler content of different ratios should produce different regression characteristics.

Thermochemical analysis of the combustion reactions of these amine fillers with oxygen indicates that the main products are nitrogen, water, carbon dioxide, and carbon monoxide. In the atmosphere the carbon monoxide is subsequently oxidized to carbon dioxide. This is an environmentally friendly exhaust with no particulate matter and no acids.

Method of Approach

The approach consisted of identifying additives to be examined, evaluating thermochemical performance, making mixes to define compatibility of additives with binder system chemistry and to define viscosities of different solids loadings for processibility, fabricating fuel grains to be test fired in labscale test motors, firing the labscale motors, and then reducing and analyzing the data. Once optimum fuel performance characteristics were obtained in the labscale motor, the procedure was scaled up and performance was verified in a larger, 11-inch motor. We also ran a test to determine the hazard classification of the solid fuel.

Labscale Test Motor

The labscale test motor had a total fuel grain length of ten inches, made up of four individual 2.5" long segments. The initial port diameter was either 0.625" or 0.83". The maximum grain diameter, including the paper phenolic sleeve was 1.50." The head end opening was 1.25" allowing some gaseous oxygen impingement directly on the end of the grain, which was not inhibited in any way. The motor case was heavy weight steel. We fired the labscale motor for either 2.5 or approximately 3.5 seconds. The shorter durations were for high oxidizer mass flux--0.25 to 0.52 lb/(sec sq in); the longer durations were for low oxidizer mass flux--0.08 to 0.14 lb/(sec sq in). Pressures for the high oxidizer mass flux firings were usually around 450 psi, while the pressures for the low oxidizer mass flux were generally around 550 psi. The two different pressures arose as a result of using two different, readily available nozzle sizes.

11-Inch Test Motor

This motor used grains made in 34" long segments. The first configuration tested contained one grain, while the second contained three grains laid end to end. Calculated thrust developed by the three grain configuration was 2500 lbf. Initial port diameters were 3" for the single grain configuration and 4" for the three grain configuration. Maximum fuel grain diameter was 8" including the paper phenolic sleeve. There was a head end section forward of the grain, approximately 6" long and lined with a thin layer of fuel which burned during the firing, raising the temperature of the incoming oxygen. There was also an aft combustion chamber approximately 7" long. The nozzles were sized based on scaling up the data from lab scale motor firings and were made of graphite.

Results

Mix Processing

The amines were used as purchased with no further size modifications. One material was coarser than the other, but both were reasonably small particles. The larger was about the size of table sugar.

MDA-HSV mixed and cast a variety of ratios of amine fillers in the elastomeric binder. The mix procedure consisted of weighing out and placing the prepolymer and curative in a warm mixer, and mixing for about 10 to 20 minutes under vacuum. The additives were then weighed out and added all at once to the mixer, the mixer was closed, vacuum was pulled, and the combination was further mixed until the solids were uniformly dispersed. The solids dispersed fairly quickly, and the resultant fluid was readily castable. Many mixes were made and cast from a

two gallon mixer to make the 8" diameter fuel grains. The cured density was measured at 1.15 g/cc for the 8" diameter fuel grains.

Cleanup and Disposal

The amines are water soluble and light dustings are easily cleaned up with a wet rag. The dirty rag can be washed, with the effluent going into an ordinary sanitary sewer. Since there are no size modifications of the solid fillers, handling/waste is minimal. The liquid hydrocarbon prepolymer is non hazardous and can be sent to a landfill after wiping up minor amounts. The curative is a diisocyanate and is toxic prior to reaction. However, the diisocyanate is always formulated to be in less than an equivalent amount, and the cured solid binder is non hazardous. Cleanup of uncured binder or straight curative with isopropyl alcohol converts any unreacted isocyanate to a non toxic urethane, and the product can be disposed of in landfills.

Labscale Motor Tests

The different ratios of fillers generated a range of regression behaviors. The regression behavior fit the standard equation for hybrid motor operation which is

$$r = a\,(G_O)^n$$

where r is the surface regression rate of the fuel in inches/second, a is an empirical constant, G_O is the oxidizer mass flux, and n is the empirical exponent.

It was determined that the exponent could be varied between 0.45 and 0.55 using a range of the amine fillers. It is desirable to have a tailorable exponent in order to have flexibility in motor design and operation.

At low oxidizer mass flux, char residue was observed on the surface of the fuel grains after a firing. At higher oxidizer mass flux, the grains were scoured clean and looked the same after the test as before, except that the port diameter was larger.

An interesting variation was axial regression rates. Since the labscale motor contained four segments, it was easy to compare weight losses in the different segments. The hydrocarbon filled fuel exhibited a large variation in weight loss between segments, while the MDA-HSV fuel exhibited minimal variation between segments. The greater uniformity in axial regression behavior of the MDA-HSV fuel will simplify design and minimize inert weight, as sections that burn out more quickly will need additional insulation while the remaining fuel in other areas burns out.

11-Inch Motor Tests

The motors ignited smoothly and exhibited no significant pressure oscillations during firing, indicating good combustion stability. There was no smoke observed behind the plume during the burn. In addition shock diamonds could be seen in the plume of the single grain configuration, a condition usually associated with high combustion efficiency. The motors exhibited smooth shutdown on oxygen cutoff with no afterburning.

The tests in the 11-inch motors indicated that motor performance could be scaled up fairly accurately. The main difference was increased combustion efficiency due to the larger aft combustion chamber, and the much longer average residence time of species combusting in the motor. The observed regression rates in the larger motor, especially the three grain configuration motor were close to that observed in the labscale motor, but were slightly higher.

The single grain configuration was fired for 11 seconds at a pressure which dropped from 920 psi to 600 psi as the nozzle eroded. The three grain configuration was fired for 8 seconds at a pressure which dropped from 480 to 420 psi as the nozzle eroded.

Combustion efficiency was found to be a function of pressure with 99% efficiency observed in the 750 psi (average) firing, and approximately 95% efficiency observed in the 450 (average) psi firing.

The regression rate was some 47% higher than that of the more widely tested hydrocarbon filled formulation. When the increased density was combined with the increased regression rate, the increase in fuel mass flow was 70%.

Axial regression was fairly uniform in the three fuel grain configuration, with the head end and center grains losing the same weight, and the aft end losing a little more. By comparison, in firings under similar conditions, the aft grain in the hydrocarbon filled formulation lost much, much more.

Fuel Flammability and Safety

To determine the shipping classification of the fuel, an International Air Transportation Authority test was conducted in which a slab of fuel, 250 mm long, 20 mm wide, and 10 mm high, was ignited at one end by a propane torch. The material is not classified as a flammable solid if the flame does not propagate the entire length of the sample within 2 minutes after ignition.

The sample of fuel tested was difficult to ignite in ambient air. When it did ignite, the flame was relatively small and remained close to the ignition point without propagating significantly. Instead of propagating, it slowly self extinguished, as an insulating char formed. As a result, this rocket fuel falls outside the category of a flammable solid. This makes it safe to handle, store, ship, and dispose of.

Discussion

MDA-HSV has developed an environmentally clean hybrid rocket fuel that overcomes the inherent hazards of solid propellants and their ingredients while exhibiting a higher specific impulse than that of class 1.3 solid propellants. This is combined with a density that is higher than previously examined hybrid rocket fuels, via use of higher levels of higher density fillers.

The MDA-HSV fuel burns cleanly, with tailorable regression characteristics that provide the design engineer with added flexibility and will minimize use of inerts such as insulation. The fuel extinguishes cleanly and quickly on oxygen shutoff, enabling motor shutdown and restart.

The MDA-HSV hybrid rocket fuel is easier and safer to clean up and dispose of than conventional propellants since uncured fuel can be cleaned up with isopropyl alcohol, and cured fuel in not hazardous. In order to obtain high performance as a rocket fuel, it is important to scour the surface clean with hot gases passing rapidly over it. At low gas flow over the surface, a small char residue was observed. Under ambient conditions, so much char remains, that air cannot get to the unburned fuel, and the fuel self extinguishes.

The exhaust from burning MDA-HSV fuel is very clean, as could be seen during the motor firings. During operation, no smoke can be seen, which is consistent with complete combustion. Axial regression was more uniform than other fuels examined which contained other fillers. This is believed to be the result of a lower energy process to remove the fuel from the surface.

From basic kinetic relationships, it can be seen that high activation energy processes are accelerated more for a given temperature increase. The basic equation was given by Arrhenius and is

$$k = Ae^{-Ea/RT}$$

where k is the rate constant, A is an empirical constant for a given reaction, Ea is the activation energy for the reaction, R is the universal gas constant, and T is the temperature in degrees Kelvin. If two conditions at two different temperatures are compared, with the higher temperature condition designated T_2 with a corresponding k_2 and the lower temperature condition designated T_1 with a k_1, then

$$k_2/k_1 = e^{[(Ea/R)(T_2-T_1)/T_1T_2]}$$

Since T_2 is larger than T_1, the exponent is always positive, and larger activation energies will produce greater increases in rate for a given temperature increase. Since temperature has been measured to be higher in the aft end of a motor than in the middle or head end, the observation of different accelerations in axial regression rates exhibited by different fuel compositions in the aft segment of the motor is consistent with different activation energies for fuel "vaporization" from the surface.

As hybrid rocket motors have different operating characteristics than their liquid or solid counterparts, their advantages and limitations are not yet fully understood. The big advantages of liquids are throttleability, ability to be turned off, and inherent safety of separately stored fuel and oxidizer. Hybrids share these characteristics, and on the fuel side are even much safer than volatile hydrocarbon fuels or hydrogen. The MDA-HSV solid fuel is especially safe in that if accidentally ignited, it forms a char layer and self extinguishes.

During operation, the MDA-HSV fuel has a significant advantage in that formulation variations can be used to produce different exponents and thus different regression rate characteristics enabling a propulsion design engineer more freedom to design, and enabling motor operation at a more constant O/F ratio, resulting in higher performance and a lower nozzle erosion rate over the entire motor burn, since the exhaust gases will not become oxidizer rich.

Combustion efficiency in hybrid motors is a function of the size of the aft combustion chamber and the pressure. At a given pressure, larger motors generally operate at higher combustion efficiency, as the fuel that comes off the surface has longer residence time in the motor enabling the combustion reactions to proceed farther toward completion before the molecules exit the chamber. Higher pressure increases the concentrations of the reacting species and causes the reactions to go faster in a given residence time. This is consistent with the higher combustion efficiency observed in the motor fired at the higher chamber pressure.

Summary

The goal of developing an environmentally friendly, high performance hybrid rocket fuel has been accomplished. The process takes commercially available, inexpensive chemicals that can be cleaned up (including chemical conversion to non toxic species) with either water or isopropyl alcohol, and converts them to a non flammable solid which burns cleanly with high efficiency in a rocket motor when hot gases scour the surface. When hot gases do not scour the surface, burning fuel develops a char layer and safely self extinguishes.

APPROACHES TO POLLUTION PREVENTION IMPLEMENTATION

SSME Component Processing Review

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ABSTRACT

The SSME "Component Processing Review" (CPR) strategy was a team concept developed to maximize the effectiveness and efficiency of production operations while complying with challenging environmental regulations. All manufacturing operations, including cleaning processes, used to produce each major component of the SSME were identified. Unit Flow Analysis was applied in the examination of each operation for its contribution as a subset of the multi-step process used to produce a high-quality and cost-efficient product. This analysis assisted in the development of new cleaning processes which have replaced ozone-depleting and other hazardous materials. These new processes have had a significant impact on the role cleaning now plays in the production process. This paper discusses how to conduct this analysis.

BACKGROUND

In the late 1980's and early 1990's, a series of new environmental regulations, including the 1994 U.S. Clean Air Act (CAA), severely limited the use of certain standard cleaning solvents which had been used in a wide variety of processes at the Rocketdyne Division of Rockwell Aerospace. The impacted solvents included ozone-depleting solvents (ODS) such as trichlorotrifluoroethane (CFC-113), and 1,1,1-trichloroethane (TCA) as well as suspected carcinogens, like perchloroethylene (Perc). These regulations presented the challenge of reducing, eliminating and, if necessary finding acceptable replacements for materials that had been used for years to successfully produce the Space Shuttle Main Engine (SSME). The Rocketdyne Hazardous Materials Elimination (HME) Team was formed in 1989 to address this challenge. This multidisplinary team included representatives from the Rocketdyne departments of Materials Engineering & Technology (ME&T), Production Operations, Quality Assurance (QA), Environmental Protection, as well as Health, Safety & Fire Engineering. During this same time period, the SSME program at Rocketdyne initiated a structural re-organization based upon the "Organizational Excellence" Team concept. This concept was used to coordinate the SSME program into a cooperative working group of smaller "teams" based upon the eight major components and four major support activities of the SSME. Each team established and maintained control over the production of their "product" (i.e., component, or facility) by utilizing team work and accountability. Each team was composed of the resources (e.g., skilled and knowledgeable personnel, tools, equipment, etc.) necessary to produce a top quality product. The "Component Processing Review" (CPR) was specifically developed to take advantage of this team-based approach. The goal of C.P.R. was to minimize the impact of changing environmental regulations on the manufacturing of each component, while simultaneously maximizing the effectiveness and efficiency of the cleaning operations used to produce each component.

APPROACH

Many strategies were used to identify, eliminate and/or replace hazardous materials used at Rocketdyne. Control systems were initiated to restrict the procurement and distribution of regulated materials. Briefings were presented to involved personnel to explain the new regulations. Specifications and drawings were reviewed to determine all engineering requirements to use these materials. The C.P.R. strategy was developed to approach this effort from the user end, by coinciding with the Unit Flow Analyses being performed by each O.E. Product Team. Unit Flow Analysis was used by each team to examine the total manufacturing process, from raw material procurement to final assembly, as applicable their respective component. Flowcharts of the fabrication sequence were created by the Product Teams to assist in identifying and defining the contribution of each production operation to the final product. This information was then analyzed to determine which factors impacted product quality, cost, and schedule, and what changes were needed to control those factors. To support C.P.R. and hazardous materials elimination, all cleaning operations, as well as other operations using hazardous materials, were identified during the development of the Unit Flow Analysis fabrication flowcharts. The flowcharts were analyzed to determine the most efficient methods to eliminate or minimize the use of hazardous materials, while also increasing the effectiveness of the cleaning operations. The results of the C.P.R. analysis were used by the appropriate Program Team to modify component production. These modifications included material and/or process replacement, process modification, fabrication sequence re-organization, and other changes to improve component production. The HME Team also used the results of the C.P.R. analysis to verify that environmentally acceptable alternatives were available for all identified hazardous materials. If none were available, projects were initiated to identify, develop and/or implement the necessary alternatives.

Various examples of how the C.P.R. analysis was applied to the SSME program to achieve the stated goals of hazardous materials elimination and production efficiency improvement are discussed below:

DISCUSSION

C.P.R. was a team-oriented approach to hazardous material elimination. The Product Team personnel utilized their working knowledge of component hardware and production operations, while members of the HME Team applied their understanding of materials, processes, and environmental regulations upon reviewing the fabrication flowcharts. The review of the first few flowcharts resulted in the recognition of a standard analysis, which consisted of 6 simple questions:

a) Why is the part being cleaned?
b) Is cleaning necessary at this point of fabrication?
c) If necessary, is the level of cleaning appropriate?
d) Can the cleaning process be simplified or reduced in scope?
e) If the process utilizes a material identified for replacement, is an acceptable material or process available for substitution?
f) If not, why and what action is being initiated to address this issue?

These questions were applied to each cleaning operation listed on the SSME component fabrication flowcharts during C.P.R. analysis.

An example of a fabrication flowchart, with the cleaning operations identified, is shown in Figure 1.

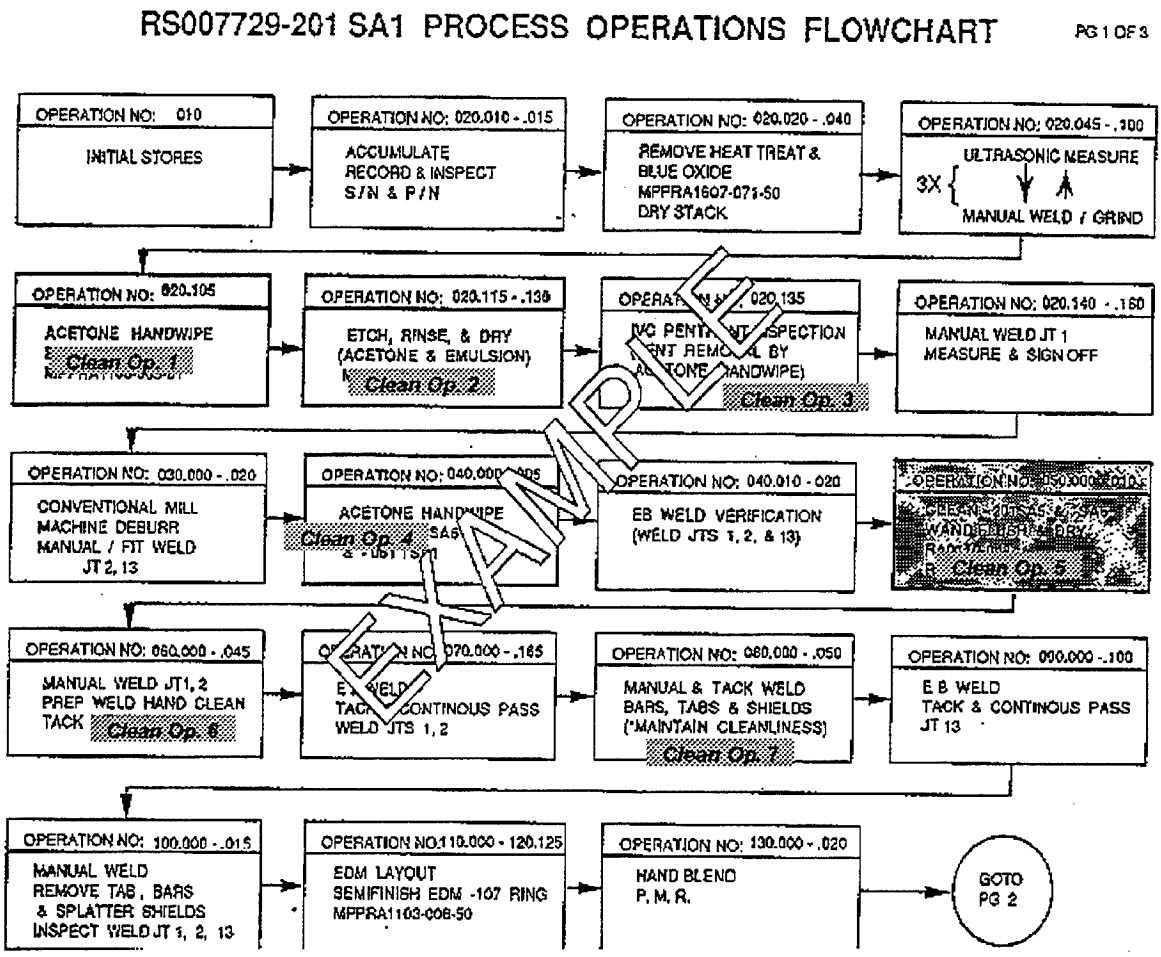


Figure 1 - Example of Fabrication Flowchart

In this example, 7 cleaning operations had been identified and the standard C.P.R. questions were applied to each. Clean Operation 1 was being performed in preparation for an etching operation prior to penetrant dye inspection. A surface must be water break-free to ensure a successful penetrant dye inspection, so the cleaning was necessary at this point in fabrication. It was also determined that hardware was being cleaned to the appropriate level. As this cleaning is a handwipe operation, it cannot be simplified without detrimentally impacting the subsequent operation. The location of Rocketdyne in the Los Angeles Basin made all production operations subject to local environmental, health and safety regulations, as stipulated by the South Coast Air Quality Management District (SCAQMD). One SCAQMD rule regulated the use of Volatile Organic Compounds (VOC), including acetone, the cleaning material used in Cleaning Op. 1, 2, 3, 4, 6 and 7. Although this material was not identified for replacement, it was designated for internal control and usage monitoring. The identification of acetone use in these operations did confirm that it was being used in accordance with all applicable regulations.

Hazardous Materials Elimination

In the illustrated example (see Figure 1), Cleaning Op. 5 did involve the use of a hazardous material identified for replacement. The hardware was being vapor degreased with the ozone-depleting solvent, TCA, to remove milling compounds in preparation for a welding operation. An acceptable aqueous cleaning process was available as an alternative, and had been proven, by a previous HME Team evaluation, to clean as effectively as the TCA vapor degreasing process. It was recommended to the Product Team to revise this cleaning operation and eliminate the use of TCA in this case. The Product team personnel, also noted that this major welding operation is the first in a series resulting in a fairly complex hardware configuration. Complex configurations limit effective cleaning options. It would be easier to make any major cleaning revisions at this stage of simple configuration rather than later in the fabrication process of this particular component. In some cases, where an acceptable alternative did not exist, the HME Team would develop a plan of action based upon the answers to the first 6 standard C.P.R. analysis questions.

C.P.R. also assisted in identifying the hardware requiring evaluation for certain HME projects and in defining criteria to be considered in certain HME projects. Perchloroethylene vapor degreasing was used to remove a high temperature wax compound used during plating operations. C.P.R. helped in the identification of 10 applications of this wax, and the hardware that needed to be included in the proposed alternative dewaxing process. The fabrication flowchart review for complex hardware assisted in identifying what contaminants are being produced or used. In one situation, the C.P.R. analysis confirmed that no organic contamination was generated during the production of a highly complex part. This allowed the original solvent vapor degreasing cleaning process to be replaced with a deionized water ultrasonic process, without impacting the achieved level of cleanliness.

Hardware material and configuration were important factors in selecting the appropriate alternative cleaning process. But in many situations, if the answers to the standard C.P.R. questions were similar, the same recommended alternative could be applied.

The SCAQMD regulation impacting the use of VOC did restrict the use of acetone and isopropyl alcohol (IPA) to flight hardware only. Except in very specific cases, no tools or equipment were to be cleaned using these two solvents. The C.P.R. process assisted in identifying tool and equipment cleaning operations. An aqueous-based cleaner was evaluated and implemented for these operations.

Cleaning Efficiency / Effectiveness

Unnecessary "standard practice" cleaning operations were also found during the C.P.R. analyses. One example was the cleaning of hardware upon receipt from a subcontractor. Some of these cleaning operations were unnecessary as the process performed at the subcontractor resulted in clean hardware (e.g., hardware from plating facilities, or dry film lubricant processors, etc.) The cleaning performed at Rocketdyne upon receipt was redundant. Another example of superfluous cleaning involved the standard practice of cleaning hardware upon removal from storage. Hardware was cleaned to a visual cleanliness level prior to being packaged and protected for storage, pending further processing. Unless the storage packaging and protection have been torn, broken, damaged or otherwise violated, the cleanliness of the hardware had been maintained, and no additional cleaning should be required. The wastefulness of this type of cleaning was especially obvious when machining or another high-contaminating process was the operation subsequent to storage. For most of these cases, the recommendation resulting from C.P.R. analysis was to replace the cleaning process performed after storage with a visual inspection to verify packaging integrity. There were cases where a high level of cleanliness was required by the process (e.g., penetrant inspection, thermal treatments, etc.) performed after storage, and deleting the cleaning was not recommended.

The recommended use of gloves during receiving and other visual inspection operations also eliminated numerous unnecessary cleaning operations. Hardware was often handled without gloves when inspected upon receipt from subcontractors or during internal visual inspections (i.e., dimensional measurements). The resulting fingerprint oils would then require removal prior to some critical processes (i.e., welding, thermal treatments, etc.) Cleaning is dictated by the contamination level, and by controlling contamination, production efficiency was increased.

A general review of all standard or automatic clean operations was performed during C.P.R. to eliminate unnecessary cleaning operations.

The majority of all HME projects addressing the replacement of various solvent-based cleaning processes chose aqueous-based alternatives as the most effective, practical and economical. Aqueous-based cleaning processes had been available and used at Rocketdyne for years, but solvent vapor degreasing using CFC-113, TCA, or in selected cases, perchloroethylene, was the cleaning process of choice. As with most production operations, the use of the wrong cleaning process at the wrong time is inefficient, and can have a detrimental impact on hardware schedule, cost, and quality. The C.P.R. analyses performed on numerous SSME details and components revealed that in many cases the hardware was being "over" cleaned by the listed aqueous cleaning process.

A very common example of this type of "over" cleaning of SSME hardware involved the removal of penetrant inspection residues. Hardware surfaces were originally cleaned to a water break-free condition to perform the dye penetrant inspection. During the inspection, the only contaminating materials used were the appropriate penetrant dye and developer. In many cases, the cleaning process used to remove these materials was very aggressive and usually involved 6 - 8 cleaning, rinsing, and drying operations. This was very wasteful, as a simple 3 - 4 operation cleaning process would remove the penetrant residues from the majority of the SSME hardware.

The order in which some fabrication processes were performed also had a direct impact of the efficiency of the cleaning operations. For instance, one hardware detail underwent two inspection processes after completing a series of machining operations. Figure 2a illustrates part of the original fabrication sequence.

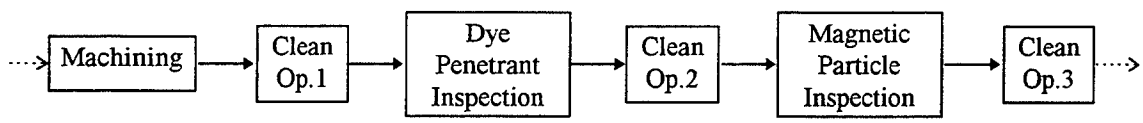


Figure 2a - Original Fabrication Sequence

Clean Op. 1 was an aggressive multi-step cleaning process used to remove the heavy machining compounds so the cleaned hardware surfaces were water break-free for the subsequent dye penetrant. The penetrant residue was removed by a fairly simple cleaning process, Clean Op. 2, just before immersing the hardware in the oil reservoir to perform the magnetic particle inspection. Clean Op. 3 was also an aggressive cleaning process to remove the oil residue. It became obvious during C.P.R. analysis that production efficiency could be increased by changing the order of the inspection operations, without loss of important information. Figure 2b shows the fabrication sequence recommended after C.P.R. analysis:

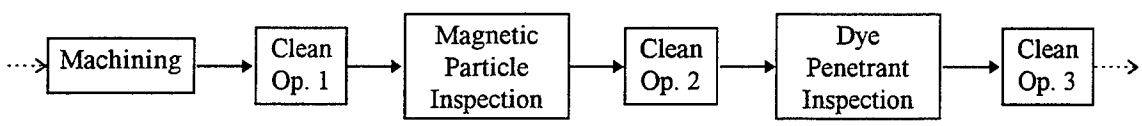


Figure 2b - C.P.R. Recommended Fabrication Sequence

This order inversion allowed the multi-step aggressive cleaning process previously used for Clean Op. 1 to be replaced with a less time-consuming cleaning process. The shorter recommended cleaning

process would clean the hardware of machining compound to the visual cleanliness level required by the magnetic particle inspection. Then a fairly aggressive cleaning process was recommended for Clean Op. 2, to remove all contamination to achieve the water break-free level of cleanliness for penetrant inspection. Clean Op. 3 could then be a mild cleaning process to simply remove the penetrant residues. In other similar cases, efficiency was improved by performing the most contaminating operation first.

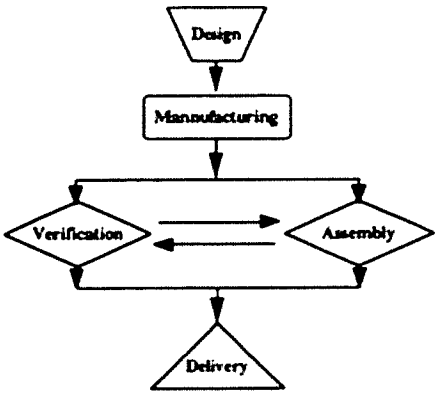
CONCLUSION

The Rocketdyne C.P.R. strategy was used to review over 1600 parts as documented on approximately 1500 fabrication flowcharts. It was a team-oriented project that utilized knowledge about environmental, health and safety regulation , the SSME hardware production, as well as cleaning processes and materials. The use of fabrication flowcharts proved a very effective method for providing information about the three factors which influence each cleaning operation: Hardware, Processes, and Contamination. Information about the hardware material substrate, design complexity, surface treatments, etc. was gained from reviewing the flowcharts. This information clearly defined WHAT was being cleaned. Cleaners can vary significantly in chemistries and properties, while the operational parameters (i.e., pressure, temperature, application method, etc.) of various cleaning equipment can also differ significantly. The acceptability of a cleaner and cleaning method is defined by the hardware being cleaned. A method acceptable for cleaning a machined metallic surface may not be acceptable for cleaning a coated non-metallic surface. The processes performed prior and subsequent to cleaning determines WHY the cleaning is being performed. The contaminants that must be removed by the cleaning process are controlled by the operation preceding it, while the subsequent operation defines the required level of cleanliness. Cleaning for general handling purposes (i.e. removal of gross contamination between machining operations) differs from cleaning necessary to achieve the water break-free surface required by processes such as welding or penetrant inspection. Three main factors were considered in the performance of C.P.R. to the cleaning of SSME hardware:

- The necessity and/or requirement for cleaning.
- The availability of an acceptable alternative for operations utilizing a hazardous material.
- The most efficient and/or effective method for achieving the necessary cleanliness level.

These considerations resulted in over 700 recommendations, which were made to the SSME program to minimize or eliminate the use of hazardous materials and to improve the effectiveness and efficiency of production cleaning.

Much of the information learned by performing C.P.R. on the SSME is applicable to another production programs. Production efficiency can be maximized for any program by considering cleaning a basic design issue. The C.P.R. process can be a proactive strategy by designing "cleanability" into the component. This would then allow cleanability to be "manufactured-in" by fabricating the component in a manner whereas much as practical, the dirtiest operations are performed when the hardware is simple and easy to clean. Then at the more complex levels of configuration, controlling contaminating processes would maintain the level of established cleanliness. If a level of cleanliness needs to be verified, the verification procedure is performed when the hardware is at the detail or simple configuration level. These verified details can then be assembled into the final product while maintaining cleanliness.



This type of proactive effort will contribute significantly to the final goal of all production programs: Delivering a top quality and cost-efficient product.

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Abstract:

Since February 1991, the Department of Defense (DoD) has required that weapon system acquisition programs incorporate environmental considerations into the development of the weapon system, including the design, test, operation, maintenance and disposal. Prior to this date, DoD's policies were oriented towards operation of facilities and installation, with the focus on the pollution control devices required for compliance, and the cleanup or restoration of problems created by past activities. Studies done by the DoD and individual services, have resulted in the conclusion that a major portion of the environmental problems experienced by the facilities and installations are a direct result of the weapon system being operated and maintained at these sites. Additional environmental policy and regulations, e.g., Executive Orders, have further specified environmental requirements for weapon system acquisition programs. The resulting problem was that there was no method established for implementing this environmental policy into an already complicated, expensive, and time consuming acquisition process.

The V-22 Osprey Aircraft Program innovatively integrated the environmental requirements into the acquisition process. The Program established a multi-disciplinary team to coordinate and implement environmental requirements. This team consists of program management personnel, environmental and materials engineers, legal counsel, and U.S. Marine Corps aircraft maintenance personnel. The team developed an environmental strategy by analyzing the aircraft system and identifying specific technical and environmental issues.

The environmental team educated as many people within the V-22 acquisition team as possible, and worked closely with the program's prime contractors - Bell Helicopter Textron, Boeing Helicopters and Allison Engine Company. Through the efforts of the government and the prime contractors, the V-22 program was able to establish and implement an effective environmental program. This program assures compliance with all environmental regulations and policies, but also provides a product that reduces the operating, support and disposal cost of the aircraft and decreases potential risk to personnel and the environment by reducing the use and generation of hazardous materials and wastes.

Introduction:

Since February 1991, the Department of Defense (DoD) has required that weapon system acquisition programs incorporate environmental considerations into the development of the weapon system, including the design, test, operation, maintenance and disposal. Prior to this date, DoD's policies were oriented towards operation of facilities and installation, with the focus on the pollution control devices required for compliance, and the cleanup or restoration of problems created by past activities. Studies done by the DoD and individual services, have resulted in the conclusion that a major portion of the environmental problems experienced by the facilities and installations are a direct result of the weapon system being operated and maintained at these sites. This presentation discusses the DoD policy on integrating environmental considerations into the acquisition process and what the V-22 Osprey program has done to implement this policy.

Acquisition Environmental History:

According to the Office of the Secretary of Defense (Environmental Security) (Salomon, 1995), DoD considers reducing the pollution associated with weapon systems critical to the defense mission for four important reasons.

It's a quality of life issue. Reducing pollution protects military personnel and their families from health and safety hazards where they live and work.
It is a military readiness issue. DoD manages over 25 million acres of land. Our forces must have continued access to airspace, land, and water for training and testing. Systems that produce little or no pollution help to preserve our access to these vital natural resources.
It's an acquisition issue. Environmental issues can increase the costs of new systems, cause delays in the development process, and reduce the performance of our systems. Pollution prevention helps us avoid these impacts to our programs.
It's a military budget issue. Pollution prevention protects scarce defense dollars, because it reduces our operating costs for environmental compliance and the risks of creating new clean up requirements in the future.

These costs are a significant part of the DoD budget. For Fiscal Year (FY) 1996, DoD's budget for environmental programs is almost $5 billion (see Table 1 for display area).

	$ Millions
Compliance	$2,205
Cleanup	$1,622
Base Closure	$457
Pollution Prevention	$322
Technology	$218
Conservation	$145
Total	$4,969

Table 1
Environmental Security FY96 Budget

Five billion dollars is a lot of money, but it only includes money specifically budgeted for environmental programs. It does not include all the money the DoD spends to comply with environmental requirements. The full cost of compliance is much higher. The remaining funding is included in other, non-environmental accounts, e.g., an acquisition program. Thus, no one knows the total amount DoD is spending for environmental compliance (Salomon, 1995).

Acquisition Environmental Policy:

DoD policy on environmental issues for system acquisition programs is contained in DoD 5000.2-R, "Mandatory Procedures for Major Defense Acquisition Programs and Major Automated Information Systems", just finalized in March of this year. These new requirements supersede the earlier requirements that were implemented in 1991. Although the policy was revised to add requirements from new laws and executive orders, and broadens the scope of pollution prevention in the acquisition process, the regulation was written to include only the purpose and the policy, and not provide procedures to implement the policy. The environmental requirements for a program include the following:

National Environmental Policy Act Compliance - Analyze actions proposed to occur in upcoming program phases that may require NEPA or Executive Order 12114 analysis.
Regulatory Compliance - Identify compliance requirements and analyze impacts on the program's cost, schedule and performance.
Pollution Prevention - Identify pollution prevention initiatives and goals and implement appropriate technologies.
Hazardous Materials Minimization - Identify hazardous materials used throughout life cycle and minimize where possible.
System Safety and Health - Identify, evaluate, eliminate and control hazards.

The acquisition process has reviews where a program's cost, schedule, and performance are reviewed. At each of these milestones, the environmental issues, analyses and accomplishments are reviewed. Figure 1 (Salomon, 1995) illustrates the acquisition process phases and milestone reviews.

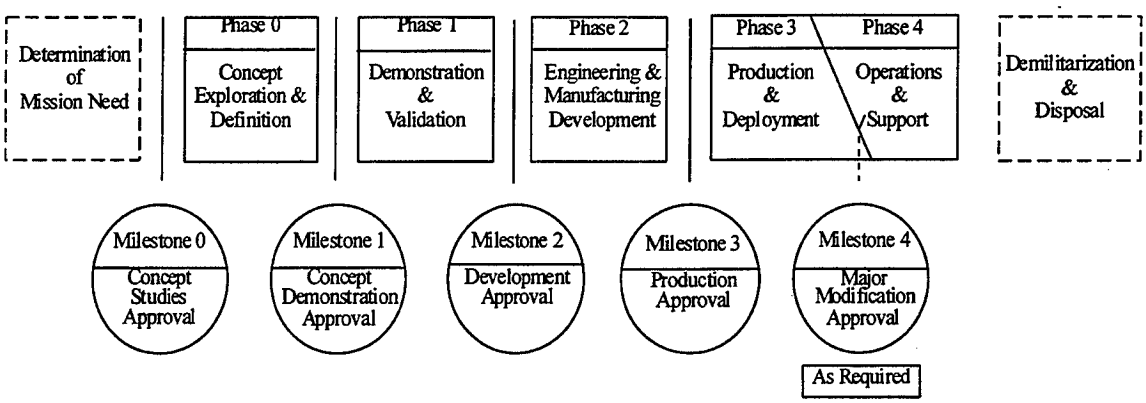

Figure 1

The procedures to implement the environmental policy are currently being written to incorporate into a deskbook for guidance to program managers. This leaves the door open to programs on how they should implement the requirements. The following is how the V-22 program implemented the requirements and highlights some of the more major accomplishments.

V-22 Program Background:

The V-22 is a multi-service, multi-mission tilt-rotor Vertical/Short Takeoff and Landing aircraft being developed for operation use beginning in the year 2001. Advanced technological design approaches are being applied to the V-22 including tilt rotor, airframe composites, oblique wing stow, modular engine, advanced avionics, "on-condition" maintenance philosophy, Built-In-Test, engine health monitoring systems and vibration analysis. The intended scenarios for V-22 combat support roles require increased speed and range, V/STOL capability, night and adverse weather capability, confined and isolated area operations and the ability to carry various internal and external payloads.

Environmental Implementation:

The V-22 Program Manager (PMA-275) has the responsibility to integrate an effective environmental program throughout the life cycle of the V-22. PMA-275 is responsible for preparing the V-22 Programmatic Environmental, Safety, and Health (ESH) Evaluation for the Milestone Decision Authority (MDA) in accordance with the DoD Regulation, 5000.2-R

To ensure the successful integration of an effective environmental program throughout the life cycle of the V-22 aircraft, PMA-275 chartered a multi-disciplinary and interactive Environmental Process Action Team (EPAT). A primary responsibility of the EPAT is to advise the Program Manager on initiatives to minimize environmental impact as a result of the V-22 Program. The EPAT defines solutions on operations, training and eventual disposal of the aircraft at the conclusion of its life cycle. The V-22 EPAT is comprised of program, environmental, materials, legal and Bell-Boeing personnel. The team provides management oversight for the V-22 environmental program, and serves as a liaison between the Program Manager and the environmental community. Open lines of communication with Bell-Boeing's V-22 Pollution Prevention Manager and other pertinent personnel are maintained to enable the EPAT to identify, define and resolve pollution prevention and environmental compliance issues that affect, or have the potential to affect the environment during all phases of the aircraft's life cycle. The EPAT membership is augmented by other government representatives [e.g., V-22 Integrated Test Team (ITT), MV-

22 Fleet Introduction Team (FIT), Resident Integrated Logistics Support Detachments (RILSDs), AIR-8.0Y], as required, depending upon the V-22 program phase. The EPAT holds quarterly meetings to:

- Determine National Environmental Policy Act (NEPA) requirements.
- Develop and monitor program contract requirements.
- Generate, track and resolve team action issues.
- Track and resolve outside environmental issues that have the potential to affect the V-22.
- Monitor contractor efforts and accomplishments (e.g., hazardous material minimization, pollution prevention, trade studies, etc.)

The EPAT promulgates information on all pollution prevention and environmental problem areas to program personnel, and coordinates its efforts with the Naval Air Systems Command (NAVAIRSYSCOM), other participating government agencies, related working groups, Integrated Product Teams (IPTs) and the prime contractors in order to maximize a timely and streamlined approach to resolving environmental issues.

Contract Requirements:

Since the implementation of the environmental requirements of Department of Defense Instruction 5000.2, Part 6, Section I, in February, 1991, the V-22 program has awarded the Airframe Engineering and Manufacturing Development (EMD) contract, the Engine Upgrade Modification contract and the Updated Drive Train contract. The modification to the airframe EMD contract to include United States Special Operation Command specific requirements is scheduled for Fiscal Year 1996. The Advanced Acquisition Contract, LRIP contract for the aircraft is scheduled for FY96, the LRIP Lot 1 contract is scheduled for FY97, and the LRIP contract for the engine is scheduled for FY97.

In addition to the following environmental contract requirements, the V-22 program also performed Ozone Depleting Substance (ODS) reviews as a result of Section 326 of the FY93 Defense Authorization Act. These reviews ensured that the government did not specify ODS requirements to the contractor.

The following is a summary of the environmental requirements that were incorporated into each contract.

Airframe.

EMD, October, 1992. This contract required the contractor (Bell-Boeing) to develop a pollution prevention program plan. Bell-Boeing was required to reduce the environmental impact of the system's operation, maintenance and repair during the system definition, design, development, test, production and deployment phases. The contract required the identification of hazardous materials/processes, justification for use, and identification of substitutes. Substitution was required based on alternative materials and processes with less impact on the environment, test data for proposed material or process substitutes, research and development, and a cost benefit analysis on life cycle costs of substitutes.

In addition to the pollution prevention requirement, Bell-Boeing was also prohibited from selecting: surface coatings containing lead, materials that include asbestos, materials that are or include ozone depleting substances, and materials with volatile organic compound content that exceeds federal, state, or local regulatory requirements where they will be required to be used.

The EMD Statement of Work (SOW) also required the contractor to perform pollution prevention trade studies for those efforts that could not be accomplished concurrently with the design of the system. The trade studies were required to be conducted after a prioritized list of trade study candidates was approved by the government.

Advanced Acquisition Contract, LRIP, proposed for FY96. The LRIP pollution prevention contract requirements have been prepared and are incorporated into the draft LRIP contract. The V-22

program tailored the requirements of the commercial specification NAS 411, Hazardous Materials Management Program, due to the memorandum signed by the Under Secretary of Defense for Acquisition and Technology, requiring programs to utilize this standard. The requirements were tailored to continue the program established under EMD. Specific changes include ensuring all vendors, suppliers and subcontractors provide all necessary information to meet the program requirements, requiring the hazardous materials report to be modified and supplied via electronic media quarterly, requiring the identification of regulatory permit requirements for the operation and support of the aircraft at operating sites, requiring 2 trade studies and requiring a demilitarization and disposal plan.

Drive Train Upgrade. This contract addressed the development, design, and qualification of an increased power capability for the EMD drive train based upon the original V-22 Full-Scale Development design. This contract does not manufacture the drive train for EMD installation. The manufacturing and maintenance related tasks are identified in the EMD contract, and are covered by EMD pollution prevention requirements.

Engine.

Engine Upgrade Program, November, 1993. Because the engine contract was a modified commercial engine, it was felt that very little could be accomplished, via pollution prevention, in the design process. Due to this rationale, the V-22 program decided to put the pollution prevention emphasis on the materials and processes used in the support and maintenance of the engine. The method used to accomplish this was MIL-STD-1388B, tasks 301 and 401. These tasks require the contractor, Allison, to identify the hazardous materials used to support the engine. The government has approval authority on these tasks, and has ensured the minimization of hazardous materials specified.

LRIP, FY97. The requirements for this contract are a duplication of those prepared for the airframe LRIP contract.

Peculiar Support Equipment (PSE).

Prime Contractor Designed Equipment. Those contracts for PSE with Bell-Boeing invoke the requirements of NAS 411 similar to the airframe LRIP contract.

Competitively Procured Equipment. A portable V-22 Hydraulic Cart is the only item of PSE currently being competitively procured. Tailored NAS 411 requirements were also included in this contract. In addition to pollution prevention requirements, engine emission requirements were specified to ensure compliance with EPA and California proposed regulations for diesel off-road engines. Environmental requirements were also used as an evaluation factor in the contract proposals.

Systems Engineering:

Environmental analysis in systems engineering is used to determine the impact on and by each system product and process alternative from quantities and types of hazardous material used as well as hazardous waste generated. Results of these analyses are factored into the system definition, design, and verification. The following is a discussion of the V-22 implementation processes.

Integrated Product Team Process.

Government and contractor IPT members were briefed by both Bell-Boeing and government EPAT members as a means to promote environmental and pollution prevention awareness, to ensure that pollution prevention is performed concurrently with system design and to provide the IPTs with government and contractor environmental and materials engineers to assist with the resolution of environmental and pollution prevention issues. Additionally, the EPAT monitors selected IPT meeting

minutes for potential environmental and pollution prevention issues and works through the IPT to resolve each issue.

Design Reviews.

Based on input by government IPT members that potential hazardous materials issues existed in or would be generated by V-22 systems and components, the EPAT monitored selected individual component and system level Critical Design Reviews (CDRs) for banned and substitutable hazardous materials and design issues that have environmental impact. In addition, the EPAT established a review process for material call-outs in pre-CDR packages. Contractor requirements included engineers to consider specification of materials as a design criteria and for pollution prevention requirements and accomplishments to be addressed in the executive CDR.

Test and Evaluation Planning.

Testing of the V-22 is a primary area of concern with respect to potential environmental impact. The EPAT reviewed the Test and Evaluation Master Plan (TEMP) very early in the environmental analysis process in order to plan and budget for potential NEPA requirements. The EPAT also maintains communication with the program test personnel to ensure environmental considerations are part of the test planning process. In addition to being actively involved in the planning process, the EPAT has integrated environmental evaluation into the standard test evaluation process. The V-22 TEMP requires environmental and pollution prevention efforts to be a phased approach beginning with early assessments during the Integrate Test/Developmental Test periods and culminating with a detailed assessment during Technical Evaluation (TECHEVAL). During TECHEVAL, an evaluation shall be conducted to determine if documented controls (technical manuals, support equipment, procedures, etc.) for residual hazardous materials adequately protects fleet personnel and the environment.

Logistics:

Prior to the contractor submitting a Logistics Support Analysis (LSA) task to the government, Bell-Boeing Materials and Processes personnel perform a materials review and provide substitutions where available. When the contractor submits an LSA task tot he government for review, the EPAT draws a materials report for the LSA Record database in order to review each maintenance task for unauthorized and substitutable hazardous materials specified for use in the task. When unauthorized or questionable materials are noted in a maintenance task, the material is flagged and the V-22 Aircraft Program Manager, Logistics (APML), and the contractors are notified and provided with EPAT assistance in determining suitable alternative materials.

Environmental Compliance and Pollution Prevention:

V-22 Program pollution prevention efforts are undertaken to minimize or avoid environmental compliance costs (e.g., occupational safety and health, emission control and hazardous waste disposal), reduce program life cycle costs, minimize environmental impacts and meet DoD and Navy environmental goals.

Pollution prevention, to the maximum extent possible, is performed concurrently within the system's engineering and logistics support analysis processes. Those hazardous materials and/or processes that are not able to be eliminated in this process are subsequently documented and prioritized to be considered for trade studies. Accomplishments in both methods are described below, as well as pollution prevention initiatives that are not V-22 specific, but that will benefit the V-22 program.

The concurrent engineering pollution prevention efforts/accomplishments described below have been categorized according to manufacturing (which includes only materials, as delivered on the aircraft), operations and maintenance.

Manufacturing.

- Reduced the quantity of cadmium plated fasteners;
- Boric-Sulfuric acid anodize authorized for use in lieu of chromic-acid anodize (on non-structural aluminum parts);
- Authorized use of non-cyanide copper plating process in lieu of caustic cyanide;
- Bell Helicopter Textron has employed the use of High Volume Low Pressure paint guns for use in aircraft painting (this will reduce VOC emissions);
- Removal of lead pigment in an adhesive (by manufacturer) utilized for composite repair;
- Elimination of asbestos gaskets in the engine;
- Elimination of asbestos in fire blankets in the engine nacelles;

Maintenance.

- Removal of 18 references to Methyl-Ethyl-Ketone (MEK);
- Removal of 8 references to Methylene Chloride;
- Substituted 10 cleaning applications with Isopropyl Alcohol;
- Substituted 46 cleaning applications with P-D-680;
- Substituted MIL-S-81733 (chromated sealant) with MIL-P-8802 (non-chromated sealant) where possible;
- Substituted titanium for carbon/BMI on aircraft work platform - less VOCs;
- Removed the requirement for a sealant remover (hazardous material), SR-125;
- Reviewed Standard Repair Procedures used in the maintenance of the test aircraft, and removed references to xylene, toluene, MEK, and a safety solvent (trichloroethane);
- Have performed field testing of environmentally preferable products during maintenance of test aircraft. Examples include Electron, as a NDI penetrant cleaner, and Prepsolv, as a substitute for 1,1,1 and MEK for cleaning.

Operation.

- Accidental fuel venting associated with the Full-Scale Development system design was corrected in redesign of the system in EMD.
- Redesign of fire suppression systems to utilize an inert gas generating system, HFC-125, and CO_2 to replace halons 1211 and 1301.

Trade Studies.

Bell-Boeing was required to review materials that are used on the V-22 EMD aircraft, and identify those that are hazardous. A list of hazardous materials to review for was agreed on by the government and Bell-Boeing prior to the review. The identified hazardous materials were then prioritized.

The V-22 Hazardous Material Prioritization System (developed by Bell-Boeing) is an objective method for prioritizing hazardous materials used on the V-22. The methodology provides a ranking of the hazardous materials based on:

- The amount of material used on the V-22,
- The toxicity of the material to human health,
- The toxicity of the material to the environment,
- The disposal, handling and storage method associated with waste products, and
- The legislation associated with the use and disposal of the material.

Amount, Human Health, Environment, Disposal and Legislation are rated using a 100 point system. The amount factor addresses the weight of material consumed or disposed of in the phases of the

V-22 life cycle of concern to the Navy, namely aircraft operation, repair and maintenance, and disposal of the V-22 at the end of its useful life. All factors are assigned points from 1 to 5, where a 5 indicates the highest level of concern.

The trade studies will include details of environmental benefits, estimated costs projected over the life of the V-22 system, effects on system performance, necessary specification changes, health benefits and intangible benefits (safer working conditions, increased productivity), design/configuration changes and material compatibility. An Engineering Change Proposal (ECP) will be required when a configuration change is required.

Bell-Boeing has provided two prioritization lists to the V-22 program. The first was provided in November, 1994, and the second in May, 1995. The first list was a result of approximately 50% of the drawings reviewed, and the second list was a result of approximately 75% of the drawings reviewed. The top 5 items from each list are provided below:

1st List	2nd List
Chromated Sealant	Chromated Sealant
Ext. & Int. Chromated Epoxy Primer	Ext. & Int. Chromated Epoxy Primer
Chromated Wet Installation Primer	Chromated Wet Installation Primer
Nickel Containing Composite	Epoxy Polyurethane Topcoat
Epoxy Polyurethane Topcoat	Non-chromated sealant

The above lists are almost identical, therefore it is not expected that the list will change significantly with the review of the final 25% of the drawings. Using this rationale, the V-22 program has agreed to the top priority candidate, chromated sealant, as one trade study. The program has identified another environmental and program concern, that was not able to be identified through the contractor's methodology. This issue, depainting the aircraft, was not identified by Bell-Boeing, because their methodology only analyzed materials delivered on the aircraft, not maintenance procedures. There is currently no method available to safely depaint those areas of the aircraft that have copper mesh impregnated composite surfaces. A summary of each trade study is provided below:

Chromated Sealants. The intent of this trade study is to establish the use of an inhibited, non-chromated polythioether sealant which is not on a Military Specification qualified products list. This sealant must show promise, not only as a replacement, but as an improvement over chromate inhibited polysulfide type sealants, while maintaining compatibility with the V-22 unique copper foil lightning strike preventive material.

Bell-Boeing is to evaluate the inhibited, non-chromated polythioether sealant (PR 1875) for use in manufacturing and repair of the V-22 aircraft. They are to use as a guide in this study MIL-S-81733, Sealing and Coating Compound, Corrosion Inhibitive, to determine sealant application, physical and performance properties necessary for the V-22 (such as brush or dip, extrusion gun, spray gun or faying surface application) and the viscosity ranges for each type, as well as acceptable solvents to be used.

V-22 Paint Removal. The advent of stricter environmental laws has created the need to replace chemical paint strippers. The most promising method of mitigating chemical strippers is plastic media blasting (PMB). Unique design characteristics of the V-22 have created the need for new PMB materials and processes that are both environmentally safe and effective for V-22 fabrication, rework and repair.

Bell-Boeing is required to develop dry media blasting operating parameters which can be used to remove paint from V-22 composite fuselage structures without causing adverse effects to the embedded copper foil lightning strike preventive material. Test panels will be coated with the approved primer and topcoat system for the aircraft. The painted panels will then be air dried at ambient conditions for seven days, followed by aging for seven days ate 150^{0}F. The determination of the extent of damage shall be

followed by other tests to compare lightning arrest capability and shielding effectiveness before and after paint removal.

Virgin media to be considered for tests shall include MIL-P-85851 Type V (acrylic), Type VI (poly allyl diglycol carbonate) and a starch blast media, or other emerging technology media. Parameters to be controlled and recorded during dry media blasting tests are particle size distribution, media flow rate, nozzle pressure, blast angle of attack and stand off distance. Nozzle type and size may be varied as required for experimentation.

Bell-Boeing is also to provide details of environmental benefits for individual tests, and to develop/identify mitigation for hazardous materials and stripping by-products resulting from test methods, as well as disposal considerations and reuse/recycling opportunities.

Pollution Prevention Metrics:

The V-22 program has been looking for a method to capture and document positive pollution prevention/environmental benefits realized by the V-22's hazardous material/waste elimination and minimization efforts from manufacture through operations and maintenance and final demilitarization and disposal of the aircraft. The first idea considered was a comparison of the CH-46s' and CH-53s' (the aircraft the MV-22 will be replacing) emissions data with that of the V-22 could be performed which would show an overall percentage decrease. It is estimated that 70% of all aircraft maintenance is performed at the depot level, therefore, it would not be necessary to obtain O and I level data. A complete toxic chemical release inventory and hazardous waste numbers starting with CY94 was obtained from the Naval Aviation Depot Cherry Point. The percentage of NADEP Cherry Point workload stemming from H-46 and H-53 aircraft for 1994 and 1995 was also available. Using the workload percentage the estimated total emissions resulting from the H-46s and H-53s were obtained. This information is now available for comparison with the V-22 data when it becomes available. The problem is that V-22 data (in sufficient quantities for comparison) will not be available for approximately 10 years. In the interim, it was determined that another method for determining V-22 pollution prevention accomplishments was needed.

The second method considered is to work with Bell-Boeing to determine and document specific pollution prevention accomplishments, e.g., specific quantity reductions of materials between the FSD program and the EMD program. Specific items have been documented, but determining the quantities per aircraft associated with each material and process, as well as the estimated life-cycle quantities and cost issues, seems to be a daunting task at the moment. The V-22 program has not determined yet whether to pursue the effort. There will be life cycle quantity and cost information associated with the trade studies, but this is only a small percentage of the V-22 program's overall pollution prevention/environmental efforts.

The V-22 program has also supported a Small Business Innovative Research (SBIR) program to develop an Environmental Life Cycle Cost Analysis Model. This research is currently being performed by Tecolote Research, Inc. The timeframe for completion of the model is in 1998, and right now they are looking at testing their methodology on the V-22 engine.

Hazardous Material Control & Management (HMC&M):

HMC&M is required for those hazardous materials that were not able to be eliminated through pollution prevention efforts. HMC&M ensures that hazardous material and hazardous waste is safely used and handled, in terms of human health and the environment throughout the life cycle of the V-22 aircraft. The V-22 program has considered HMC&M from a overall perspective, as well as individually by specific testing and operating sites. Efforts and accomplishments are described below.

Hazardous material and hazardous waste information is documented in MIL-STD-1388.2B, Logistics Support Analysis Record (LSAR). This information is used to develop procedures for safe use, storage and disposal of hazardous materials and wastes to be integrated into the Integrated Logistics Support Plan (ILSP), maintenance plan, supply support documents, test plans, installation procedures, technical manuals and preventive maintenance

requirement cards (MRCs). The EPAT receives monthly listings of hazardous materials from the finalized maintenance tasks in the LSAR database to ensure appropriate HMC&M considerations have been documented.

An Occupational Health Hazard Assessment (OHHA) Report was prepared for the program in accordance with MIL-STD-882B, Task 206, and DI-SAFT-80106. This document identifies the potential occupational health hazards to personnel involved with the operation, support maintenance, repair, and disposition of the V-22. It identifies any potentially dangerous personnel health exposure levels to physical agents and hazardous materials that may occur with the occupational involvement of personnel with the aircraft. The OHHA assesses the hazards and recommends controls to minimize the associated risk. The assessment identifies necessary requirements for the use of protective clothing and equipment, the safe exposure limits to physical agents and hazardous materials, the measurement devices necessary to quantify safe exposure levels, engineering controls, and hazardous material safe handling requirements so that exposure levels are reduced to acceptable levels.

The EPAT reviewed the OHHA along with the program's System Safety Manager. The EPAT detailed specific instances where Bell-Boeing either did not adequately address the hazards associated with a material, or the efforts required to ensure safe use and handling. These comments were provided to the System Safety Manager to incorporate in the overall comments back to Bell-Boeing. The OHHA report is regularly scheduled for updating and resubmittal over the rest of the EMD contract. The EPAT will continue to monitor this effort.

Conclusion:

All DoD weapons system acquisition programs could utilize the environmental management approach developed by the V-22 program, and many programs could benefit from the specific pollution prevention technology accomplishments. The key factors to the program's success have been the hazardous material minimization methodology established by Bell and Boeing and by the tremendous support from the government's environmental team. Our effort to provide continuous input and guidance to Bell and Boeing has made a significant difference in how they are managing their pollution prevention program, what the priorities are for the program and how best to implement changes.

References:

Salomon, Lt. Col. Roy and Cathy Kim, "Weapon System Pollution Prevention" prepared for Mr. Gary Vest, Principal Deputy Under Secretary of Defense for Environmental Security, December, 1995, pp. 1 and 5.

METHYL CHLOROFORM ELIMINATION FROM THE PRODUCTION OF SPACE SHUTTLE SOLID ROCKET MOTORS

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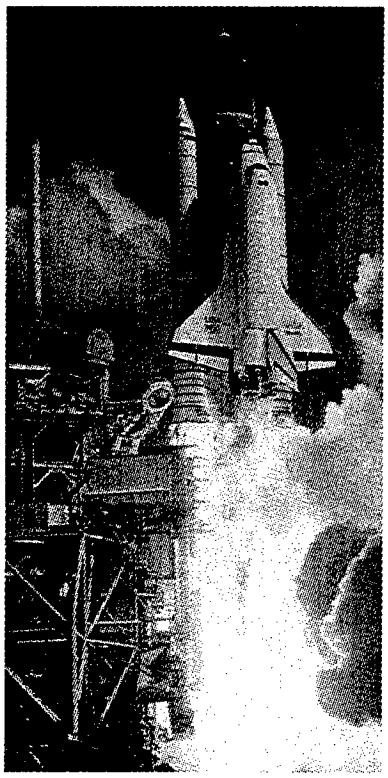
ABSTRACT



Thiokol Space Operations manufactures the Reusable Solid Rocket Motors used to launch America's fleet of Space Shuttles. In 1989, Thiokol used more than 1.4 Mlb of methyl chloroform to produce rocket motors. The ban placed by the Environmental Protection Agency on the sale of methyl chloroform had a significant effect on future Reusable Solid Rocket Motor production. As a result, changes in the materials and processes became necessary.

A multiphased plan was established by Thiokol in partnership with NASA's Marshall Space Flight Center to eliminate the use of methyl chloroform in the Reusable Solid Rocket Motor production process. Because of the extensive scope of this effort, the plan was phased to target the elimination of the majority of methyl chloroform use (90 percent) by January 1, 1996, the Environmental Protection Agency deadline. Referred to as Phase I, this effort includes the elimination of two large vapor degreasers, grease diluent processes, and propellant tooling handcleaning using methyl chloroform. Meanwhile, a request was made for an essential use exemption to allow the continued use of the remaining 10 percent of methyl chloroform after the 1996 deadline, while total elimination was pursued for this final, critical phase (Phase II). This paper provides an update to three previous presentations prepared for the 1993, 1994, and 1995 CFC/Halon Alternative Conferences, and will outline the overall Ozone Depleting Compounds Elimination Program from the initial phases through the final testing and implementation phases, including facility and equipment development. Processes and materials to be discussed include low–pressure aqueous wash systems, high–pressure water blast systems, environmental

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shipping containers, aqueous and semi-aqueous cleaning solutions, and bond integrity and inspection criteria. Progress toward completion of facility implementation and lessons learned during the scope of the program, as well as the current development efforts and basic requirements of future methyl chloroform handcleaning elimination, will also be outlined.

INTRODUCTION

The Reusable Solid Rocket Motors (RSRMs) used to lift the Space Shuttle from its launch pad at Kennedy Space Center (KSC) are manufactured by Thiokol Corporation at its facility in Promontory, Utah. This manufacturing process uses large quantities of methyl chloroform (TCA), which has recently been banned by the Environmental Protection Agency (EPA) and international mandates (Montreal Protocol). As a result of these new regulations, Thiokol and NASA have embarked on a significant journey to identify and implement suitable alternatives for methyl chloroform without compromising the safety, reliability, quality, or performance of the solid rocket motors. This paper provides an outline of this program, known as the Ozone Depleting Compound (ODC) Elimination Program.

A plan was established in 1990 by Thiokol in partnership with NASA's Marshall Space Flight Center (MSFC) to eliminate the use of TCA in the production process. Because of the extensive scope of this effort, the plan was phased to target the elimination of 90 percent of TCA use (Phase I) by January 1, 1996, the EPA deadline. Meanwhile, a request was made for an essential use exemption to allow the continued use of the remaining 10 percent of the TCA after the 1996 deadline, while total elimination was pursued for this final, critical phase (Phase II).

THE MANUFACTURING PROCESS (THE OLD VERSUS THE NEW)

The RSRMs each provide more than 3,000,000 lb of thrust during lift-off of the Space Shuttle. Because of their large proportions (each motor is 126 ft long and 12 ft in diameter), RSRM production presents unique challenges (Figure 1). Specialized equipment and manufacturing techniques are required that are unique to our fabrication facilities and processes.

Two minutes into the launch of a Space Shuttle orbiter, the RSRMs separate from the external fuel tank and fall, slowed by parachutes, into the ocean. They are then recovered and returned to KSC for disassembly, inspection, preservation (using HD-2 grease), and preparation for shipment back to Utah. In Utah, the remaining insulation is removed from the motor casings and nozzle hardware. The grease and paint is then removed, and the hardware is inspected, refurbished, and returned to production.

Each motor consists of four casting segments (Figure 1), which are made up of 11 separate steel sections, most of which are nearly 13 feet long and 12 feet in diameter. The previous process used a thick film of HD-2 grease as the shipping container, which required a considerable quantity of TCA to vapor degrease the components. With the new process, the sections are received from our Refurbishment Center in climate-controlled shipping containers in a grease-free condition. The individual sections are inspected, cleaned, and then assembled into casting segments. The segments are, in turn, prepared by the priming and painting of exterior surfaces and the application of primer, adhesive, and insulation to interior surfaces.

The casting segments are then transported to the large-motor casting pits, where they are loaded with solid propellant. During the propellant casting process, they are placed in the vertical position in submerged

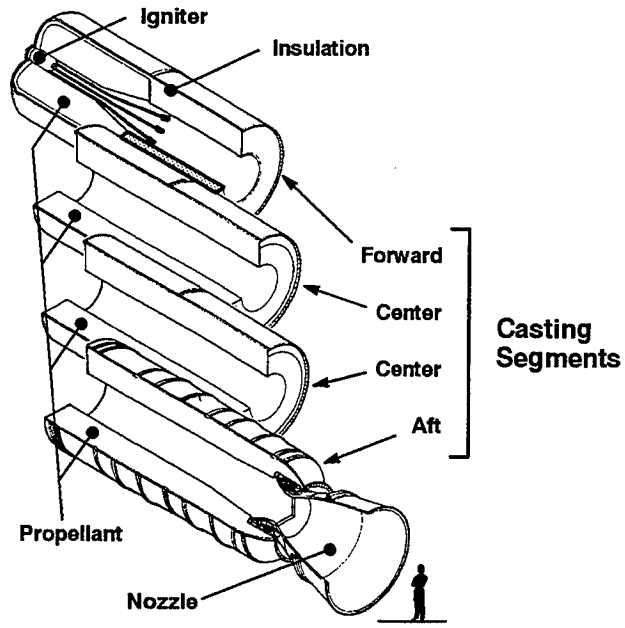

Figure 1. Space Shuttle RSRM Propellant Configuration

casting pits. A Teflon®-coated mandrel is positioned in the center of the segment to shape the propellant grain. A liquid, viscous form of the propellant is cast under vacuum into the segment and around the mandrel, then allowed to cure and solidify.

Another major component of the motor is the nozzle assembly, which controls the discharge of hot gases from the motor during flight. In nozzle production, a total of nine steel and aluminum housings are processed in the same basic manner as the case hardware, with the exception being the post-refurbishment and cleaning processes. Glass-cloth phenolic insulators and carbon-cloth phenolic liners are then bonded to the housings. These components are ultimately assembled to form the nozzle.

The last step in RSRM processing is the preparation for shipment. Cast segments are sent to the Final Assembly Center, where they are X-rayed and system tunnel floor plates bonded in place. Also, the nozzle is installed in the aft segment, and the igniter installed in the forward segment. The segments and support hardware then are either stored or shipped to KSC, where they will be stacked on the launch pad and prepared for launch.

ODC ELIMINATION PLAN/PROGRAM

Because of the large quantities of TCA used in RSRM production, it was necessary to divide our plan into phases that would allow the most efficient use of resources. Analysis showed that a significant amount of TCA could be eliminated by concentrating on several major categories. The program was, therefore, phased (Figure 2): Phase 0 eliminated the obvious generic uses of TCA where another product could be used on nonflight hardware (general cleanup of support tools, work stations, etc.). These "grassroot" changes were implemented immediately and had a significant impact on our TCA use. Phase I was designed to eliminate 90 percent of the material, based on 1991 consumption figures. It concentrated on the two large vapor degreasers in the Refurbishment and Production centers, and on the material used to prepare tooling

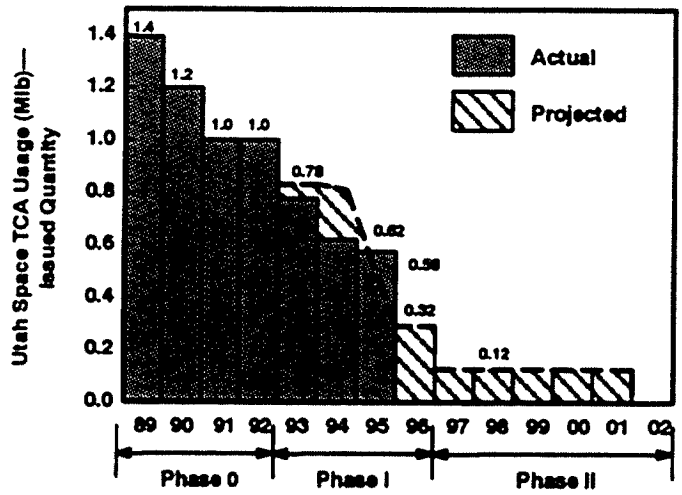

Figure 2. Actual and Projected Reduction in TCA Usage

for the propellant mixing and casting processes. Phase II will be dedicated to the elimination of the remaining 10 percent of TCA usage, which is mainly handcleaning used to prepare hardware surfaces for critical bonding and assembly, as well as rubber activation.

Since eliminating all emissive uses of TCA by the January 1, 1996, deadline would not be possible, Thiokol applied to the Solvents, Coatings, and Adhesives Technical Options Committee of the United Nations Environmental Program (UNEP) for an essential use exemption. This exemption, which allows for the purchase of TCA for emissive use after 1995, was granted in October of 1994 for two years. A request for an extension of an additional four years was recently approved by the Montreal Protocol committees at the December 1995 UNEP session in Vienna, Austria. The master program schedule for the entire RSRM ODC Elimination Program is shown in Figure 3.

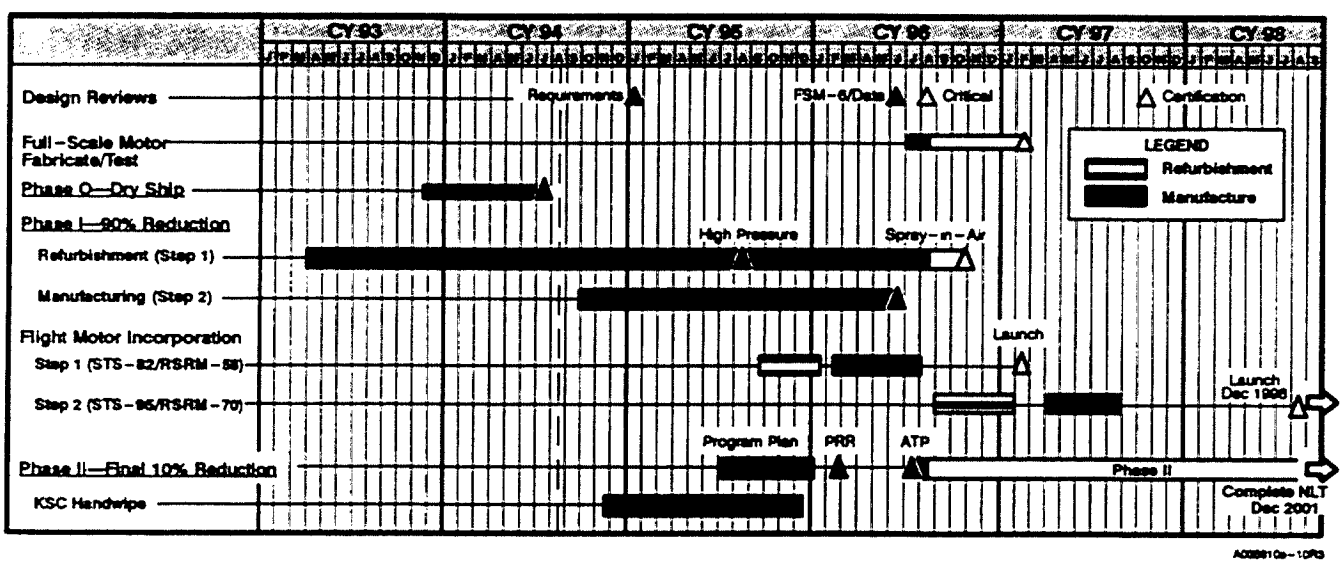

Figure 3. Master Schedule for TCA Replacement

CLEANER DOWNSELECTION STUDY

Thiokol began the TCA elimination process by searching for both a substitute cleaner and a new process to replace vapor degreasing. The enormous amount of available industry data was reviewed, and numerous candidates were selected for testing. After a technical and programmatic assessment of 150 different products was completed, testing was performed using 15 different aqueous and semi–aqueous cleaners for spray and immersion applications. From these, two cleaners (DuBois Jettacin® and Brulin 815 GD®) were chosen because of their exceptional cleaning ability and resulting bond strengths. Simultaneously, spray cleaning was selected over immersion as the new process mainly because of the size and unique configuration of the hardware.

Cleaning and bonding tests were performed in a 24–in. fixed workpiece, oscillating nozzle, spray machine manufactured by Progressive Recovery, Inc. Two significant conclusions resulted from this testing: 1) bond adhesion values from specimens cleaned with the new chemicals were much higher than the baseline TCA values (Figure 4) and 2) the use of the selected cleaners in a spray application indicated a

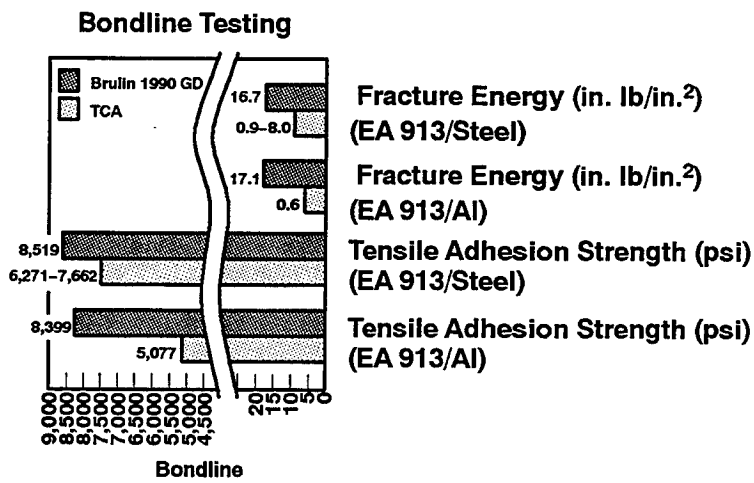

Figure 4. Summary of Brulin 1990 GD® Testing

foaming problem. The first result overcame the belief that nothing could equal TCA for its cleaning ability. The second result showed that the wrong cleaners were selected for the chosen process, indicating that a new approach was necessary (Vendor information for both the Brulin and Jettacin specified the cleaners primarily for immersion applications.).

SIGNIFICANT EMOTIONAL EVENT

From contacts made at the 1994 Precision Cleaning Show, Thiokol engineers visited a supplier of spray cleaning systems (R. G. Hanson of Bloomington, Illinois) to investigate the foaming problem. Testing in mid–scale machines manufactured by Proceco confirmed that the use of Brulin 815 GD and Jettacin in spray applications leads to excessive foam generation. Based on these results, Thiokol redirected its efforts to select and evaluate a low–foaming aqueous cleaner.

Brulin 1990 GD was selected because of its similarity to Brulin 815 GD, with which an extensive experience base had been established, and because it was formulated specifically for spray applications. To

reduce test scaling effects, a 40–in. spray cleaning system (Proceco Typhoon®) was purchased to support the testing (Figure 5). The Proceco machine is a three–stage system with recirculated wash, recirculated rinse, and a fresh water rinse–to–drain stage. A 25–hp booster pump was added to the wash cycle to allow variable pressure up to 250 psig for testing purposes.

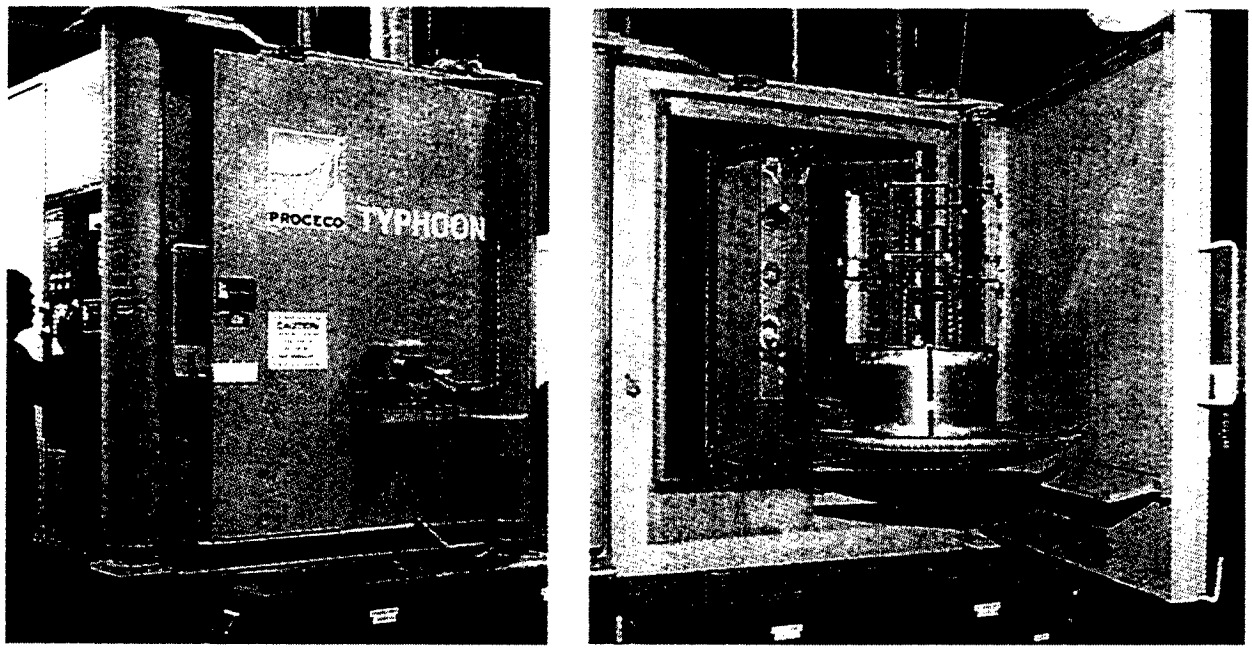

Figure 5. Proceco 40–in. Spray Cleaning System

FINAL PARAMETERS

As supported by industry information, Thiokol's testing with the Brulin 1990 showed that best bond results were obtained with a wash solution at 160°F and a flow rate of 150 gal/min. There was little difference between a spray pressure of 140 and 70 psig, but the higher pressure aided in cleaning difficult part geometry. The best bonding results also correlated with second stage (first rinse) parameters of 150°F and 50 psig at 150 gal/min. The third stage (second rinse) was an elevated–temperature, low– pressure rinse flowing at 4.7 gal/min. These parameters have been incorporated in additional testing that included full–scale hardware.

PROCESS CHANGES: THE REFURBISHMENT CENTER (PHASE I, STEP 1)

Early Elimination Efforts

Early efforts were made to eliminate non–critical uses of TCA in the refurbishment process. In particular, 44,000 lb of TCA were used each year to dilute preservative grease in order to ease its application to hardware. To eliminate this use, dilution ceased and the use of grease as an in–process preservative was greatly reduced.

The next goal was to eliminate the use of preservative grease completely. Since most of the components are high–strength carbon steel, corrosion is a significant concern. Thiokol turned to the use of environmen-

tally controlled shipping containers (Figures 6 and 7) to allow transportation between refurbishment and manufacturing sites without the use of preservative grease. The shipping containers have been implemented for all hardware and have proven to be very effective. This change also aided in the reduced use of TCA since intermediate steps of vapor degreasing were eliminated.

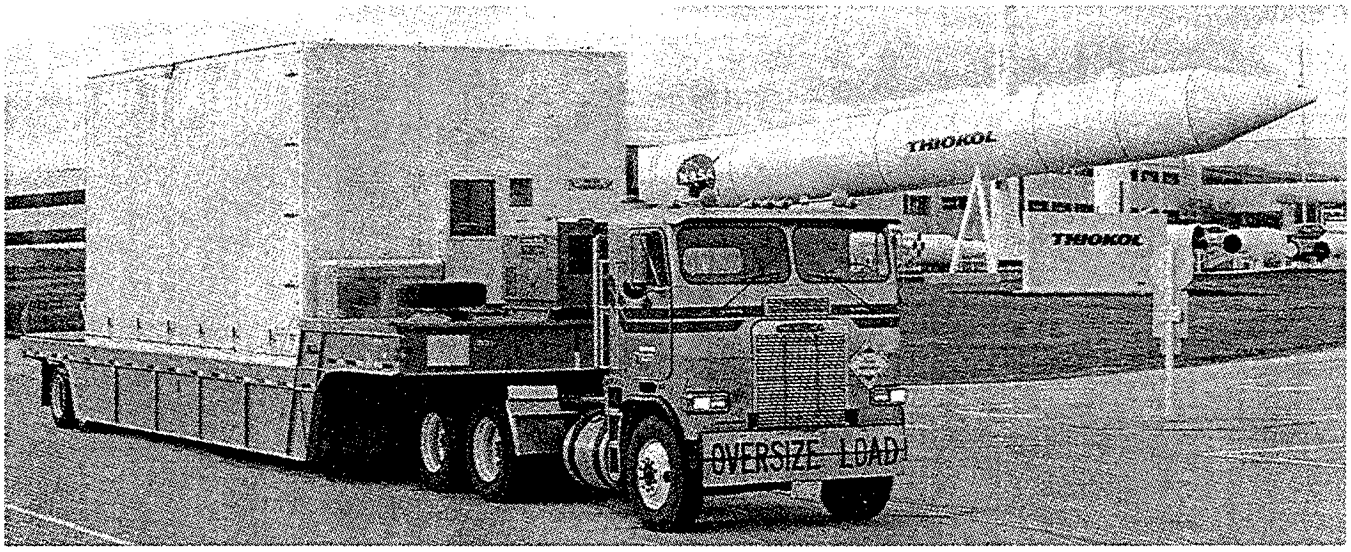

Figure 6. Environmentally Controlled Shipping Trailer

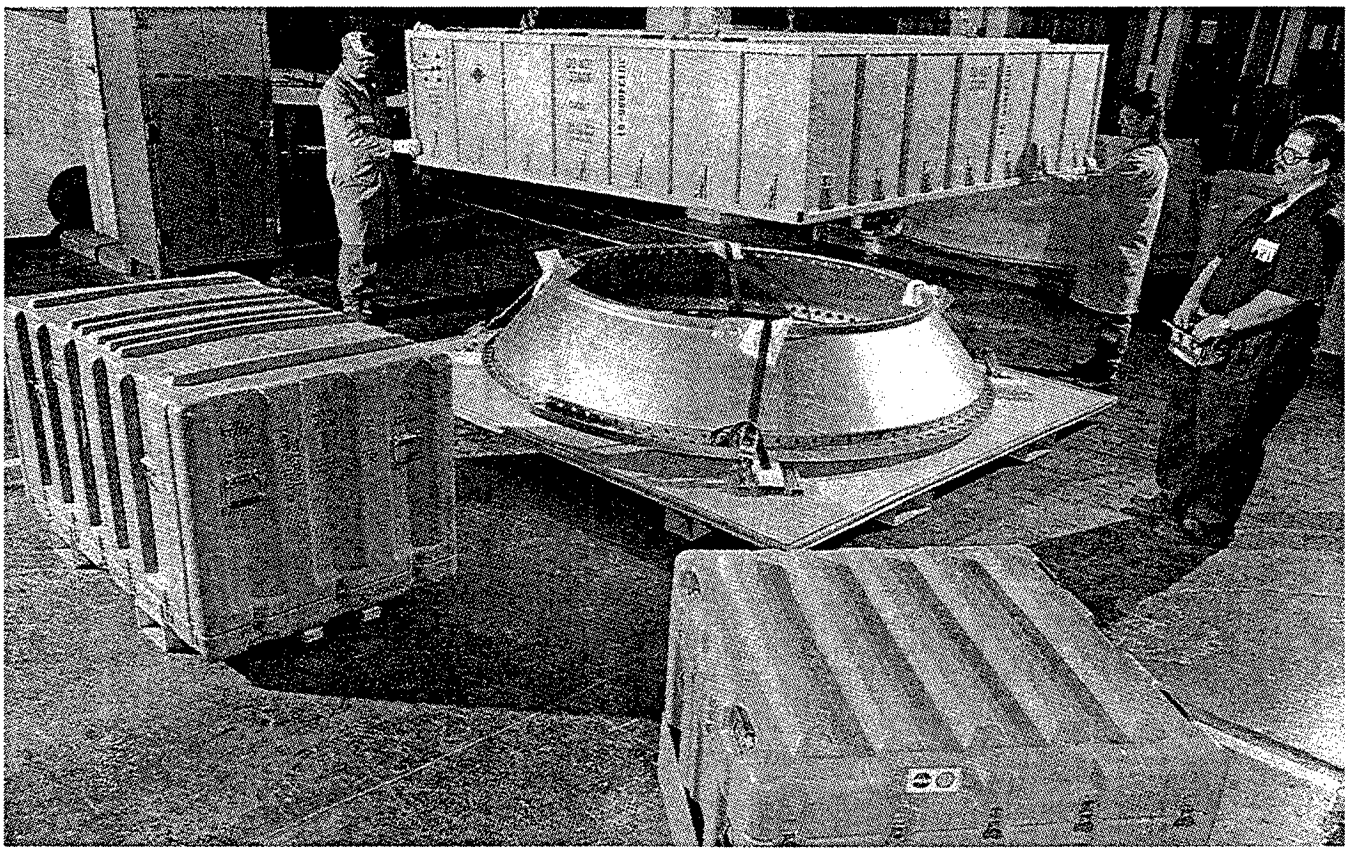

Figure 7. Environmental Shipping Containers

High-Pressure Water Blast

During the previous (TCA) refurbishment process, process and inspection materials were removed in a vapor degreaser. Based on the 1991 data, this degreaser accounted for nearly 50 percent of the TCA used in motor production. As part of the ODC Elimination Program, two high-pressure water blast (HPWB) systems (Figures 8 and 9) (built by Progressive Technologies, Inc., of Grand Rapids, Michigan) were installed. Using jets of water at pressures reaching 30,000 psi, these blast systems strip grease, Chemlok®, and residual materials from the interior and paint from the exterior of the rocket motor cases in a fraction of the time the previous vapor degreasing and grit blast cycles required. These systems are now qualified and have replaced not only vapor degreasing, but also the process of removing postflight materials from metal hardware as well. The systems have multi-axis computer numerically controlled robots that allows precise control of nozzle stand-off and position, both of which are critical to proper operation.

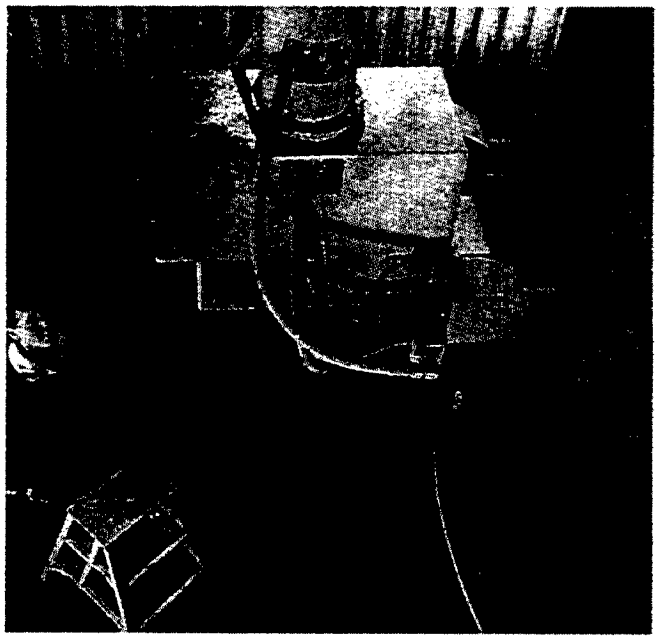

Figure 8. Case Cylinder HPWB System

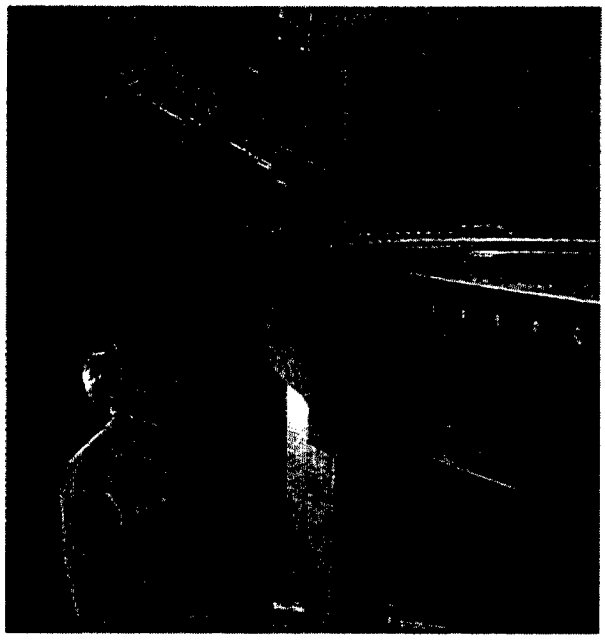

Figure 9. Nozzle/Dome/Igniter HPWB System

Testing and subsequent production cycles using these systems have shown exceptional cleaning capabilities using high-pressure water. Also, the water blast removes insignificant amounts of metal from the components, and eliminated repetitive grit-blast cycles, thereby extending useful life of the expensive, long-lead metal components.

Large Spray Cleaning System

Occasionally, hardware is not in a configuration to be cleaned by high-pressure water (e.g., painted hardware, large tooling, etc.). In these cases, a large spray cleaning machine (Figure 10) using Brulin 1990 GD will be the primary cleaning system. The machine will include three stages—all recirculated—and will have two wash booms that will traverse the hardware axially. The system will have a footprint of 14 ft by 14 ft and a maximum working height of 16 ft. This system (manufactured by Proceco, Inc.) is on track for use by the third quarter of 1996.

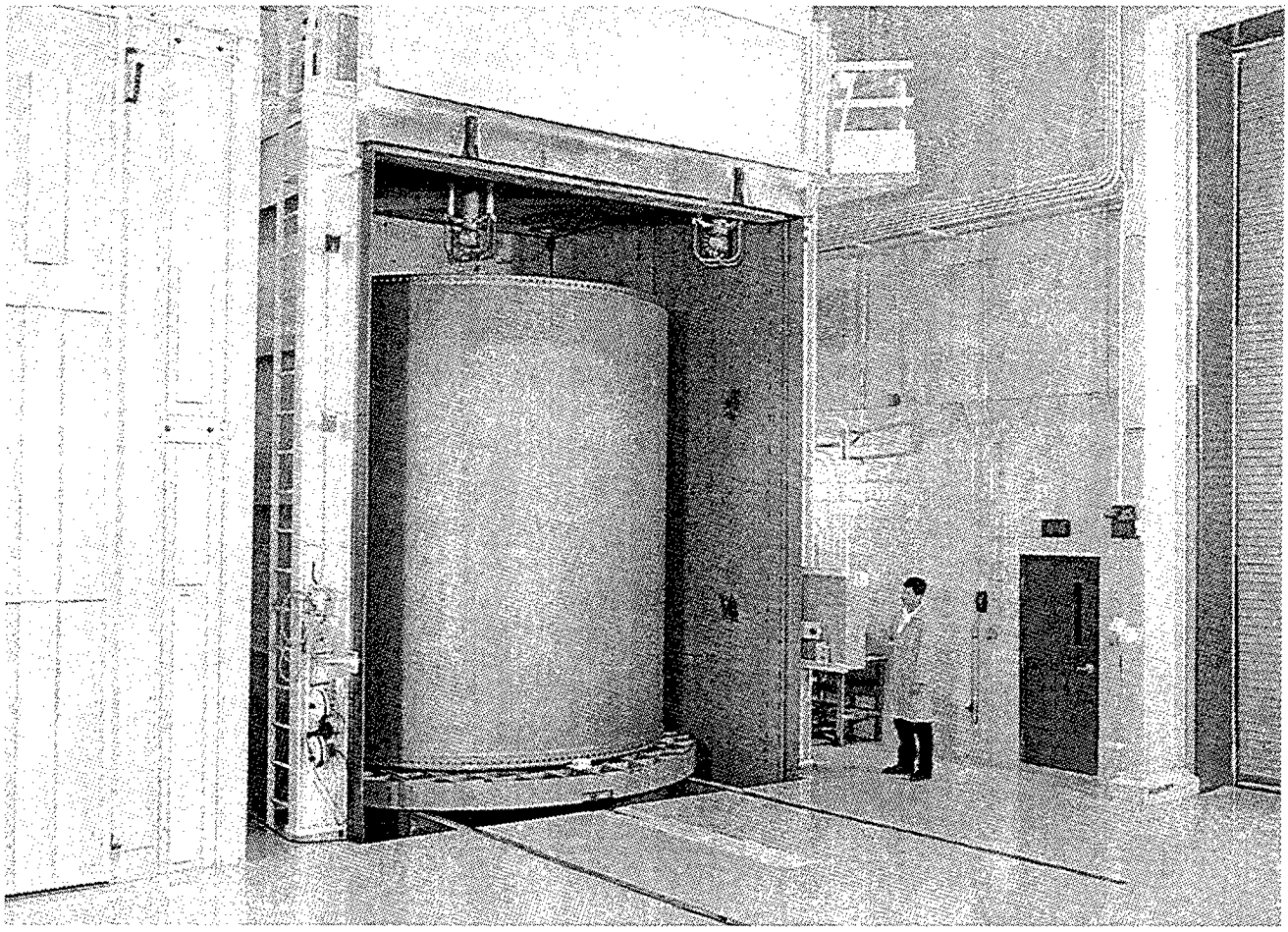

Figure 10. Large Proceco Aqueous Spray Cleaning System

Small Parts Cleaner

The refurbishment process also relies on a small vapor degreaser for cleaning many small parts (e.g., igniter chambers, tooling, bolts, pins, etc.). This unit will be deactivated and replaced with a small spray cleaning system similar to the system mentioned above. The spray machine, a Proceco Typhoon, will use the same aqueous solution as the large machines (Brulin 1990 GD) and will consist of three stages, similar to the unit used for early testing (see Figure 5).

PROCESS CHANGES: THE PRODUCTION CENTERS (PHASE I, STEP 2)

Large Spray Cleaning System

All case and nozzle hardware is currently cleaned in a large vapor degreaser before painting and bonding as the first stage of production (as opposed to refurbishment as mentioned in Step 1). Use of this degreaser accounts for nearly 205,000 lb of TCA consumption each year. This use will be eliminated by incorporating another large Proceco spray cleaning system. Similar to the Refurbishment Center's machine, this system consists of three recirculated stages and uses Brulin 1990 GD as the cleaning agent (Figure 10).

The facility to house this large system, along with the companion grit blast system, was completed earlier this year. The new systems were operational the second quarter of 1996.

Extensive testing has been conducted on subscale samples and full-scale components to ensure current bond integrity was met or exceeded. Process simulation articles (partially constructed full-scale items) will be fabricated using the new cleaning system to prove-out the process changes. The final demonstration test of the cleaning capability and compatibility will be accomplished using full-scale static test motor to be fired in the first quarter of 1997. At present, flight production using the new systems is scheduled to start in April 1977 following complete evaluation of the postfire test motor.

Small Parts Cleaner

Currently, the igniter metal components—made from D6AC steel—are vapor degreased in TCA before bonding in a process very similar to the larger components. This step will be directly replaced with spray cleaning using Brulin 1990 GD. Completed on schedule in January of 1996, process qualification has incorporated the Proceco Typhoon that was used for testing and the development phase (see Figure 5).

Mix/Cast Tooling Cleaning

During the propellant mixing and casting processes, more than 15,000 lb of TCA are used each year for the handcleaning of tooling and support hardware (Figure 11). A small vapor degreaser, which was used for cleaning test specimens and some igniter components, has already been shut down and replaced with

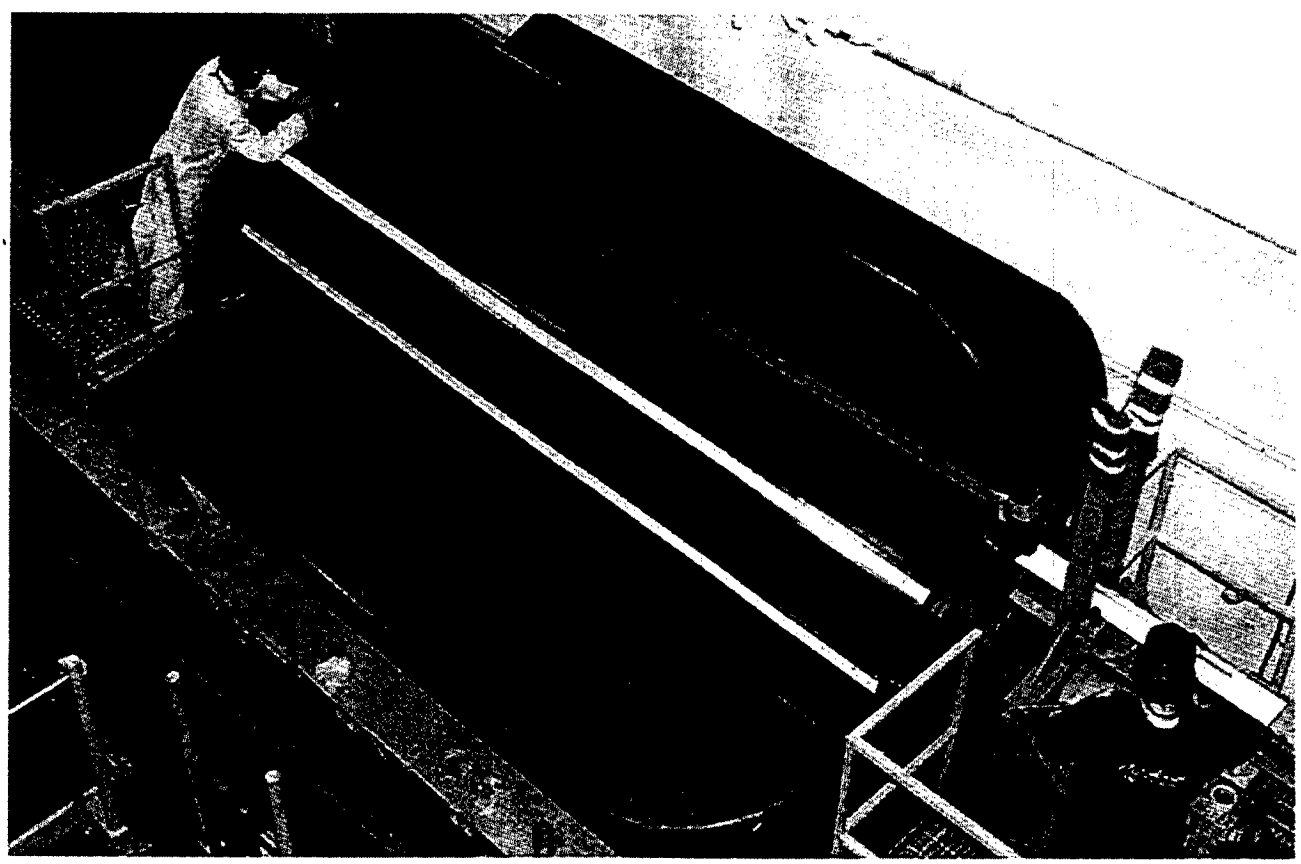

Figure 11. Propellant Casting Core Cleaning Operation

alternate processes. Studies were also performed on organic, inorganic, aqueous, semi–aqueous, and alcohol–based cleaners to determine suitable replacements for TCA to remove propellant from tooling and equipment. Cleaning ability and material compatibility were studied. Because of the explosive hazards associated with processing high–energy solid propellant, flammability and conductivity of the cleaners were also primary considerations. After preliminary investigation of 36 cleaners, 10 were chosen for closer scrutiny. Finally, PF Degreaser® (PT Technologies) and Ionox BC® (Kyzen Corporation) were selected as replacement candidates. Further testing—now concluded—has determined that one solvent cannot replace TCA in all applications due to the unique polymer characteristics of the propellant and various states of cure. Implementation of these two cleaners was completed in June of 1996, and the new cleaners are in use on production tooling with good results.

THE NEXT STEP: HANDCLEANING ELIMINATION (PHASE II)

The Phase II effort, originally scheduled to take place in 1997 through 2001, has been accelerated to start mid–1996. Phase II will target the elimination of the remaining 10 percent of TCA use. Though it is a smaller quantity of material compared to Phase I, this TCA accounts for in excess of 500 distinct applications on a wide variety of substrates, soils, and process materials. These substrates include steel, aluminum, glass and carbon phenolic, rubber, paint, cork, and other miscellaneous materials (Figures 12 and 13). TCA

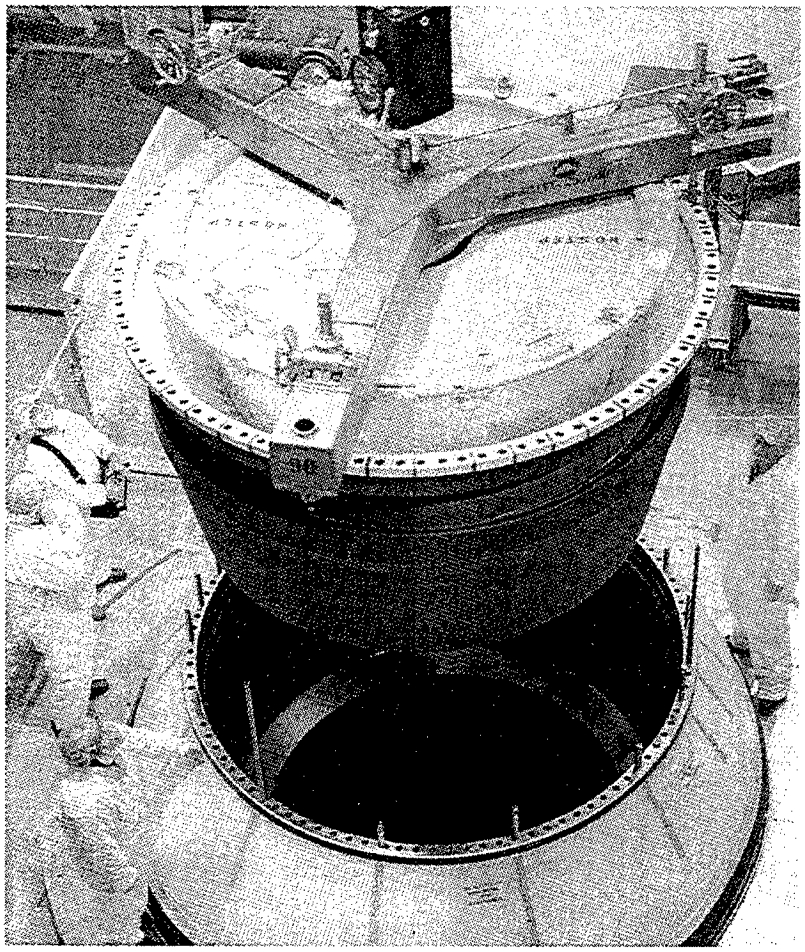

Figure 12. Handcleaning of Nozzle Phenolic Insulator

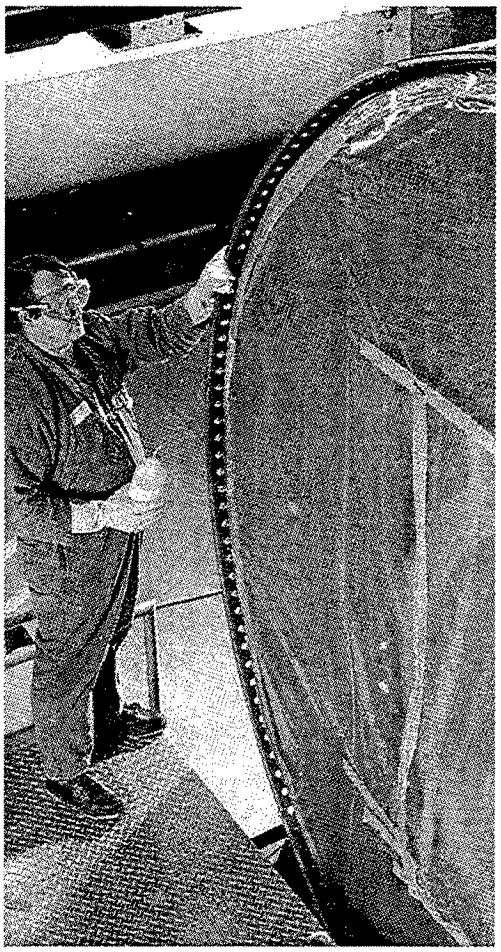

Figure 13. Handcleaning During Nozzle Installation

is mostly used for final hand cleaning of the hardware bonding and non-bonding surfaces, hand cleaning of tooling for use in critical applications, and rubber activation. These are considered the most critical uses of TCA in rocket motor manufacture. Cleaners must be proven compatible with the substrates and yet be capable of removing up to 35 different contaminants.

After an extensive review of existing cleaners, available literature, and existing test data, approximately 30 cleaners have been selected for preliminary examination. The cleaner candidates are now being tested with fabrication and support materials from the applicable processes for compatibility, electrostatic energy characteristics, bonding qualities (where applicable), toxicity, and personnel safety. Following these preliminary tests, the field of candidates will be reduced to five or six of the most likely choices. More thorough tests will be performed during the next few years on these new cleaners to ensure the safest and highest quality end products are delivered with the new cleaning processes.

It is during this phase of our TCA Elimination Program that we have been looking to the precision cleaning industry as well as other aerospace and non-aerospace users for advice and recommendations as to which types of cleaning solutions and application media would be effective on our soils and substrates. As part of our participation at various industry gatherings (such as the Precision Cleaning Expositions), we have been seeking information and samples of potential candidates that are likely to meet our handcleaning requirements.

Originally part of Phase II—and initiated two years ahead of schedule—was Thiokol's effort to replace TCA for cleaning applications for assembly and stacking operations at KSC. In many cases, the KSC processes mirror those performed at the main production facility in Utah. A battery of tests completed by Thiokol in June 1995 fully evaluated the cleaning capability and overall bonding effects on all material and hardware interfaces. The candidate cleaners have been selected based on replacements used by other Space Shuttle contractors to ensure compatibility and reduce duplication of effort. The two cleaners selected are Reveille (DuBois Corporation) for all metal surfaces and substrates and isopropyl alcohol for cork surfaces and substrates. Flight incorporation of the new KSC processes was recently completed and has been used on the last few Space Shuttle flights.

LESSONS LEARNED

These efforts to eliminate TCA in rocket motor production have not come easy. They have consumed thousands of man-hours and an enormous amount of resources. But more significantly, they have required a change in attitude, a different way of looking at the way we produce rocket motors. In many cases, a complete paradigm shift had to occur before the real thought process could occur. The biggest hurdle some of us had to face was that we assumed there was no other process or material combination that could clean our hardware as well as hot TCA vapor degreasing or ambient TCA handcleaning. What we have found as a result of our ODC elimination activities is that there are processes and materials available that are capable of cleaning as well, if not better than TCA. All we have to do is talk to the precision cleaning industry, other users (both aerospace and non-aerospace), accept their suggestions and recommendations, and then very carefully evaluate these options based upon our own specific requirements, knowledge, and expertise. Recent observations of postflight hardware remind us that any process change, particularly internal bondlines affected by the dynamics of launch and motor operation, need to be developed at a pace that allows for extensive engineering evaluation followed by testing in simulated or actual end-use environments, up to and including when necessary, full-scale static tests. Interaction of these various changes in conjunction with dissimilar or adjacent interfaces must also be considered and carefully screened during the testing process.

Another important lesson learned was the technology spin–offs that have resulted from these new processes. The implementation of the high–pressure water blast systems, for instance, has allowed Thiokol to dramatically improve a number of other postflight processes involving the cutting and removal of remaining insulation materials from the metal hardware. Operator–sensitive, hand–held water blast processes that exposed personnel to an elevated level of risk have been replaced by the automated systems, significantly increasing the through–put and minimizing exposure to the hardware as well. In some cases, the condition of the hardware is significantly improved, resulting in enhanced postflight inspection and database integrity. Over time, these new processes will continue to benefit our entire program through safe, efficient processing of the expensive metal components.

CONCLUSION

Thiokol has aggressively acted over the past four years to meet the January 1, 1996 deadline for the elimination of TCA use. In reviewing our processes, extensive amounts of TCA (780,000 lb) were quickly eliminated from the manufacturing process by implementing subtle, common sense changes. Testing and investment in leading–edge technology are enabling Thiokol to redirect the manufacturing process and reduce the use of TCA by over 900,000 lb by the target date. Implementation of the high–pressure water blast systems in our Refurbishment Center, and other "grease–free" changes, have allowed Thiokol and NASA to exceed our TCA reduction targets in the last three years (see Figure 2). Furthermore, coordinating with the EPA and UNEP for the necessary exemptions, all emissive uses of TCA will be suspended by the end of this century. Environmentally sound manufacturing practices that maintain the safety and reliability of the RSRMs are the primary goal of Thiokol Corporation.

SPACE SHUTTLE REUSABLE SOLID ROCKET MOTOR (RSRM) HAND CLEANING SOLVENT REPLACEMENT AT KENNEDY SPACE CENTER (KSC)

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SUMMARY

At Kennedy Space Center (KSC), Thiokol Corporation provides the engineering to assemble and prepare the Space Shuttle Reusable Solid Rocket Motor (RSRM) for launch. This requires hand cleaning over 86 surfaces including metals, adhesives, rubber and electrical insulations, various painted surfaces and thermal protective materials. Due to the phase-out of certain ozone depleting chemical (ODC) solvents, all RSRM hand wipe operations being performed at KSC using 1,1,1-trichloroethane (TCA) were eliminated. This presentation summarizes the approach used and the data gathered in the effort to eliminate TCA from KSC hand wipe operations.

BACKGROUND

USBI's Solid Rocket Booster (SRB) and Thiokol's RSRM hardware have large interfaces requiring bonding operations to close-out the interface joints between the hardware. USBI had qualified replacement cleaners for their hand wipe applications that previously used TCA. Thiokol had planned to delay replacement of TCA in its close-out operations while continuing to operate under an Essential Use Waiver granted by the Montreal Protocol. Once the operational difficulties of cleaning different sides of the SRB/RSRM interface with different cleaners was realized, Thiokol committed to attempt a joint implementation of the same cleaners. USBI had down-selected to five primary cleaners for testing: Reveille, PF Degreaser, isopropyl alcohol, Prime and Jettacin.

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APPROACH

Using the timeless scientific method, the first step was to define the problem. All hand cleaning operations were identified and observed when possible. A matrix was developed that identified all of the substrates cleaned, the purpose of the cleaning (i.e. cosmetic, inspection, preparation for bond), any subsequent bond lines and what testing would be required to qualify a new cleaner in that specific application. Additional informational items were included in the matrix for internal use such as operating instructions affected, hardware location and facility location where each operation was performed.

A hypothesis was formed. Since the USBI selected cleaners passed all of SRB's qualification steps with several common substrates and bond lines, these same cleaners would be a good selection for RSRM hand wipe cleaning, and would support implementation of a common cleaner. The five cleaners chosen by SRB and a cleaner chosen by the Thiokol Mix and Cast work center, Ionox BC, were chosen as replacement candidates for testing.

TESTING

Testing required for qualification of the new cleaners in the RSRM operations at KSC were defined utilizing the matrix which had been prepared during problem definition. Testing included compatibility, corrosion, dry time and tensile adhesion. USBI had already completed testing on several of the same substrates and some of the same bond lines. Wherever possible USBI data was utilized to prevent duplication of effort and to save program money. Also, to the extent possible, the test methods utilized by USBI were used to ensure data comparisons would be valid.

Compatibility testing for non-metallic materials utilized ASTM D471 as a guide. Compatibility data was gathered for each substrate the candidate cleaners would potentially come in contact with. Three substrate specimens were tested with each cleaner. Initial measurements, including mass, volume and hardness, were taken prior to testing. The specimens were immersed in the test cleaner for 22 hours. After this initial immersion period, mass, volume and hardness was measured again. The samples were re-immersed for an additional 48 hours, for a total of 70 hours. The same parameters, mass, volume and hardness, were again measured at the end of testing. The percent change from pre-test measurements was calculated for both immersion times. The percent changes for each of the three specimens for each candidate cleaner were compared to the three specimens tested with TCA for each substrate. An analysis of variance was conducted on the percent changes in mass, volume and hardness to determine if the candidate cleaner caused significantly more change, statistically similar change or statistically less change than the TCA. Change in a substrate as a result of a hand wipe cleaning operation is undesirable. The ideal cleaning fluid would totally remove any contaminant from the substrate surface yet have no effect on the substrate itself. For these reasons, more change than TCA was classified as "worse" than TCA. The same amount of change as TCA was classified as "comparable" to TCA. Less change than TCA was classified as "better" than TCA.

Paint compatibility testing was performed on all of the paint and coatings materials the cleaners would contact using ASTM F502 as a guide. The affected coatings were applied to panels of typical surfaces and allowed to fully cure or dry. Half of each panel was exposed to the candidate cleaner for thirty minutes at 100 degrees F. The panels were then allowed to fully dry for 24 hours. Paint hardness was determined using graphite leads of decreasing hardness at a 45 degree angle to determine the lead that would not rupture the surface but would leave a black mark. The number of lead changes between the exposed and unexposed areas (i.e. 4H to 2H = -2) was statistically compared to the number of lead changes caused by TCA. The ANOVA technique described above was again used to classify results as worse, comparable or better than TCA.

A total immersion corrosion test was performed on metal substrates that are cleaned using ASTM F483 as a guide. Three coupons of each metal substrate were prepared for each cleaner. The specimen dimensions were measured and the surface area calculated. Coupons were cleaned per the standard, which included cleaning with TCA and MEK. The coupons were dried in an oven and cooled in a desiccator. After the coupons were completely dried, they were weighed. The coupons were immersed in the test fluids for 24 hours at 100 degrees F. The coupons were again rinsed, dried, cooled and weighed. The coupons were then returned to the test fluids for an additional six days. After being immersed for a total of seven days, the coupons were rinsed, dried, cooled and weighed for the last time. The effect of the cleaning fluid on the metallic coupons was calculated as mg/cm^2 lost per 24 hours. The results were statistically analyzed with the ANOVA technique to determine if the test fluids were worse, better or comparable to TCA.

Because the candidate replacement cleaners have different evaporation rates than TCA, dry times were determined for each cleaner on each substrate family. Two coupons of each substrate were prepared and weighed for each cleaner tested. One of the coupons from each set was contaminated and reweighed. This ensured that the presence of contaminant would not affect the dry time. The contaminated and uncontaminated coupons were cleaned. Organic cleaners were tested by wiping with a dampened wiper followed by a dry wipe with a clean wiper. Aqueous cleaners were tested by wiping with a dampened wiper followed by wiping with a water dampened wiper prior to a final dry wipe. Each of the coupons was weighed at ten minute increments for one hour. The results were then graphed to see when evaporation was essentially complete.

The majority of bond lines were tested using anvil tensile adhesion buttons shown in Figure 1. The tensile buttons were made from the same steel that the RSRM case material is made from. In most cases this steel material did not represent the substrate being tested. The substrates that were cleaned and subsequently bonded on the hardware were identified. The affected substrates were bonded onto the steel button. The surface of this affected substrate was prepared to mimic the surface being cleaned on the actual hardware. This surface was then contaminated with contaminants specific to that substrate. The substrate was then cleaned with candidate cleaners as well as TCA as a control. The test adherend was then bonded to the cleaned substrate. Because this work represents processing of loaded segments at KSC, all of the cures are performed at ambient temperatures. In the majority of cases, the test adherend was either EA934NA, a structural adhesive used to bond preformed cork to the mated joints or K5NA, a cork-filled ablative compound used to fill-in between cork runs and a variety of other

close-out locations. Bond testing was conducted after three aging conditions: immediately after cure (no aging), after 4-weeks accelerated aging and after one-year ambient aging at KSC.

Figure 1 - Button-to-Button Specimen Configuration

Bond lines involving the application of paint or coatings were tested using a Paint Pneumatic Adhesion Tensile Test Instrument (PATTI) tester. Whatever substrate the coating was applied to on the hardware was prepared. The substrate to be coated was contaminated with contaminants representative of the real process. The surfaces were then cleaned with the candidate cleaners or TCA. After the surface dried, the coating was applied and allowed to cure at ambient conditions. After the coatings had fully cured or dried, depending on the coating, small buttons, called PATTI dollies, were bonded to the coating using a quick drying high strength cyanoacrylate type adhesive. The dollies were then removed with the PATTI tester and the adhesion strength of the coating to the cleaned substrate was measured. Like the anvil buttons mentioned above, testing was conducted after cure, after 4-weeks accelerated aging and after 1-year ambient aging.

RESULTS

Data generated from testing with the new cleaners was compared to engineering requirements as well as to the TCA samples for similarity. In many cases the TCA samples far exceeded the engineering requirements for a given bond line. One of the criteria for the new cleaners was that they met all engineering requirements. Although not a hard requirement, it was desirable for the new cleaners to perform as well or better than TCA.

Non-metallic and paint compatibility as well as corrosion results were reported as better than, comparable to or worse than TCA. These results were derived from an analysis of variance (ANOVA)

of raw data performed in triplicate. This is essentially a three day soak test and does not represent what would occur to a substrate during a cleaning operation. These results provide a comparison of the effects TCA and Reveille have on a substrate after extended exposure. Because Reveille was the final cleaner of choice, discussion of the results will be limited to a comparison of Reveille to TCA. Table 1 shows Reveille results from the compatibility tests on non-metallic substrates as they compared to TCA. Of the testing performed by Thiokol, Reveille only resulted in two substrates with any changes greater than those caused by TCA. Reveille caused more change in silica-filled EPDM rubber mass and volume than TCA; but a comparable change in hardness. Reveille was still qualified for cleaning this substrate due to bonding results which will be discussed later. The second substrate with which Reveille had a more adverse effect on mass and volume change was teflon tape. This tape was prepared by folding a length over onto itself. From this portion of tape, a one inch square coupon was cut for testing. After the testing was complete, the teflon side of the tape appeared unchanged, but the adhesive came unadhered from itself and the two layers of tape, connected by a fold, were curled up. Based on visual examinations it was concluded that the cleaner had affected the mass and volume of the tape adhesive, not the teflon itself. During the cleaning operation in question, the tape is already adhered to a surface and contact with any cleaners is unintentional and incidental. In this respect, Reveille did prove to be effective at removing tape residue, one of the more tenacious contaminants. Based on the testing, observations and field situation, there were no concerns with using Reveille around teflon tape. For all other substrates tested, Reveille was better or comparable for all parameters measured.

Paint compatibility test results are presented in Table 2. With the paint compatibility, the only parameter measured was hardness. Reveille was milder on the surfaces coated with Chemlok than TCA. Reveille was comparable to TCA with the other coatings tested.

Table 3 summarizes corrosion test results. A decision was made early in this program not to introduce aqueous cleaners onto bare metal surfaces. All of the cleaners tested were organic and non-corrosive. No corrosion was detected on any of the samples. There was no distinguishable difference between TCA and Reveille for any of the metal substrates tested.

Dry time results were gathered in the form of reduction of mass over time. The measurements were graphed to determine when weight loss became negligible. Measurements and bonding results supported a thirty minute dry time on all substrates tested. Further testing showed that non-porous surfaces such as metals and painted surfaces were effectively dry after fifteen minutes. Bond testing supported the fifteen minute dry times on non-porous surfaces as well.

Substrate	Better	Comparable	Worse
Carbon Cloth Phenolic		Mass, Volume, Hardness	
Glass Cloth Phenolic		Mass, Volume, Hardness	
EPDM		Hardness	Mass, Volume
Kapton	Mass	Volume	
Polysulfide	Mass, Volume, Hardness		
Connector Potting Compound	Mass	Volume	
Teflon Tape			Mass, Volume
Viton	Mass, Volume	Hardness	
Solvent Wash Bottles	Mass	Volume	
Spray Bottles		Mass, Volume	
MIL-R-6855 Electrical Insulation	Mass, Volume		
STW3-3134 Electrical Insulation	Mass, Volume		

Table 1 - Reveille Non-Metallic Compatibility Results as Compared to TCA

Substrate	Results
Chemlok 205/Chemlok 236A	Better
Rust-Oleum Primer	Comparable
Rust-Oleum Paint	Comparable
Hypalon Paint	Comparable

Table 2 - Reveille Paint Compatibility Results as Compared to TCA

Substrate	Results
Mild steel	Comparable
Cadmium plated bolts	Comparable
D6AC steel	Comparable
Stainless groundstrap/conductive adhesive	Comparable

Table 3 - Reveille Corrosion Results as Compared to TCA

Tensile adhesion results for button-to-button tensile adhesion tests are reported in Table 4. Also within the table are some of the stricter engineering requirements of the bond specimens. With no exception, the Reveille bond strengths exceeded the bond requirements by more than two and a half times and often up to five times. Previous testing conducted by USBI showed that cork may be too porous for the slower drying organic cleaners. For this reason, Reveille was not tested on cork. As noted within Table 4, cork substrates were cleaned with isopropyl alcohol (IPA). After initial testing, additional testing was performed to confirm the acceptability of a fifteen minute dry time on non-porous surfaces. All sample sets tested with a fifteen minute dry time are noted. All other sample sets were bonded after a thirty minute dry time. Several of the bond lines have no bond requirement. In these cases, hazards analyses assume there is no bond in these areas for various reasons. In these cases, close comparison to TCA became the requirement within this test plan. There are some cases where the average value for Reveille bond specimens is slightly lower than that of TCA. These tend to be in the noise level of the test, but have been evaluated individually. In the cases of K5NA/K5NA - 4 week, cork-Hypalon/K5NA - 4 week, Carbon Cloth Phenolic/RTV/Glass Cloth Phenolic - 4 week, Inconel/K5NA - 0 time and Rust-Oleum Primer/K5NA - 0 time, there was zero percent adhesive failure at the test interface. Therefore, any differences, large or small cannot be attributed to the cleaner but rather to material variability. The Rust-Oleum Paint/K5NA demonstrated negligible adhesive failure, less than ten percent, within that sample set. In the remaining cases, the difference in TCA and Reveille averages fell into one of the following categories, removing concern: 1) differences were within the noise level of the test and had strengths exceeding both the general requirement for K5NA of 100 psi and the general requirement for EA934 NA of 1000 psi by over three times, 2) there is no requirement for the bond, yet the specimens exceeded the general requirement for both K5NA of 100 psi and the general requirement for EA934 NA of 1000 psi by over three times. Compatibility data mentioned previously for EPDM showed that when immersed for 70 hours, Reveille was more harsh on this substrate than TCA. For this reason the EPDM/K5NA bond line was scrutinized more closely. One significant difference between TCA and Reveille bond specimens was the failure mode. All of the TCA specimens, both 0-time and 4-week failed exclusively at the test interface. Adhesive failures are generally undesirable. With the Reveille specimens, the 0-time had an average of 21% adhesive failure at the test interface for the 0-time specimens, while the 4-week specimens exhibited no adhesive failures at the test interface. While the Reveille specimens appear to be significantly stronger, since they did not fail primarily at the test interface, no statistical evaluation can be made to confirm statistical significance of the difference between the cleaners.

Bond Line		Hazards Req't, psi	TCA Results, psi	Reveille Results, psi
Cork/K5NA	0-Time 4-Week	50	149.1 145.1	154.6 (IPA) 158.1 (IPA)
K5NA/K5NA	0-Time 4-Week	100	514.7 308.6	538.7 268.7
EPDM/K5NA	0-Time 4-Week	100	390.9 367.3	525.0 409.9
Cork-Hypalon/K5NA (15 min dry)	0-Time 4-Week	50	195.7 212.2	201.3 200.5
Carbon Cloth Phenolic/RTV/ Glass Cloth Phenolic	0-Time 4-Week	0	160.0 137.9	161.5 131.8
Mild Steel/EA934 NA	0-Time 4-Week	0	1320.8 1858.2	2665.0 3027.8
Inconel/K5NA	0-Time 4-Week	0	695.9 562.8	681.7 547.9
Inconel/EA934 NA	0-Time 4-Week	0	4496.8 5149.0	3650.2 5047.0
Stainless Steel/K5NA	0-Time 4-Week	100	573.1 513.8	582.4 503.5
Chemlok 205-236A/K5NA	0-Time 4-Week	100	584.5 521.5	632.6 573.2
Rust-Oleum Primer/K5NA (15 min dry)	0-Time 4-Week	100	647.4 771.2	634.2 851.5
Rust-Oleum Primer/EA934 NA (15 min dry)	0-Time 4-Week	1000	2449.4 4472.8	2149.4 3449.6
Rust-Oleum Paint/K5NA (15 min dry)	0-Time 4-Week	100	580.2 816.1	633.1 998.2
Rust-Oleum Paint/EA934 NA (15 min dry)	0-Time 4-Week	1000	3599.8 5236.0	3391.0 4976.4

Table 4 - TCA and Reveille Button-to-Button Tensile Adhesion Results

PATTI tensile adhesion results are reported in Table 5. The cork substrate was prepared using isopropyl alcohol instead of Reveille for reasons stated previously. Reveille exceeds all requirements

by a factor of four to more than eighteen times. As with the previous tensile specimens, the engineering requirement for these bond lines are listed within the table. While Reveille does not always exceed the average TCA values, in every case, Reveille specimens displayed less adhesive failure at the test interface. Since both TCA and Reveille exceed the requirements significantly and they differ trivially, none of these bond lines present any concern.

Bond Line		Hazards Req't, psi	TCA Results, psi	Reveille Results, psi
K5NA/Hypalon Paint	0-Time 4-Week	100	711.4 862.7	630.2 835.7
Cork/Hypalon Paint	0-Time 4-Week	50	711.6 1166.8	711.2 (IPA) 922.6 (IPA)
D6AC Steel/Rust-Oleum Primer (15 min dry)	0-Time 4-Week	1000	3448.6 3823.0	4524.2 4406.4

Table 5 - TCA and Reveille TCA PATTI Tensile Adhesion Results

CONCLUSIONS

Reveille was comparable to or better than TCA in respect to compatibility for all non-metallic substrates tested except two, EPDM and teflon tape. These are discussed in detail in the "RESULTS" section. Reveille does appear to be acceptable despite these results for use on both EPDM and teflon tape. Reveille was comparable to or better than TCA in regard to affects the cleaners have on painted surfaces. TCA and Reveille were statistically comparable in respect to corrosive effects on metallic surfaces. Neither TCA or Reveille produced detectable corrosion. Dry times on all substrates were thirty minutes or less, causing no effect on KSC processing time lines. On non-porous surfaces acceptable dry times were demonstrated at fifteen minutes.

Reveille was an acceptable non-ODC cleaner for preparing all non-cork surfaces for bonding. Isopropyl alcohol was an acceptable non-ODC cleaner for preparing all cork surfaces for bonding. Subsequent bond strength of systems cleaned with Reveille, or isopropyl alcohol in the case of cork, exceeded all engineering requirements and were comparable with TCA.

The selection and use of Reveille in RSRM hand wipe operations at KSC supports the mutual commitment of Thiokol/RSRM and USBI/SRB to jointly implement common replacement cleaners to the maximum extent possible. This ensures minimum inventory, minimum waste streams, economy of

scale in purchasing, and minimizes the risk technicians will inadvertently employ the wrong cleaning chemical.

ACKNOWLEDGEMENTS

This paper is the result of a large effort put forth by many people. This team determined testing requirements, made USBI test data available, conducted necessary testing, reported testing, worked on training input and supported implementation of cleaners at KSC. The team was a group comprised of NASA, USBI and Thiokol employees. NASA team members included Leigh Key and Darrell DeWeese from MSFC; Cathy Clayton and Lori White from USBI; Russ Bakes, Lance Christopherson and Blake Bradford from Thiokol in Utah; Chet Cooper and Jeff Cook from Thiokol at KSC; and Frank Smith from Huntsville Space Ops (HSO) Quality, Becky Brown and Scott Taylor from HSO testing, and especially Tony Thornton and Charlie Davis who prepared all of the bond specimens and conducted the compatibility, corrosion, paint compatibility and dry time testing; consistently did things right the first time and were proactive and alert enough to catch engineering mistakes.

CLEANING: VERIFICATION AND INSTRUMENTATION—I

Elimination of Ozone Depleting Chemicals - Cleanliness Verification Alternatives

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ABSTRACT

Historically, cleanliness verification of Space Shuttle Main Engine (SSME) hardware was primarily performed by flushing the hardware with 1,1,1-trichloroethane or other ozone depleting solvents. An aliquot of the flush solvent was filtered and analyzed for nonvolatile residue and particulate matter. Due to environmental regulations, the use of 1,1,1-trichloroethane has been eliminated at Rocketdyne. Two methods have been selected for nonvolatile residue determination which do not require the use of ozone depleting chemicals, an aqueous method that utilizes total organic carbon analysis and a gravimetric cyclohexane technique. An aqueous method has been selected to replace solvent techniques for particulate analysis. Laboratory qualification testing has been completed using hardware and contaminants representative of those encountered in production. The transition from research and development to full production implementation has been completed and the particulate and nonvolatile residue techniques are currently being utilized in manufacturing processes.

BACKGROUND

1,1,1-Trichloroethane (TCA) is an ozone depleting compound and was banned from manufacture in December 1995. In the past, TCA was the solvent primarily used for cleanliness verification of rocket engine hardware. After flushing critical hardware surfaces, an aliquot of the final flush solvent was collected, filtered for particulate analyses and gravimetrically analyzed for nonvolatile residue (NVR). Rocketdyne's goal was to have alternate cleanliness verification procedures implemented by January 1996. Two NVR replacement methods were selected for qualification testing - an aqueous method and a cyclohexane solvent method.

The aqueous method was adapted from a NASA-KSC method utilizing a total organic carbon analyzer (TOCA). The hardware is ultrasonically agitated in heated deionized water and an aliquot of the water injected into the TOCA for determination of carbon content. Laboratory testing determined this method was acceptable for Rocketdyne applications. Further testing was required on hardware to demonstrate feasibility and to qualify the technique for production use.

Solvent methods were evaluated for use where the aqueous method was not viable - e.g., large hardware or items damaged by ultrasonic agitation. The ideal solvent would be a non-ozone depleting compound readily available in high purity and have high volatility, low residue after evaporation, and an exposure limit greater than 100 ppm. After researching the available literature, a list of candidate chemicals was compiled. These chemicals were tested for NVR content and the ability to remove contaminants typically used at Rocketdyne. The three top performing solvents were cyclohexane, ethyl acetate and HCFC 225. (HCFC 225 was heated to 100°F in order to increase its cleaning capabilities). The HCFC 225 solvent was eliminated because of its high toxicity and also because it is classified as an ozone depleting compound (ODC). Ethyl acetate was eliminated because it did not have high solubility for waxes and greases. Cyclohexane showed cleaning efficiencies similar to TCA for the contaminants tested and was selected as the most viable candidate to replace TCA for solvent cleanliness verification processes.

With the aqueous precision cleaning techniques already implemented, it was logical to investigate an aqueous method for particulate verification. This method consists of collecting 500 ml of the final deionized water used to rinse the part. The water is filtered and the filter media analyzed for particulate matter. As with the NVR replacement techniques, the next phase would be hardware level testing to show feasibility and to qualify this method.

TEST PROCEDURES

NVR Verification Testing

Qualification testing of each proposed method was performed per the guidelines of MSFC-SPEC-164 Rev. B. Hardware-scale testing was conducted to compare the accuracy of the proposed methods of cleanliness verification with the previously used TCA method. Test hardware was contaminated with typical manufacturing soils and was then verified by the aqueous method, the cyclohexane flush method, and the TCA flush method.

Test hardware (Table 1) was selected to represent a variety of sizes, configurations and materials. Photographs of several hardware pieces are shown in Figures 1 and 2.

Test Item	Part Number	Material	Surface Area (sq. ft.)
High Pressure Fittings (38 total)	N/A	300 Series CRES	1.0
GOX Control Valve Housing	RS010142	Inconel 718	0.8
Pogo Baffle	N/A	Inconel 625	1.7
Main Injector Body Section	RS009138	Inconel 718	0.5
HPFTP Rotor Seal	RS007592	Haynes 188, A286	1.8
Valve Shaft Assembly	RS008262	Inconel 718	0.8
HPOTP Inlet Vane	RS007743	K-Monel	1.8
Pogo Z Baffle Assembly	G1R0012666	Inconel 718 Casting,	3.7
HPOTP Jet Ring	RS007757	A286, 347 CRES, Nickel	0.9
HPOTP Turbine Nozzle	RS007750	MAR-M-246 Casting	2.1
Flexible Line Assembly	RES1222	Inconel 625/718	1.4
Pneumatic Control Assembly	R0019451	Anodized 7075 Aluminum	5.0

Table 1. Test Hardware

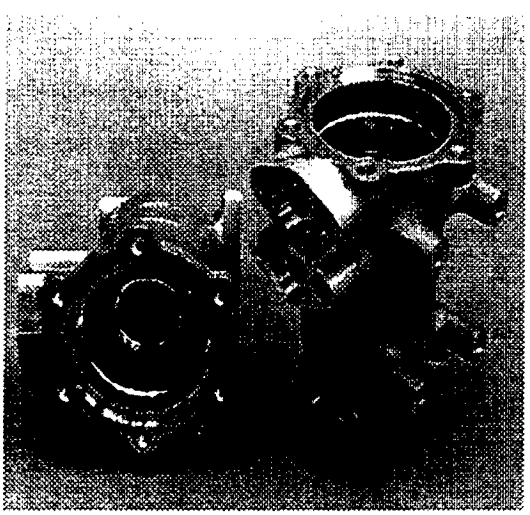

Figure 1. Gox Control Valve Housing

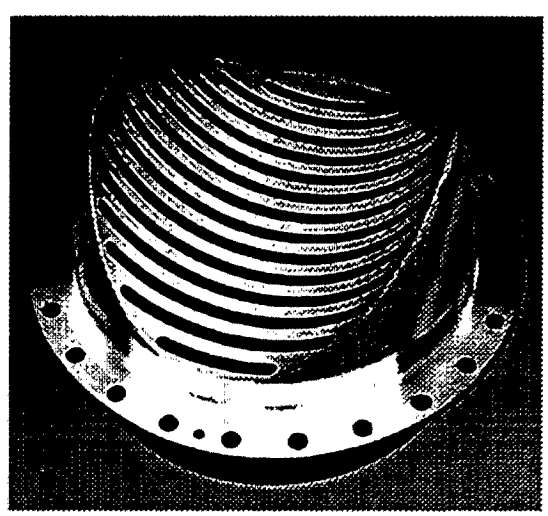

Figure 2. Pogo Z Baffle Assembly

Soils used during test included single component contaminants (Table 2) and a contaminant mixture comprised of the following:

22 wt. %	Cool Tool	22 wt. %	MIL-H-83282 Hydraulic Fluid
22 wt. %	Centerpoint Lube	22 wt. %	Preservative Oil
4 wt. %	IIa Dye Penetrant	4 wt. %	Turco 4215 Additive
4 wt. %	IVc Dye Penetrant		

Contaminant	Description
Cool Tool Monroe Fluid Technology	Hand-applied cutting & tapping fluid containing paraffinic oil
MIL-H-83282 Hydraulic Fluid Bray Oil Co.	Synthetic hydrocarbon hydraulic fluid containing triphenyl phosphate
Rust Foil L-492 Preservative Oil Franklin Oil Co.	Solvent-dispersed corrosion preventive compound containing aliphatic hydrocarbons and mineral oil
Centerpoint Lube Chicago Manufacturing & Distributing Co.	High viscosity, grease-like extreme pressure machining lubricant containing petroleum oil, wax, and rosin ester
Turco 4215 Additive Turco Products	Nonionic detergent containing diethylene glycol monobutyl ether and nonylphenoxypoly (ethyleneoxy) ethanol
Bio-Pen P6F-4 (IVc Dye Penetrant) Ardrox Inc.	Fluorescent, water-washable dye penetrant
Bio-Pen P6R (IIa Dye Penetrant) Ardrox Inc.	Detergent-based, visible, solvent-removable dye penetrant

Table 2. Contaminant Descriptions

Single contaminant tests were performed to establish the capability and variation of each technique. Final qualification tests were performed using the contaminant mixture and a broader range of hardware. Specific hardware selected for tests were based upon the limitations of the verification technique - e.g., the aqueous method is only intended to be used on moderate sized hardware due to the limitations in the sensitivity of the TOC analysis. However, there is no size limitation with the use of cyclohexane and larger hardware could be included. All of the hardware was verified with the TCA technique to provide a baseline. Testing was repeated to obtain a minimum of five replicates per condition. The test matrix used is shown in Table 3.

Hardware	Contaminant	Number of Test Runs		
		Aqueous TOC	TCA NVR	Cyclohexane NVR
Gox Control Valve	Cool Tool	5	5	3
	MIL-H-83282	4	3	3
	Mixture	8	5	5
Pogo Baffle	Preservative Oil	3	5	3
High Pressure Fittings	Cool Tool	4	5	3
Main Injector Body Section	IVc Dye Penetrant	3	5	4
HPFTP Rotor Seal	Turco 4215A	3	5	3
Valve Shaft Assembly	Mixture	7	5	-
Pnuematic Control Assembly	Mixture	-	5	5
Flexible Line Assembly	Mixture	-	5	5
Pogo Z Baffle Assembly	Mixture	7	5	5
HPOTP Inlet Turning Vane	Mixture	7	5	-
HPOTP Turbine Nozzle	Mixture	-	5	5
HPOTP Jet Ring Assembly	Mixture	7	6	-

Table 3. NVR Test Matrix

Hardware Preparation - Hardware was initially cleaned and verified, and then contaminated with approximately 0.5 to 10 mg of contaminant per square foot of hardware surface area. The contaminant was placed in locations where residues would be likely to remain after a cleaning operation, such as threaded holes, dead-end cavities, small orifices and internal surfaces. The hardware was then heated at 200°F for 2 hours to remove any volatile constituents, allowed to cool to room temperature and analyzed for NVR by one of the following techniques. Hardware contaminated with Cool Tool and IVc Dye Penetrant was not heated due to the low volatility of these contaminants.

TCA Nonvolatile Residue Analysis - The surfaces of the contaminated hardware were flushed with 500 ml of TCA. The solvent was collected, filtered and a gravimetric NVR performed by evaporating the TCA to a volume of 10 - 20 milliliters using a rotary evaporator or steam bath. The solvent was then transferred to a constant weight container which had been pre-weighed to the nearest 0.1 mg. The pan was placed in a constant temperature oven set at 221 to 230 °F and heated for 1.5 hours. It was then cooled to room temperature, weighed and returned to the oven for 30 minutes. These steps were repeated until a constant weight (less than 0.3 mg difference) was obtained. The initial container weight was subtracted from the final weight to obtain the measured NVR. The measured NVR value was adjusted by subtracting the NVR of an equivalent amount of unused solvent. The resulting value is the NVR reported.

Cyclohexane Nonvolatile Residue Analysis - Verification using cyclohexane was performed using a method similar to the TCA method. The only exception was that the final oven drying temperature used during the analysis was lowered to a range of 185 to 195°F. The standard drying temperature specified for the TCA method is 221 to 230°F. Use of this elevated drying temperature with cyclohexane causes excessive evaporation of the contaminant residue. This was verified by performing gravimetric NVR analysis using each of the two drying temperatures on standard solutions of contaminants in cyclohexane. Results showed lower drying temperature provided the more accurate results.

Aqueous TOC Nonvolatile Residue Analysis - Aqueous verification was performed by ultrasonic agitation of the part in deionized water and analysis of the water for total organic carbon content. A stainless steel container, the smallest size available which would accommodate the part, was ultrasonically cleaned. The pan was filled with deionized water which had been filtered through activated charcoal to remove residual organics. The pan was suspended in a Blackstone 25 kHz ultrasonic bath which had been heated to 125°F. After the water temperature reached 125°F, the ultrasonics were activated for 10 minutes and a 200 µl sample of the water withdrawn using a 250µl syringe. The sample was injected into a Rosemount/Dohrmann DC-190 High Temperature Combustion Total Organic Carbon Analyzer (TOCA), and the total carbon content was measured and verified to be less than 0.5 mg/liter.

The contaminated hardware was then placed in the filled stainless steel pan and allowed to heat for approximately 10 minutes until the part and water temperature equilibrated. The part was ultrasonically agitated for 10 minutes, minimum. Larger, more complex parts were agitated for 10 minutes, inverted, and agitated for an additional 10 minutes. A minimum of three separate samples were analyzed for TOC and the average value recorded. The volume of water in the stainless steel pan was measured and the equivalent NVR calculated as follows:

$$NVR = \frac{TOC \times V}{Cc}$$

Where: NVR = nonvolatile residue, mg
TOC = total organic carbon of sample, ppm or mg/liter

V= volume of water, liters
Cc = organic carbon fraction of the residue
(mg TOC / total mg contaminant)
= 0.59 for Cool Tool
= 0.61 for Turco 4215 Additive
= 0.66 for Centerpoint Lube
= 0.71 for Hydraulic Fluid
= 0.72 for Dye Penetrant
= 0.74 for Preservative Oil
= 0.68 for Contaminant Mixture

Cc is the weight fraction of organic carbon in a given material. If the weight fraction of organic carbon in a material is known, then the total concentration of the material in solution can be determined from the measured TOC.

To determine the carbon content of the test contaminants, standard solutions were prepared over the range of 1 to 10 mg contaminant/liter of water. The TOC of each solution was measured and plotted against the solution concentration. A regression analysis was performed to fit the data to the equation of the form y = mx. The value of m is the carbon weight fraction of the contaminant or Cc. The Cc of the contaminant mixture was calculated by a weighted average of the single component carbon contents.

Particulate Verification Testing

Nine pieces of hardware of varying size and complexity were selected for particulate verification testing (Table 5). See Figures 3 and 4 for photographs of several of these pieces. Verification was performed using the current TCA method and the proposed aqueous method. Wherever possible, hardware was obtained in duplicate to allow for testing in parallel. In this way verification using each method (TCA and aqueous) would be performed on hardware which was subjected to nearly identical cleaning processes and environmental conditions.

Test Item	TCA Method # Test Runs	Water Method # Test Runs
Injector Post	6	6
Flexible Line Assembly	6	6
Main Propellant Valve Actuator Cylinder	6	6
Main Oxidizer Gate Valve Cylinder	6	6
HPOTP Inlet Turning Vane	5	5
GOX Control Valve Housing	5	5
Inducer Casting	5	5
Main Combustion Chamber	2	4
HPOTP Turbine Nozzle	5	5

Table 5. Particulate Analysis Test Matrix

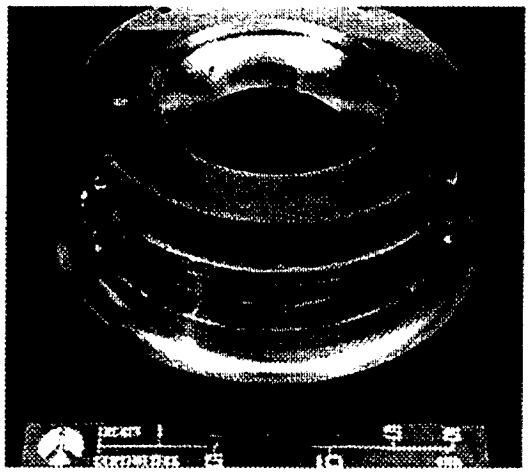

Figure 3. HPOT Inlet Turning Vane

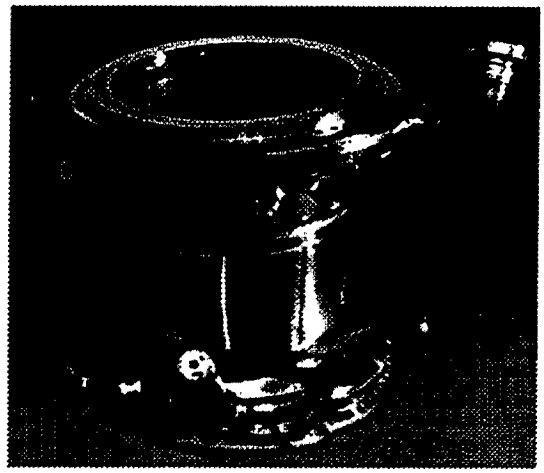

Figure 4. Main Combustion Chamber

The hardware was precleaned in an aqueous parts washer with Turco 4215NC-LT at 150° F, rinsed with a deionized water spray at 120° F and oven dried at 160 °F in an air circulating oven. The hardware was not precision cleaned in order to ensure the presence of particulate matter for quantitative data collection. Verification was performed by flushing the hardware with 500 ml of deionized water or TCA, collecting all of the fluid, filtering through a 0.45μ filter and analyzing the filter media for particulates in two size ranges, 400 - 800μ and greater than 800μ. These ranges were chosen based upon the particulate cleanliness requirements for the SSME.

RESULTS

NVR Results

The accuracy of each NVR cleanliness verification method was assessed by calculating the fraction of the contaminant detected. This normalizes the data to allow a comparison among the three methods.

$$\text{Fraction of contaminant detected} = \frac{\text{measured NVR (mg)}}{\text{amount contaminant placed on part (mg)}}$$

The fraction of contaminant detected for each of the tests performed using the single component contaminants is presented in Figure 5. As shown, some values in excess of 1.0 were obtained, indicating that the measured NVR was slightly higher than the amount of contamination placed on the part. This is attributed to the inherent variability of each of the analytical techniques and in general, represents absolute variations on the order of a fraction of a milligram.

The average detection capability and standard deviation were calculated for each method. In calculating the average, all values greater than 1.0 were set equal to 1.0 to avoid skewing the average. However, the standard deviation was calculated using the actual data to show the variability of each technique. As shown in Figure 5, both the aqueous method and the cyclohexane method were 83% effective in detecting the contaminants. The baseline TCA method was 82% effective. The standard deviations of the aqueous and cyclohexane methods were equivalent to or slightly less than that of the TCA method.

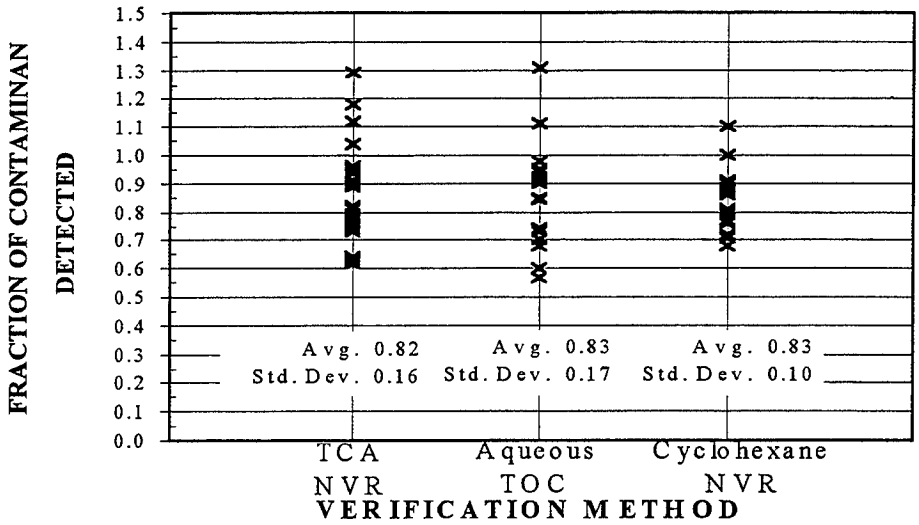

Figure 5. Comparison of Verification Techniques Using Hardware Contaminated With Single Component Contaminants

The results of the testing performed with the contamination mixture are shown in Figures 6 and 7. For the particular hardware tested, the aqueous method showed a 91% detection capability and a standard deviation of 0.10 as compared to an 88% detection capability and a standard deviation of 0.22 for the TCA verification method. The cyclohexane method showed an 89% detection capability and a standard deviation of 0.13 as compared to an 89% detection capability and a standard deviation of 0.31 for the TCA method.

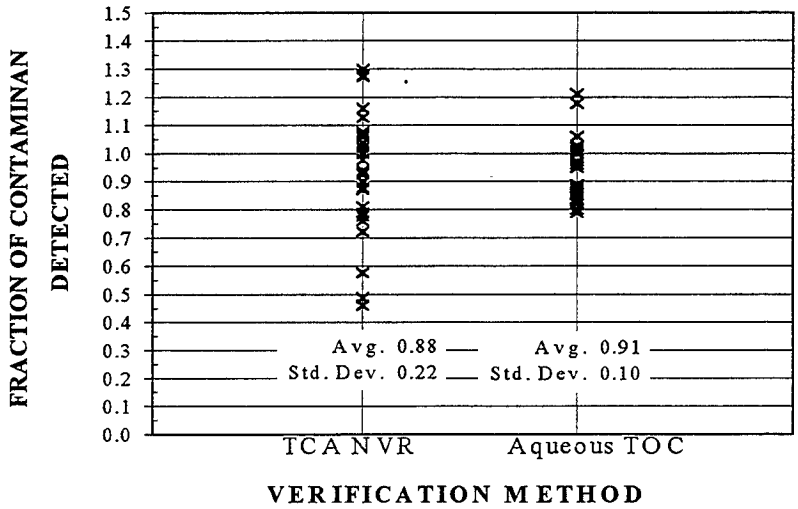

Figure 6. Comparison of Aqueous Verification Method to TCA Verification Method Using Hardware Contaminated with Mixture

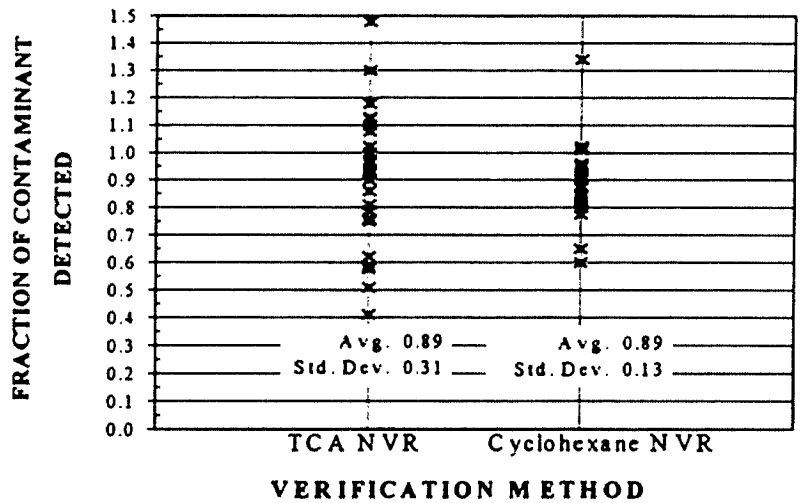

Figure 7. Comparison of Cyclohexane Verification Method to TCA Verification Method Using Hardware Contaminated with Mixture

Particulate Results

Particulate data was analyzed by combining the results for each hardware type and by combining the results for all hardware tests. The cumulative number of particles detected for all hardware tests are shown in Figure 8 and the results for tests conducted with the Main Combustion Chamber and the High Pressure Oxygen Turbopump (HPOTP) Inlet Turning Vane are shown in Figures 9 and 10. As shown, water is just as efficient as TCA for removing particulates in the size range of interest for SSME requirements. Examination of the individual hardware runs showed that in only one case (one test item) did the TCA remove a larger number of particulates than the water. In this case the difference was not significant; the TCA removed only one more particle on average in each size range.

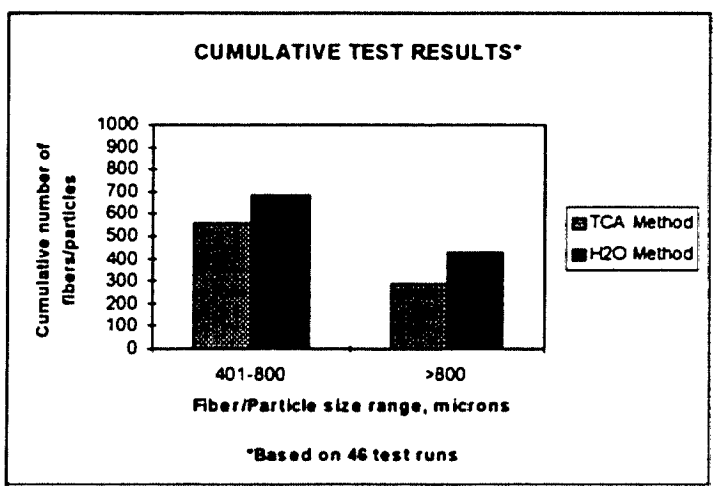

Figure 8. Cumulative Test Results of Particulate Verification Testing

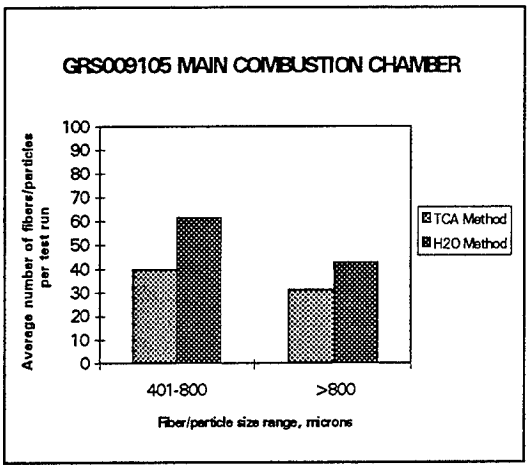

Figure 9. Particulate Test Results for Main Combustion Chamber

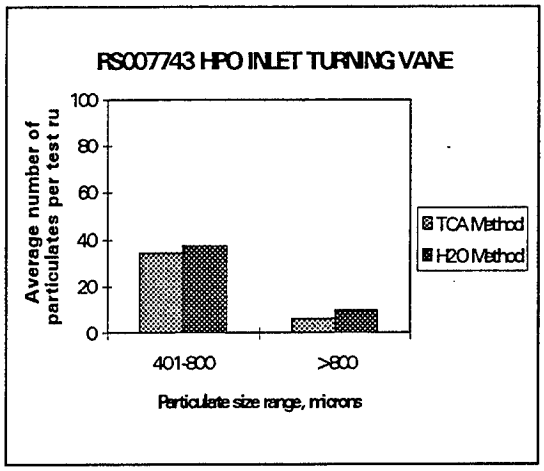

Figure 10. Particulate Results for HPOTP Inlet Turning Vane

DISCUSSION

Based upon the testing performed, it has been demonstrated that the TOC aqueous method and the cyclohexane solvent method are as accurate and show equivalent or less variation than the previously utilized TCA method for NVR cleanliness verification. However, each of the new verification methods has certain limitations. Only moderately sized hardware can be verified using the aqueous method due to the detection limits of the TOCA. The size limitation is approximately 12" x 12". Hardware containing dry film lubricants cannot be subjected to the ultrasonic agitation as it is detrimental to the coatings. Based upon a separate study of the effects of ultrasonic agitation on aluminum, bare aluminum should not be verified using the aqueous method. It is acceptable to use this method on anodized or chem filmed aluminum provided the exposure duration does not exceed 10 minutes. Finally, the aqueous method was not sufficiently developed to detect silicone greases, fluorinated greases or paraffin waxes.

The cyclohexane method should not be used on hardware containing non-metallics such as neoprene, silicone, butyl or ethylene propylene elastomers due to material degradation by the solvent. Cyclohexane, as well as the previously used TCA method, is not effective for detecting silicone greases or fluorinated greases. Cyclohexane is flammable and classified as a VOC. Therefore special precautions must be taken while handling this material to conform to safety and environmental restrictions. Finally, cyclohexane is incompatible with oxidizers and every precaution must be taken to ensure oxidizer hardware is adequately dried.

In this study, TCA and water yielded comparable results for particulate verification of SSME hardware. Based upon these results, aqueous particulate verification was proven to be an acceptable alternative to the previous TCA method. In addition to the obvious advantages of utilizing water to flush the hardware, (i.e.- low cost, convenience, safety), the aqueous method allows for sampling at the end of the cleaning process and eliminates the need for an intermediate drying step prior to particulate verification. This offers a verification process which is faster and more convenient. However, additional tests may be required to qualify the use of water for systems with particulate requirements differing from that of SSME.

IMPLEMENTATION

The proposed verification techniques were approved by NASA-MSFC and the process of implementation was initiated. The implementation process consisted of training manufacturing personnel

with the new techniques and instrumentation, changing applicable documents and installing specialized equipment.

Aqueous Particulate Verification

Particulate verification was easily implemented as hardware is predominantly precision cleaned by aqueous methods. At the conclusion of the cleaning operation, a final DI rinse is performed and a 500 ml sample is collected for particulate verification. No additional equipment was required for implementation of this method.

Aqueous NVR Verification

The TOCA was relocated from the experimental laboratory to the production precision cleaning facility. The system required some modifications to become compatible with the clean room environment. An air compressor was purchased and connected to a TOC gas generator to replace the compressed air bottle previously used in the laboratory. A custom acrylic enclosure was built for the TOCA printer to reduce fiber generation from the printer paper. Manufacturing inspection personnel received extensive hands-on training from laboratory personnel to become adept in the operation of the TOCA system.

Hardware verified by aqueous/TOC method is analyzed immediately after particulate verification. This eliminates an intermediate drying step that is required if solvent verification is performed. If either method can be used, the aqueous method of verification is the preferred technique.

The TOC analysis is performed as outlined in the testing procedures discussed earlier. The hardware is placed in a clean sampling pan filled with the approximate amount of water needed to completely cover the hardware. To reliably detect an NVR level of 1 mg/sq. ft., the maximum water volume to surface area ratio is 3 liters / sq. ft. The hardware is positioned in the sampling pan so dead openings are faced upward and no openings are closed off by the sampling pan. Hardware with critical surfaces may be protected using a Teflon screen placed between the hardware and the sampling pan. After reaching temperature equilibrium, the hardware is ultrasonically agitated for 10 minutes. Larger and more complex pieces of hardware may require rotation and additional ultrasonic agitation. Sample volumes of 200 microliters are injected into the TOCA and the average TC reading is recorded. The volume of water used in the sampling pan is measured using a graduated cylinder. The NVR is calculated as detailed earlier using a Cc value of 0.68, which is a conservative value of the weight fraction of organic carbon in shop contaminants typically used at Rocketdyne.

Solvent NVR Verification

Implementation of the use of cyclohexane required special consideration because cyclohexane is flammable and classified as a VOC. Verification using this technique requires special equipment to ensure safe handling and compliance with environmental regulations. Every effort was made to provide a safe and efficient means of verification using the cyclohexane method. Hardware selected for solvent verification must be dried before flushing with cyclohexane. After the hardware has been dried and cooled to room temperature, it is placed in the cyclohexane flushing system for sampling. (Because of the additional drying step involved and the required safety procedures, this method requires more time for completion than other techniques.) The hardware is flushed with 500 ml of cyclohexane and a gravimetric NVR is performed. Cyclohexane is not compatible with oxidizers and special precautions are taken to ensure hardware is adequately dried. Currently, all hardware flushed with cyclohexane is subsequently exposed to a vacuum oven drying process. After the final drying procedure, a hydrocarbon analyzer is used to determine if any residual cyclohexane remains on the hardware.

Glove Box Flushing System

A flushing system (Figure 11) was fabricated to provide an inert atmosphere for flushing hardware with cyclohexane. The system minimizes personnel exposure to cyclohexane vapors and eliminates potential fire hazards. The flushing system is similar in operation to an ordinary glove box. Gaseous nitrogen is used as a purge gas and also as a pressurant to pump solvent through the system. An additional nitrogen line aids in drying the hardware and the interior of the box after flushing is complete.

An oxygen analyzer monitors the oxygen content inside the system. The analyzer is coupled to an automatic valve which restricts cyclohexane flow when the oxygen content inside the system exceeds 5.0 %. The box can accommodate hardware up to approximately 3 feet in length. Hardware exceeding this limit is verified using a handwipe method.

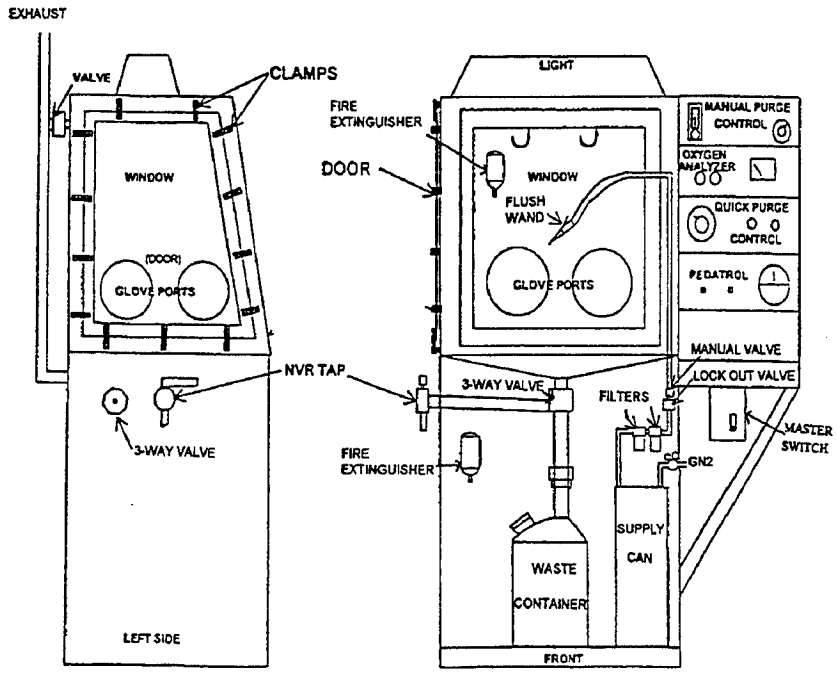

Figure 11. Glove Box Flushing System

The upper portion of the system contains the flushing area where hardware is placed for verification sampling. Cyclohexane is filtered through 5 and 10 micron filters prior to contact with the hardware. The solvent can be sprayed through one of several wand tip designs to accommodate specific hardware configurations. A three way valve allows the solvent to flow directly into the waste container or into the sampling port.

The cabinet beneath the flushing area also contains a nitrogen atmosphere during glove box operation. The cabinet contains two 5 gallon capacity stainless steel canisters - a solvent waste container and a pressurized solvent supply container. These canisters are designed for easy installation and removal using quick disconnect fittings. The bottom of the cabinet contains a catch basin for retaining solvent in the event of a spill.

Line Flushing System

A separate flushing system was developed to accommodate propellant and pneumatic lines that could not be verified in the glove box due to size limitations. (See Figure 12). This system is used for lines with an inside diameter of 0.5 inch or less. Lines having a larger inside diameter are verified using a handwipe method. The system consists of an inlet and outlet manifold with a selection of threaded connections available in varying sizes for installation of the lines. The solvent is pumped from a stainless steel supply can, through the lines, and directly into a clean sampling flask using an OmniSpense Dispenser equipped with a systolic pump. The cyclohexane is immediately analyzed for gravimetric NVR. After flushing with solvent, the hardware line is purged with gaseous nitrogen which is vented outside the room. A series of valves control the flow of cyclohexane and nitrogen through the system.

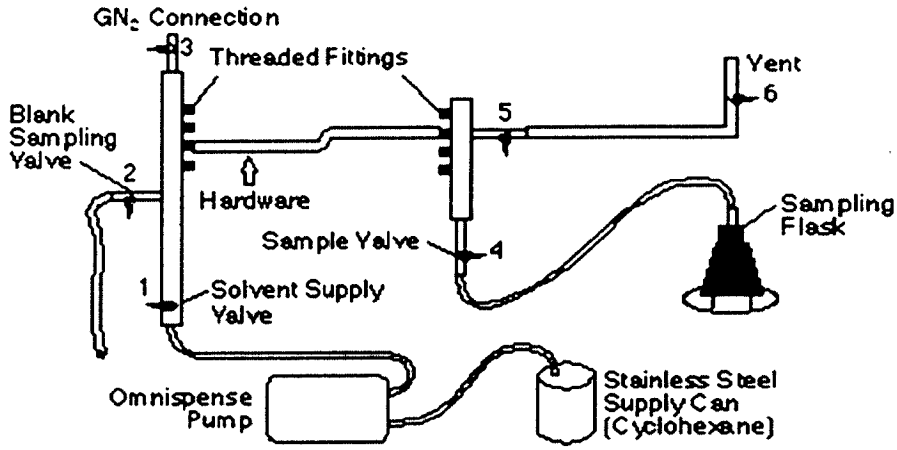

Figure 12. Line Flushing System

Handwipe Cleanliness Verification

A handwipe cleanliness verification method was developed for hardware that cannot be verified by the aqueous or cyclohexane method due to size limitations or material incompatibility. Hardware is wiped with a non-linting polyester cloth or swab which has been dampened with distilled grade cyclohexane. The residue on the cloths or swabs is extracted with cyclohexane using ultrasonic agitation or a Soxhlet extractor. The solvent is then analyzed by gravimetric NVR or quantitative infrared hydrocarbon analysis.

CONCLUSIONS

The verification techniques selected to replace the TCA methods of verification have been through laboratory evaluation, hardware-scale demonstration, qualification testing and production implementation. These methods have been shown to be equivalent to the previously used techniques for NVR and particulate verification for Rocketdyne applications. These methods are successfully being utilized on a day-to-day basis in the manufacturing processes at Rocketdyne.

ACKNOWLEDGMENTS

Gene Morgan, Bud Simpson and Bill Hoult were responsible for the design, fabrication and installation of specialized equipment required for successful implementation of the techniques. Special thanks to Susan Stern for providing the particulate test data. The authors also wish to thank Susan Lim, Ray Skowronski, Mary Maseda, Steve Klee, Margarite Sylvia, Sonya Reid and Carole Elm for their diligent efforts in completing all the required testing in support of this project.

THE USE OF HFC (CFC FREE) PROCESSES AT THE NASA STENNIS SPACE CENTER

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Sciences Laboratory

ABSTRACT

The search for ozone depleting alternative chemicals was heightened when, in 1990, the more than 65 countries that had signed the Montreal Protocol agreed to phase out CFCs completely by the year 2000. In 1992, then-president Bush advanced this date for the United States to January 1, 1996. In 1991, it was realized that the planned phase out and eventual elimination of ozone depleting chemicals imposed by the Montreal Protocol and the resulting Clean Air Act (CAA) amendments would impact the cleaning and testing of aerospace hardware at the NASA Stennis Space Center. Because of this regulation, the Test & Engineering Sciences Laboratory has been working on solvent conversion studies to replace CFC-113.

Aerospace hardware and test equipment used in rocket propulsion systems require extreme cleanliness levels to function and maintain their integrity. Because the cleanliness of aerospace hardware will be affected by the elimination of CFC-113; alternate cleaning technologies, including the use of fluorinated solvents have been studied as potential replacements. Several aqueous processes have been identified for cleaning moderately sized components. However, no known aqueous alternative exists for cleaning and validating T&ME and complex geometry based hardware. This paper discusses the choices and the methodologies that were used to screen potential alternatives to CFC-113.

BACKGROUND

Over the last 20 years, CFC-113 has emerged as the workhorse solvent for cold cleaning components/hardware and propellant (gas and cryogenic) systems for NASA. This was due to a combination of factors, but primarily because it was considered the safest and the most environmentally benign of the chlorinated solvents. As a result of increasing regulations we are faced with the pressure to evaluate new solvent chemistries and to accomplish the same surface cleanliness without incurring regulatory burdens.

Hydrochlorofluorocarbons (HCFCs) were initially proposed as possible substitutes for CFCs, because as a class, these chemicals have a lower ozone depleting potential than CFCs. The EPA, however, has classified HCFCs as an interim alternative that will also be phased out, and some HCFCs have been found to be potentially carcinogenic. Next, a number of perfluorocarbons (PFCs) were developed as replacements for CFCs, but the EPA has condemned these compounds as potential contributors to global warming because of their extremely long degradation times. In addition, PFCs have high boiling points and may co-distill contaminants during Non Volatile Residue (NVR) determination, resulting in a false positive NVR.

Volatile Organic Compounds (VOCs) are highly regulated under the CAA and describes a class of compounds that break down quickly after being released into the atmosphere and contributes to ground level smog. Cyclohexane, toluene, and hydrocarbon blends have been re-labeled as substitutes for ozone depleting solvents. These are VOCs with their own environmental and health concerns.

A drop-in replacement solvent might be the ultimate goal, but the reality is something quite different. Almost all substitutions tend to be application specific or require some modification in the process. Alternatives must be able to not only effectively remove soils, but they must also fit into the regulatory framework.

Solvents for CFC conversion must be responsive to the following:

- Ability to remove contaminants (good solvency with oil, greases, and particulates)
- Not implicated in ozone depletion
- Low global warming potential
- VOCs
- Flammability and compatibility with oxygen systems
- Low toxicity
- Fast drying time
- Material compatibility (i.e. corrosion, absorption and etc.)

The ability (drying time) of the solvent to remove itself from the hardware is important for the cleaning of T&ME (pressure gauges, transducers, flowmeters...etc.). The difficulty in incorporating aqueous cleaning processes for T&ME, which have complex shapes and negative geometries (cavities, crevices, orifices and blind holes) is that water is not easily removed. A primary risk to be concerned with is component corrosion. This is brought about by the aggressiveness of DI water to re-ionize itself. The DI water is very unstable in the deionized state and wants to revert back to the ionic state. Experience has shown that DI water has reacted to various metals and platings; some almost instanteously, and some in a time dependent basis. Some corrosion by products are metal oxides and hydroxides which may have a determinal effect on the component.

Another concern is the removal of the surfactants and other additives (i.e. saponifiers, deflocculants, anti-foaming agents...etc.) that are used to increase the cleaning capabilties of the DI water. The surfactant and/or the additives may concentrate in small cavities and ignite in oxidizer systems.

APPROACH

A gravimetric experiment was designed to evaluate the contaminant removal efficiency of the candidate solvents. The goal during the selection of contaminants was to find representative substances that are difficult to remove during component cleaning. The contaminants used in this study represent a wide array of contaminant types and were chosen based on discussions with Lockheed Martin, Rocketdyne, Johnson Control, and GB Tech personnel. Environmental, toxicity, and physical property testing were not performed. Rather, candidate solvents were

selected for testing after reviewing the EPA regulations, vendor literature and meetings with personnel from SSC,WSTF, KSC and Rocketdyne.

Regulations reviewed were:

> Significant New Alternatives Policy (SNAP). SNAP under Title VI of the CAA is intended to expedite movement away from ozone depleting compounds. It empowers the EPA to identify and restrict chemicals that contribute to ozone depletion or global warming. They have ranked many of the traditional aqueous, semi aqueous, and hydrocarbon solvents acceptable within certain guideline restrictions.
>
> National Emission Standards for Hazardous Air Pollutants (NESHAPs). Title III of the CAA establishes the NESHAP program. NESHAP lists 189 Hazardous Air Pollutants (HAPs). Typical HAPs include TCA, perchloroethylene, trichoroethylene (TCE), methylene chloride, certain glycol ethers, MEK and MIBK. This program requires extensive reporting and record keeping requirements.

The solvents selected included an HFC and a new HCFC. The experimental process was benchmarked to CFC-113 to determine the cleaning effectiveness of the candidate solvents. The types of metals used in the test hardware include stainless steel, brass and phosphorus-bronze. Many of the hardware parts have blind holes and internal cavities that are difficult to clean and dry.

SOLVENT STUDY

Solvent Selection

Solvent selection is dependant on a number of parameters and was evaluated against the acceptance criteria. The solvent down select parameters and associated criteria is summarized below.

Down Select Summary

Parameter	Tests Performed	Criteria
NVR Removal Efficiency	Gravimetric	75% Efficiency
Flammability	Literature	Nonflammable
Environmental	SNAP/ No HAPs	EPA Approval
Material Compatibility	Literature	Technical Data
Oxygen Compatibility	Impact	No reaction
Physical Properties	Literature	Technical Data
Toxicity	Literature	MSDS Data

Test Solvents

The physical properties and the environmental and safety features for the solvents that were tested are listed in Table 1 and 2 respectively. The tables also served as a selection matrix to assess the down select parameters for each solvent. Three solvents were selected as potential candidates and were compared to the control solvent CFC-113. The solvents investigated are: (1) A mixture of 45% 3,3,-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225-ca isomer) and 55% 1,3,dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225-cb isomer); the mixture is referred to as HCFC-225, (2) 1,1,1,2,3,4,4,5,5,5 decafluoropentane known as HFC 43-10mee (Vertrel XF®), (3) and an azeotropic mixture of 62% HFC43-10mee and 38% trans-1,2-dichloroethylene known as HFC 43-10mee / 38% DCE (Vertrel MCA®). The Vertrel MCA® solvent used in this study did not contain nitromethane as a stabilizer.

After reviewing the physical properties and the environmental and safety features, a qualitative judgement was made to test all candidate solvents. HFC 43-10mee was eliminated during the preliminary NVR testing because it removed only 44% of the NVR. The criteria for NVR removal efficiency was 75%.

Table 1

PHYSICAL PROPERTIES

Properties	CFC-113 (Control)	HCFC-225	HFC 43-10mee	HFC 43-10mee / 38% DCE
Boiling Point (°C)	47.6	54	55	39
Density (g/cc, @ 25°C)	1.57	1.55	1.58	1.41
Viscosity (cps, @ 25°C)	0.68	0.03	0.67	0.66
Vapor Pressure (mmHg, @ 25°C)	336	283	226	464
Flash Point (O°C)	None	None	None	None
Surface Tension (dynes/cm)	17.3	17	14.1	15.2
LOX Impact Reactions (WSTF) n=20	0/20	0/20	0/20	0/20
Latent Heat of Vapor. (cal /g)	36.1	34.6	31	43.3

Table 2

ENVIRONMENTAL & SAFETY FEATURES

Features	CFC-113 (Control)	HCFC-225 45%ca / 55%cb	HFC 43-10mee	HFC 43-10mee / 38% DCE
PEL (ppm)	1000	{50}	{200}	{200}
Atmospheric Lifetime	90	ca ~ 1.6 cb ~ 5.1	20.8	≈15
VOC (Most States)	No	No	No	No / Yes
Ozone Depletion Potential (CFC=1)	0.8	0.03	0	0.0
Global Warming Potential (CO_2=1)	4500	ca ~ 170 cb ~ 530	1310	890

{ } Manufacturer's acceptable exposure limit (AEL), PEL values have not been established for the test solvents.

Selected Contaminants

The following contaminants that were used are listed in Table 3. One gram of each contaminant was combined and is referred to as the SSC mix. The SSC mix was diluted with 200ml of CFC-113 and was used as a carrier solvent to dope all test hardware in this study.

Table 3

CONTAMINANT TYPES

5 Component mixture (SSC Mix) of:	
Mineral Oil	Mixed Hydrocarbons / Petroleum Based
Hydraulic Fluid 83282	Ester Based Hydrocarbon
Silicon Oil	Polydimethylsiloxane
Krytox 240AC	Perfluoroalkypolyether
Vacuum Grease	50/50 Mix - Krytox & Petroleum Based

Test Hardware

The test and measurement equipment used represented a variety of gauge and instrument types, including high and low pressure Bourdon tube type pressure gauges (with and without bleed ports), pressure transducer, and a rotameter type flowmeter. The criteria for the selection of the test hardware included materials of construction, configuration, and range. In addition, 6" x 6" stainless steel witness (flat/simple geometry) plates were used to measure the solvent's performance based on geometrical variables and to assess solubility characteristics. The T&ME hardware used in this study are listed in table 4.

Table 4

TEST HARDWARE DESCRIPTION

Item	Range	Material	Configuration
Gauge	0-4000 psig	Stainless	Open / Bleed Port
Gauge	0-30 psig	Stainless / Bronze	Open / Bleed Port
Gauge	0-5000 psig	Stainless	Closed / No flow thru
Gauge	0-3000 psig	Brass / Bronze	Closed / No flow thru
Transducer	0-400 psig	Stainless	Closed / Internal threads
Flowmeter	18 SCFM	Stainless	Open / AN fittings

Test Procedure

All test hardware articles were cleaned, and the cleanliness level was verified to meet Level 1 per NASA/SSC 79.001 (<1mg. NVR/.09m^2). All hardware NVRs were determined gravimetrically. The cleaned articles were doped with a known amount of the NVR mixture (SSC Mix). The solvent carrier (CFC-113) was used to contaminate the articles by adding the appropriate volume to the internal surface areas.

For the initial test all T&ME items were contaminated with 200uL (5 mgs. of NVR) of the standard mix solution. All doped articles set for a minimum of 72 hours under ambient conditions. Closed-ended gauges were filled and evacuated with the test solvent four times (50mL/flush). The flushes were combined for NVR determination. Open gauges, flowmeters, and pressure transducers were flushed with 200 mL of solvent for NVR determination. Flow meters were purged with nitrogen (@100cc/min) to remove the carrier solvent. NVR determinations were determined gravimetrically by evaporating 200 mL of the test solvent to a volume of 10mL. The concentrated fluid was transferred to a tared aluminum weighing pan and heated in an oven at 105°C (221 °F) for 1.5 hours. The weighing pan was cooled to ambient temperature by placing it in a desiccator for 30 minutes. The remaining residue was weighed and recorded for each test solvent. In addition, a background NVR level was established for each solvent. After the initial

test, all test hardware were recleaned, and a second series of tests were performed. 400uL (10 mgs. of NVR) were used (in the second series) to dope all the test articles. NVR measurements were repeated to determined the amount of NVR removed from each test article.

After each rinse, the percent NVR removal was calculated using the below equation:

$$\%Removal = \frac{NVR\ Removed}{Doped\ NVR} - Solvent\ Background\ NVR \times 100$$

TEST RESULTS

Tables 5 through 7 contain the NVR removal (solvent cleaning) results of the T&ME items and witness plates that were doped with contaminants contained in the SSC mix.

All the solvents were able to remove the contaminants from the SSC mix. The cleaning results show a small dependance on configuration. The rotameter type flow meters with their complex geometry gave the lowest removal efficiencies. Also, gauges cleaned in the closed end configuration resulted in a lower NVR removal than the open ended gauges. This small dependance on configuration is probably attributed to the test solvents having high density and low viscosity. These properties are desirable for obtaining low surface tension, which improves the solvent's ability to wet complex surfaces.

HCFC-225 showed the best performance of the three solvents tested. Unfortunately, the EPA has recently decided to ban production of HCFC-225 in the near future. Also, this solvent has the highest toxicity (lowest AEL) of the candidate solvents.

The data contained in the below graph is a summary of the average per cent removal for each solvent and compares cleaning efficiences among the test articles.

SOLVENT PERFORMANCE SUMMARY

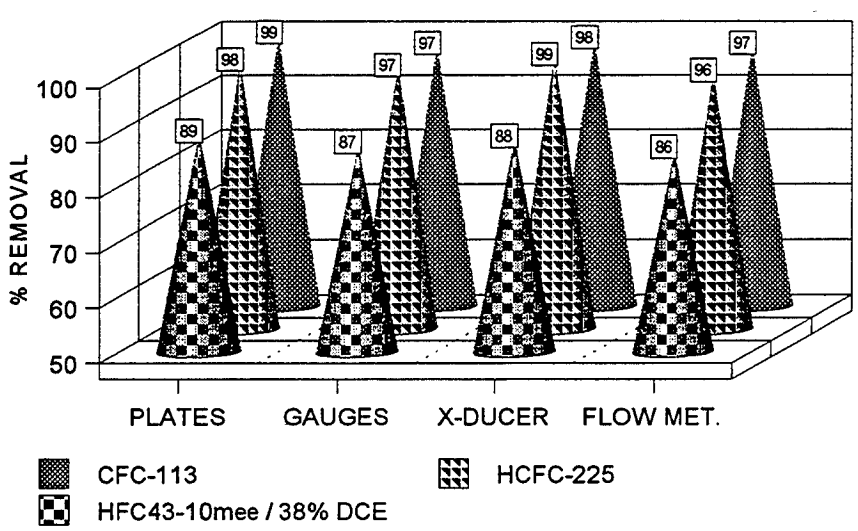

Table 5

NVR REMOVAL EFFICIENCY FOR CFC-113 (CONTROL)

Item	*Range / Configuration*	*NVR Added (mgs)*	*NVR Removed (mgs)*	*% Removal*
Gauge	0-4000 psig / Open	5 / 10	4.88 / 9.83	97.95
Gauge	0-30 psig / Open	5 / 10	4.95 / 9.92	99.10
Gauge	0-5000 psig / Closed	5 / 10	4.86 / 9.63	96.75
Gauge	0-3000 psig / Closed	5 / 10	4.91 / 9.38	96.00
Pressure Transducer	0-400 psig / Closed	5 / 10	4.92 / 9.80	98.20
Flowmeter	18 SCFM / Open	5 / 10	4.85 / 9.68	96.9

Table 6

NVR REMOVAL EFFICIENCY FOR HFC 43-10mee / 38 % DCE (Vertrel MCA®)

Item	*Range / Configuration*	*NVR Added (mgs)*	*NVR Removed (mgs)*	*% Removal*
Gauge	0-4000 psig / Open	5 / 10	4.43 / 8.79	88.25
Gauge	0-30 psig / Open	5 / 10	4.39 / 8.68	87.30
Gauge	0-5000 psig / Closed	5 / 10	4.30 / 8.52	85.60
Gauge	0-3000 psig / Closed	5 / 10	4.37 / 8.58	86.60
Pressure Transducer	0-400 psig / Closed	5 / 10	4.92 / 9.80	87.75
Flowmeter	18 SCFM / Open	5 / 10	4.85 / 9.68	85.95

Table 7

NVR REMOVAL EFFICIENCY FOR HCFC-225

Item	*Range / Configuration*	*NVR Added (mgs)*	*NVR Removed (mgs)*	*% Removal*
Gauge	0-4000 psig / Open	5 / 10	4.96 / 9.87	98.95
Gauge	0-30 psig / Open	5 / 10	4.90 / 9.74	97.70
Gauge	0-5000 psig / Closed	5 / 10	4.87 / 9.58	96.60
Gauge	0-3000 psig / Closed	5 / 10	4.80 / 9.67	96.35
Pressure Transducer	0-400 psig / Closed	5 / 10	4.92 / 9.80	98.95
Flowmeter	18 SCFM / Open	5 / 10	4.85 / 9.68	96.20

Table 8

SOLUBILITY & NVR RECOVERY RESULTS (mgs)

Solvent	*1st Rinse*	*2nd Rinse*	*3rd Rinse*	*4th Rinse*	*Total NVR Removed*
CFC-113 (Control)	20.13	2.24	0.76	0.64	23.77 mgs.
HFC43-10mee / 38% DCE	17.40	3.45	1.74	1.03	23.62 mgs.
HCFC-225	22.12	1.28	0.53	0.31	24.21 mgs.

To further evaluate the effectiveness of each of the candidate solvents, a solubility test was performed where witness plates (6"x 6", 0.25ft^2) were contaminated with 25 mgs. of the SSC mix. The witness plates were rinsed with 4, 50 ml rinses of the test solvent and an NVR level was determined for each rinse (Table 8).

OXYGEN IMPACT TESTING

Oxygen compatibility testing (NASA/WSTF) by mechanical impact per ASTM D 2512 was conducted on HCFC-225 and HFC43-10mee / 38% DCE (Vertrel MCA®) without the nitromethane stabilizer. Vertrel MCA® with the nitromethane stabilizer did not pass the LOX impact tests. The products were tested in the bulk form (sample thickness ≈0.05 in.) at ambient pressure in liquid oxygen (LOX) using an impact energy of 98J (72 ft-lb). The candidate solvents successfully passed the test with zero reactions out of 20 tests.

CONCLUSION

- HCFC-225 has a similar performance profile to CFC-113. HCFC has the highest toxicity (lowest AEL) of the candidate solvents. HCFC is regulated under title VI of the Clean Air Act and production will be banned in 2015.

- All solvents passed the LOX compatibility evaluation and showed no reactions to the mechanical impact.

- HFC 43-10mee / 38% DCE offers an acceptable cleaning efficiency for removing contaminants from T&ME.

FUTURE EFFORTS

Preliminary testing of hydofluoroether-7100 (HFE-7100®) looks promising. Its performance for removing contaminants from witness plates is comparable to HFC43-10mee / 38% DCE. HFE-7100 (methoxy-nonafluorobutane) has favorable environmental properties. It has one of the lowest toxicological profiles, with a time weighted average exposure (AEL) of 600ppm (eight hour average). The solvent is practically non-irritating to the eyes, and is not considered a mutagen.

The EPA has recently approved HFE-7100® as acceptable under the SNAP program and has VOC exemption. The solvent is nonflammable and has recently passed LOX impact tests.

Further NVR testing is required to evaluate the hydrofluoroether's effectiveness for removing contaminants from T&ME and complex geometry hardware.

Investigate new NVR techniques: The present method of analysis (i.e. NVR via Infrared Spectroscopy) may not be utilized for the new solvents (HFCs and HFEs are opaque to the IR spectrum for evaluating hydrocarbons), thus requiring the Gravimetric method, which is labor intensive and could delay component processing. For example, the present IR/NVR method takes ≈ 15-20 minutes/sample, whereas, the gravimetric method takes 2 - 3 hours/sample.

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The Search for a Replacement for CFC 113 in the Precision Cleaning and Verification of Shuttle Hardware

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1.0 Introduction

Increasingly stringent regulations regarding the production and use of chlorofluorocarbons (CFCs) have been enacted due to these compounds' detrimental effects on atmospheric ozone. CFC 113 (trichlorotrifluoroethane), used extensively in the past for many different manufacturing processes at Rockwell International, Space Systems Division, is being phased out due to a 1996 production ban. The identification, testing, and implementation of new materials and/or procedures for use as replacements for CFC 113 in these processes is the focus of several ongoing research efforts.

The majority of the hardware used with or on the Shuttle requires high levels of cleanliness, for both operational requirements and because of compatibility concerns. Certain types of hardware, most notably those from oxidizer systems and especially assembled components, currently require the use of CFC 113 for both their precision cleaning and subsequent cleanliness verification. CFC 113, because of its high vapor pressure, low toxicity, nonflammability, and ability to solubilize many common contaminants, has been used at Rockwell, as well as many other companies, to both remove and verify the removal of contaminants from these types of hardware. The identification and testing of potential replacement fluids for CFC 113 in this application is the subject of this report. Candidate fluids representing many different classes of materials were screened as to their efficacy in removing common Shuttle service and manufacturing fluids. The two best candidates from these screening tests were then selected, and compatibility/exposure and component cleaning tests are ongoing.

2.0 Background (Current Process)

Hardware, after being machined and/or manufactured, is precleaned to remove the majority of the machining oils, tube-bending lubes, and other manufacturing-associated contamination. In general, an aqueous cleaner (such as Brulin 815GD) is used for this precleaning step. Following this process, the hardware is removed to a cleanroom and precision cleaned and verified according to a standard Rockwell procedure. In this procedure, the use of CFC 113 for subsystems requiring a certain non-volatile residue (NVR) level, such as for oxygen or nitrogen tetroxide service, are specified. Other

systems, such as the Auxiliary Power Unit System, already utilize non-CFC solvents such as isopropyl alcohol. Parts which have been in service but were removed for some reason also are required to be precision cleaned and verified before reinstallation.

Verification is accomplished by flushing or rinsing the part with fluid and collecting 100 milliliters (ml) for every square foot of area rinsed (with a minimum of 100 ml collected). This fluid is then filtered (0.45 or 0.8 micron absolute) and a particle count and size determination (manual) is performed on the filter patch. The NVR of the fluid is determined, either gravimetrically, by evaporation of the solvent, or by infrared spectrophotometry, utilzing the hydrocarbon absorbance at 3.4 microns to obtain the concentration of hydrocarbon-containing materials present. Following this verification, the part is dried, either with nitrogen, argon, vacuum, heat, or a combination; the drying procedure being dependent upon the type of part or assembly being cleaned.

A typical Rockwell cleanliness level requirement for the allowed number of particulate matter and non-volatile residue is as follows:

Cleanliness Level	Particle Size (microns)	Maximum Number of Particles per Sample	Maximum NVR per 100 ml
100A	< 25 25-50 >50-100 >100, Nonmetallic >100, Metallic	No silting 68 11 1 0	1 mg

3.0 Screening Test Procedures

The suitability of candidate fluids for use in removing NVR was evaluated by determining the solubility of various contaminants in these fluids. This was accomplished by attempting to rinse these contaminants off of a substrate using a given volume of fluid, and then determining the percent contaminant removed. The screening test was designed so as to provide information on the solubilities of common contaminants in the selected candidate fluids relative to CFC 113.

3.1 Candidate Fluids, Selection Criteria

Candidate fluids were selected from as wide a range of different classes of solvents as possible, including aqueous, organic, volatile methyl siloxane, and halocarbon. In all of

the above cases, NVR determination cannot be done using infrared spectrophotometry (due to either interference from carbon-hydrogen bonds of the fluid itself, or other intrinsic properties of the fluid). The requirements for gravimetric NVR include an evaporation temperature for the solvent of 105 +/- 5°C; in consideration of this, candidate fluids with relatively high boiling points (greater than approximately 150°C) were discarded. An effort was made to find fluids which could function as nearly as a drop-in replacement as possible. Also, only those fluids which could be obtained with low initial NVR contents were considered, in order to avoid the introduction of contamination from the solvent itself. (With a verification solvent, no additional fluid is allowed to enter the part subsequent to the verification step, or the part would have to be re-verified as clean.) The following list represents those materials which were screened for contaminant removal:

Table 1: Candidate Fluids

Candidate Fluids
Freon TF (CFC 113)
Isopropyl Alcohol
H_2O
Hexane
Cyclohexane
Ethyl Acetate & H_2O (6.1% w/w* azeotropic mixture)
H_2O & 100 ppm Triton-X 100 (surfactant)
Ethyl Acetate, H_2O, & Ethanol (7.8% & 9.0% w/w* azeotropic mixture)
Dow-Corning OS-20 (octamethyldisiloxane)
DuPont Vertrel XF (HFC 43-10 *mee*)
DuPont Vertrel MCA (HFC 43-10 *mee* & trans 1,2-dichloroethylene azeotropic mixture)
Asahi Glass Asahiklin (AK) 225 (HCFC 225 *ca* & *cb*)
Tribolube F-197 (perfluorinated fluid)
Borothene (halocarbon)

*%w/w = percent by weight

3.2 Contaminants, Selection Criteria

Contaminants were chosen to represent the different classes of materials used in manufacturing processes and in assembly of parts and systems, as well as some common Shuttle service fluids and materials. The materials selected represent to some extent the worst-case conditions for contamination; the data should be interpreted as a comparison of

the candidate fluid with the control fluid, Freon TF. The following list details the contaminants chosen and the type of material:

Table 2: Contaminants for NVR Determination

Contaminant	Type of Material
Dow-Corning DC-33	Silicone grease
Braycote 601	Perfluorinated grease (Teflon-filled)
Mil-H-83282	Hydraulic fluid, ester-based
Mil-H-5606	Hydraulic fluid, hydrocarbon-based, with acrylic
Houghto-Draw	Tube-bending lube, for stainless steel; hydrocarbon-based
Titanlube	Tube-bending lube, for titanium; hydrocarbon, ester, & polyisobutylene

3.3 Test Procedures

Aluminum 6061-T6 panels (1.5 by 3 inches) were used as the substrate for the contaminants. The panels were precleaned initially by immersing in a 10-20% Brulin 815GD aqueous cleaner bath for 20 minutes, followed by a hot water dip (1-2 minutes), gaseous nitrogen purge, and then oven dry. Each panel was weighed (to the nearest tenth of a milligram), contaminated with one of the listed contaminants on one surface (10 to 150 milligrams, depending upon the density of the contaminant), and then reweighed. The contaminated panel was air-dried for a minimum of four hours and/or dried for one hour at 150 +/- 10 °F. Each was then rinsed with 40 ml of the chosen fluid, allowed to air dry, and then weighed again. The panels were cleaned between each test with CFC 113 and acetone to remove any residual contamination from the previous test.

3.4 Results and Discussion

The data obtained using the procedure in the previous section was used to calculate the percent of each contaminant removed from each panel by a given fluid as follows:

$$\% \text{ Removed} = \frac{(\text{Weight of Contaminated Panel - Weight of Rinsed Panel})}{(\text{Weight of Contaminated Panel - Initial Weight of Panel})} \times 100$$

These results are presented in the following table:

Table 3: Removal Efficiencies of Candidate Fluids

Fluid	Contaminant, Percent Removed					
	DC 33	Braycote 601	Mil-H-83282	Mil-H-5606	Houghto-Draw	Titanlube
none	3	0	0	78	0	1
Freon TF	80	91	100	100	100	100
Isopropyl Alcohol	95	1	99	94	94	13
H_2O	7	3	75	91	4	5
H_2O & 100 ppm Triton X-100	5	3	81	86	1	1
Hexane	96	1	100	100	100	100
Cyclohexane	95	1	100	100	99	100
Ethyl Acetate & H_2O	85	0	99	99	98	62
Ethyl Acetate, Ethanol, & H_2O	70	4	97	100	99	99
OS-20	96	0	97	91	23	6
Vertrel XF (HFC 43-10 *mee*)	7	75	52	87	5	4
Vertrel MCA	43	24	100	92	100	75
AK 225	85	87	100	100	100	16
90% Vertrel XF & 10% AK 225	9	60	63	90	11	3
70% Vertrel XF & 30% AK 225	10	71	79	92	4	3
Tribolube F-197	5	91	9	80	< 1	<1
Borothene	78	< 1	99	100	100	85

The control (no fluid) results for the Mil-H-5606 hydraulic fluid indicate that it contains approximately 80% volatile components; this should be considered when assessing the removal efficiencies of the fluids for this contaminant. These results are meant only to be a rough measure of the solvency of these various contaminants in the selected fluids. The Freon TF was able to remove most of the contaminants fairly cleanly. None of the fluids (including Freon TF) was completely effective at removing the Braycote 601 perfluorinated grease (the Teflon particles tend to remain behind). Braycote 601 is,

however, LOX and propellant compatible and is used only during assembly and on the vehicle. Also, complete removal of this grease from assembled parts may not be desirable for operational reasons.

Of the solvents tested, cyclohexane, hexane, the ethyl acetate/water/ethanol azeotrope, Borothene, Vertrel MCA, and AK 225 seemed to be the most effective at removing the majority of the given contaminants. AK 225 was probably the most effective of all of the solvents tested; it removed all of the contaminants fairly readily except the Titanlube.

4.0 Certification Testing

It was decided at this stage of the testing to focus on those fluids which could be used for cleaning oxidizer or oxygen systems. Due to concerns expressed about potential entrapment of the fluid in complex and/or assembled parts and other drying difficulties, it was decided to discontinue testing of non-oxidizer compatible fluids. Using this added criterion, the two remaining candidates from those which showed adequate performance in the screening tests are the Vertrel MCA and the Asahiklin 225.

Two separate types of tests need to be done in order to certify a new cleaning fluid for use on Shuttle Orbiter hardware. The first test is an exposure test, to ensure that the fluid is compatible with Orbiter component materials. The second test involves the cleaning of actual Shuttle hardware and components, of varying complexities, to ensure that these fluids can clean and verify the cleanliness of complex assembled hardware to the same level of performance as CFC 113. Both of these tests are currently ongoing at Rockwell. The test matrices and procedures are presented in the following sections and preliminary results will be provided as they become available.

4.1 Compatibility Testing

4.1.1 Material Selection Criteria

Materials were selected so as to represent all of the materials with which the two fluids could come in contact during the cleaning and verification procedures. For similar materials of the same chemical class or family, the one which would be most likely to exhibit degradation or corrosion was chosen. The following list represents those materials selected for exposure testing:

Teflon PTFE
Rulon AR (Glass-filled Teflon PTFE)
Tecfluorocote (Teflon coating)
Braycote 601
Kalrez 1045
EPR (Ethylene Propylene Rubber)
Kynar (Polyvinyldene Fluoride)
Vespel SP-21 (Polyimide/Graphite)
Everlube 811 (Sodium Silicate Dri-Lube)
Tilube 1175 (Dri-Lube)
Neoprene C557
Viton V0747
Aluminum 2014-T6*
Aluminum 7075-T73
Aluminum Bronze
CRES 302
CRES 440C, RC 55
CRES 301 Full Hard Sheet
E-Brite Z6-1*
CRES 446
CRES 17-4 PH, H 1025
AM 350, SCT 850
CRES 15-7 RH950*
Custom 455, H950*
CRES 15-5 PH, H900
CRES 17-4 PH, H1025
CRES 17-7 PH, CH900*
Inconel X750
Inconel 718
Invar 36
Titanium 6Al-4V*
Phosphor Bronze
Solder (60 Sn; QQ-S-571)
Brass (36000)*
Kennametal K 96
Braze (72Au-22Ni-6Cr)
Solder (96Sn-4Ag)
Tungsten Carbide
Tungsten
Columbium (Niobium) 103
Beryllium-Copper
Aluminum, Anodized Coating
Aluminum, Chemfilmed

* stress specimen

4.1.2 Specimen Preparation

The majority of the materials were prepared as coupons for the exposure testing. Those remaining materials (marked with an asterisk in the preceding section) were exposed as stress specimens; a bolt was placed through a machined c-ring and tightened to 95% of yield to create a specimen with transverse tensile stress. All of the metallic specimens were polished (a minimum of one face) so as to provide a fresh metal surface for exposure. The samples were weighed, measured, and, in the case of the non-metallics, the hardness was determined using a Shore A or Shore D durometer.

4.1.3 Exposure Conditions and Test Procedures

The samples were immersed in the selected fluids in sealed containers at ambient conditions (22 +/- 3 °C) for a ninety day exposure. The samples will be removed at thirty and sixty day intervals and inspected for any evidence of degradation or corrosion, including changes in weight or dimensions. At the conclusion of the ninety day exposure, the samples will be removed and reweighed, measured, and the hardness determined. The percent swell of the elastomers will be determined both immediately after removal from the fluid and after being air-dried for a period of one week. The fluids will be evaporated

to dryness post-test and the non-volatile residue (NVR) analyzed using infrared spectrophotometry (IR) and/or energy dispersive x-ray spectroscopy (EDS).

4.2 Component Cleaning Tests

Component cleaning tests will be done next as the final phase of the certification, following assurances that the fluids are compatible with the components' materials. Ten pieces of Orbiter hardware, of varying complexities (including several different types of valves and quick disconnects), will be contaminated and then cleaned using Vertrel MCA and AK 225, and the results compared to CFC 113. The contaminants used will include mineral oil, Mil-H-83282 and Mil-H-5606 hydraulic fluids, DC 33, Braycote 601, Houghto-Draw, and a standard particle-size dust.

5.0 Discussion and Conclusions

Of the solvents and fluids screened thusfar, the Vertrel MCA and Asahiklin 225 seem to have the most desirable properties for precision cleaning and verification, in terms of ability to solubilize contaminants, physical properties, and compatibility issues. Testing of these two fluids with Orbiter hardware and component materials is being done currently in order to certify their use. However, evaluation of other alternate cleaning methods is also continuing. Testing of additional solvents or solvent mixtures will be done as they are made available for testing; one potential candidate class of fluids in this category are the hydrofluoroethers which are currently being developed by 3M. Another area of future research involves using water for verification, utilizng a total organic carbon analyzer for quantification of the amount of non-volatile residue present. This technique could potentially be useful for the verification of aqueous cleaned parts, or for other parts where entrapment (drying difficulties) and compatibility are not concerns.

EVALUATION OF AK-225®, VERTREL® MCA AND HFE A 7100 AS ALTERNATIVE SOLVENTS FOR PRECISION CLEANING AND VERIFICATION TECHNOLOGY

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Abstract

The National Aeronautics and Space Administration (NASA), Kennedy Space Center (KSC) Materials Science Division conducted a study to evaluate alternative solvents for CFC-113 in precision cleaning and verification on typical samples that are used in the KSC environment. The effects of AK-225®, Vertrel® MCA, and HFE A 7100 on selected metal and polymer materials were studied over 1, 7 and 30 day test times. This report addresses a study on the compatibility aspects of replacement solvents for materials in aerospace applications.

INTRODUCTION

Based on the Montreal Protocol of 1987, the global agreement signed by the United States and 23 other nations, the National Aeronautics and Space Administration itself in 1991 initiated a timetable for the reduction and eventual phaseout of the use of ozone depleting substances at its respective centers. Kennedy Space Center (KSC) used thousands of pounds of Freon™ 113 (CFC-113) each year for precision cleaning and validation of well over 200,000 piece parts that are used for shuttle operations. Typical components include valves, regulators, flex hoses, fittings, etc. In answer to the 1987 mandate, KSC developed an aqueous precision cleaning process that addresses approximately 80% of the CFC-113 usage. The remaining 20% require an alternative solvent. The focus of this study was to evaluate AK-225®, Vertrel® MCA and HFE A 7100 as alternative solvents to CFC-113 for precision cleaning and validation of common metal alloys and polymers that are used at Kennedy Space Center.

The three solvents are already being marketed by their respective manufacturers as viable alternatives to CFC-113. They have key physical characteristics in common such as non-flammability, low toxicity, little to zero ozone depletion, low global warming potential, evaporation rate, and compatibility with plastic and metals that make them excellent candidates for use in the KSC environment. Solvent properties are detailed in Table 1.

Table 1: Solvent Properties

Physical Properties	CFC-113	AK-225 (Asahi Glass Co.)	HFE A 7100 (3M™)	Vertrel (DuPont)
Boiling Point (°C)	47.6	54	60	39
Liquid Density (g/ml)	1.57	1.55	1.50	1.42
Surface Tension (dyn/cm)	17.3	16.2	13.6	16.2
Freezing Point (°C)	-35	-131	-135	-80
Solubility in Water (ppm)	170	210	<10	140
Vapor Pressure (mmHg)	368	137-175	195	228
Viscosity (cp)	0.68	0.59	0.61	0.49
Heat of Vaporization (cal/g)	35.1	32	30	43.3
Evaporation rate (ether=1)	1.3	0.9	***	***
Vapor Density (air=1)	6.5	7.0	8.6	***
Flash Point (°C)	None	None	None	None
ODP	0.8	0.03	0	0
GWP	4500	370	500	1000
Atmospheric Lifetime (years)	110	8	5.5	<21

The solvent AK-225®, manufactured by Asahi Glass Co., is a hydrochlorofluorocarbon (HCFC) that is nearly identical to CFC-113 in cleaning ability, boiling point, compatibility with plastic and metals, nonflammability, and evaporation rate. At the same time it is 25 times less harmful to the stratospheric ozone layer than CFC-113. Vertrel® MCA is a hydrofluorocarbon (HFC) with trans-1,2 dichloroethylene. According to DuPont, Vertrel is nonflammable, has zero ozone depletion and has low global warming potential. This solvent is also being marketed to replace 1,1,1-trichloroethane (1,1,1-TCE), hydrofluorocarbons and perfluorocarbons (PFC) in many applications. The hydrofluoroether (HFE) A 7100 solvent, developed by 3M, is described with similar characteristics and was developed to address limitations of some perfluorocarbon applications that are considered ozone depleting.

EXPERIMENTAL METHOD

Six types of materials representative of those used in shuttle operations were selected for this study, three types of metal alloys and three types of polymers. The metal alloys were aluminum, brass and stainless steel. The polymers were Teflon™, Vespel™ and Viton™. A description of the diameter, thickness and surface condition of each sample coupon is given in Table 2.

Table 2: Sample Description

Materials	Diameter (inches)	Thickness (inches)	Surface Condition
Aluminum	3/4	1/8	Smooth
Brass 230	3/4	1/16	Smooth
Brass 260	3/4	1/8	Smooth
Stainless Steel	3/4	1/8	Smooth
Vespel-1	3/4	1/16	Smooth
Vespel-21	3/4	1/16	Smooth
Vespel-211	3/4	1/16	Smooth
Viton	3/4	1/8	Rough
Teflon	3/4	1/4	Smooth

The coupons were initially weighed and measured for thickness. For the solvents AK-225 and Vertrel, triplicate samples of each material were totally immersed for the time intervals 24 hours, 7 days and 30 days. Only Vespel

and Viton were tested for the HFE A 7100, due to a limited supply of the solvent, for the same time span of 24 hours, 7 days and 30 days. The solvents were used at 100% concentration as provided by the manufactures and the temperature was kept constant at 25°C. One sample of each material was also immersed in water as a control or reference. The test method for the aluminum, brass, and stainless steel samples was adapted from the ASTM F483 Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals. The test method for Teflon, Viton and Vespel was adapted from the ASTM D-471 Test Method for Rubber Property-Effect of Liquids. At the end of each time span, the samples were rinsed and dried. The weight and thickness was measured again. Surface characterization was performed using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

RESULTS

The aluminum, stainless steel and brass 230 and 260 test samples were evaluated for weight and visual changes in accordance with ASTM F483. The results are detailed in Tables 3-5 (see Appendix). In general, there was minimal change in the weight of the samples for both AK-225 and Vertrel. A negative weight loss indicates that microscopic debris or particulates were removed from the samples. There was no change in thickness for any of the metal samples, therefore only weight change is reported. All the samples had some discoloration and slight pitting (indicative of incipient corrosion), but only after 30 days (720 hours). The Brass-260 showed discoloration and pitting after only 1 day (24 hours) of being immersed in the reference solvent (distilled water). Stainless steel and aluminum had some pitting and discoloration in water, but only after being immersed for 30 days.

The polymer samples were evaluated for weight, thickness and hardness changes in accordance with ASTM D-471 procedures. In general, there were no changes in the hardness measurement. The results for the weight and thickness changes are listed in Tables 6-9 (see Appendix).

For the solvent AK-225, there was a considerable weight change in the Viton as compared to the Vespels and Teflon (see Table 6). The Vespel samples performed best of the three samples. Vespel SP-1 had the smallest change in weight in comparison to Teflon. The Viton weight is also presented in percentage to illustrate the significant weight change. Most of the thickness changes were negative, indicating weight loss due to removal of microscopic debris. However, for Viton, the positive change indicated that the sample adsorbed some of the solvent.

The average weight increase for Teflon and Viton (see Table 7) was higher in the AK-225 solvent than in the Vertrel solvent. As expected, the weight increase was smaller in the reference solvent than in either AK-225 or Vertrel. Although there did not seem to be a noticeable change in the Vespel samples, they seemed to perform better in the HFE A 7100 solvent (see Tables 8 and 9) as opposed to AK-225 or the reference solvent. Teflon and Viton also performed better in the HFE A 7100 than in Vertrel.

After the physical properties were measured, the samples were analyzed using x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to detect the differences in particular elements and the surface topography for each sample. The metal samples contained a thin carbon and oxygen layer that masked the metallic peaks. The carbon and oxygen peaks were monitored for changes in intensity as compared to the different test lengths. No significant changes were observed for any of the metals except for aluminum. The intensity of the oxygen peak was twice as high after 720 hours in AK-225 and the reference solvent than after 24 hours in the same solvents. The Vertrel solvent had the same effect on aluminum, but not to the extent as AK-225 or the reference solvent.

Teflon and Viton were monitored for fluorine and carbon peaks. No significant changes were observed in the Teflon samples. However, the Viton sample showed a slightly higher fluorine peak after a 720 hour test length. The Vespel SP-1 and SP-21 samples showed oxygen, carbon, nitrogen and a trace of silicon. Vespel-21 also contained oxygen, carbon, nitrogen and a trace of silicon. The carbon concentration was higher in Vespel-21 than in Vespel-1. Vespel-211 showed fluorine, in addition to oxygen, carbon, nitrogen. No significant changes were observed in any of the Vespel samples in either AK-225 or Vertrel.

X-ray photoelectron spectroscopy results show the distinct chemical characteristics for each of the Vespel samples. Vespel SP-1 has a higher carbon to oxygen ratio than SP-21 or SP-211. Vespel SP-211 has the highest fluorine content and Vespel SP-1 has the highest nitrogen content. For all three of the Vespel samples, the fluorine concentration increased for the HFE A 7100 solvent. In general the carbon and oxygen concentration were slightly reduced after 30 days. This is consistent with the fact that the solvent is removing some of the surface deposits such as CO and CO_2. Almost every sample that is exposed to air will have a thin layer of physically adsorbed atmospheric deposits. At the same time that the deposits are removed by the solvent, the fluorine in the material is exposed. The same phenomena was observed with the Viton samples. The XPS analysis of the Viton samples showed carbon, oxygen and fluorine. There were no significant changes other than the cleaning effect in the concentration as explained above.

The surfaces of the samples were extensively analyzed using scanning electron microscopy (SEM). The polymer samples were gold coated prior to the analysis to avoid image distortion due to charging. Each of the samples analyzed was photographed at the three magnifications: 14-20 x, 100x and 500 x. The metal samples showed less particulate after 30 days in the solvents than after 24 hours. No significant surface damage was observed in any of the samples by any of the solvents. The Viton sample showed a weave pattern on the surface, at the lower magnification, but at higher magnification this pattern was actually observed to be striations perpendicular to each other. The surface of the Vespel samples had a scale appearance and the Teflon surfaces were very smooth. No physical damage was observed on any of the polymer samples with any of the solvents.

CONCLUSION

The metal samples performed extremely well in both AK 225 and Vertrel. No significant weight or thickness changes were measured. XPS and SEM showed no surface damage in any of the samples. Aluminum showed a high oxygen increase in both AK 225 and in Vertrel as well as in water, the reference solvent. This is a typical oxidation reaction in aluminum. An aluminum oxide layer is always present in aluminum samples exposed to the environment.

For the polymer samples, the results varied. The Vespel samples showed no significant change in the AK-225 solvent. However there was an increased weight gain for Teflon in the AK-225, that was noticeably higher than in the Vertrel solvent. Most samples showed a negative change in thickness in both solvents. As expected, the changes in the reference sample were less than the changes in either AK-225 or Vertrel. Both solvents proved to be incompatible with the Viton sample. In general, the Viton samples showed larger weight and thickness changes in AK-225 than in Vertrel.

The performance of the HFE A 7100 was evaluated on Vespel and Viton samples only. Two of the Vespel samples had thickness increases of 2.5% after 30 days. Thirty days is an extreme condition and not representative of a real production environment. No significant weight changes were observed for the Vespel samples. The Viton samples showed significant weight and thickness changes and in general did not perform very well in this particular solvent. XPS and SEM results showed no significant changes in the surface chemical composition or in the surface topography of the samples.

ACKNOWLEDGMENTS

The authors wish to recognize and thank Joe Curran and Mike Springer of I-NET Incorporated, for their contribution to this study.

APPENDIX

Table 3: Solvent AK-225 Metal Results

Table 4: Solvent Vertrel MCA Metal Results

Table 5: Reference Solvent Metal Results

Table 6: Solvent AK-225 Polymer Results

Table 7: Solvent Vertrel MCA Polymer Results

Table 8: Reference Solvent Polymer Results

Table 9: Solvent HFE A 7100 Polymer Results

Table 3: Solvent AK-225 Metal Results

AK-225		
Sample	**Avg Weight Change** (mg)	**Visual Observations**
Aluminum		
24 hours	0.03	N/V
168 hours	0.10	N/V
720 hours	-4.03	Slight pitting
Brass-230		
24 hours	0.33	N/V
168 hours	-0.27	N/V
720 hours	0.67	Slight pitting, Dull
Brass-260		
24 hours	-0.07	N/V
168 hours	-0.57	N/V
720 hours	-0.33	Discoloration, Pitting
Stainless Steel		
24 hours	0.10	N/V
168 hours	0.23	N/V
720 hours	-1.70	Pitting, Black spots on surface, shiny surface in some areas

N/V - No Visual changes Observed

Table 4: Solvent Vertrel MCA Metal Results

VERTREL MCA		
Sample	**Avg Weight Change** (mg)	**Visual Observations**
Aluminum		
24 hours	-0.13	N/V
168 hours	-0.07	N/V
720 hours	-0.03	Slight pitting
Brass-230		
24 hours	4.5	N/V
168 hours	-0.27	N/V
720 hours	-2.8	Slight pitting, Dull
Brass-260		
24 hours	-0.10	N/V
168 hours	-0.27	N/V
720 hours	-0.60	Discoloration, Pitting
Stainless Steel		
24 hours	-0.07	N/V
168 hours	-0.07	N/V
720 hours	-0.07	Slight pitting & etching, Dull, Accretions

N/V - No Visual changes Observed

Table 5: Reference Solvent Metal Results

REFERENCE SOLVENT (Distilled Water)		
Sample	**Avg Weight Change** (mg)	**Visual Observations**
Aluminum		
24 hours	0.00	N/V
168 hours	0.10	N/V
720 hours	3.20	Slight pitting & discoloration
Brass-230		
24 hours	N/R	N/R
168 hours	N/R	N/R
720 hours	N/R	N/R
Brass-260		
24 hours	0.50	Discoloration, Pitting
168 hours	-0.20	Discoloration, Pitting
720 hours	-0.20	Discoloration, Pitting
Stainless Steel		
24 hours	0.10	N/V
168 hours	0.20	N/V
720 hours	6.60	Slight pitting & etching, Dull

N/V - No Visual changes Observed N/R - Not Reported

Table 6: Solvent AK-225 Polymer Results

AK-225		
Sample	**Avg Weight Change** (mg)	**Thickness Change** (%)
Teflon		
24 hours	16.7	-4.23
168 hours	-0.20	-3.87
720 hours	80.9	-5.73
Vespel SP-1		
24 hours	1.73	-0.36
168 hours	0.45	-0.83
720 hours	1.91	3.70
Vespel SP-21		
24 hours	1.21	-0.90
168 hours	3.28	0.00
720 hours	3.62	2.80
Vespel SP-211		
24 hours	-0.23	-0.30
168 hours	4.31	-0.53
720 hours	4.26	2.50
Viton		
24 hours	498.8 (31.0%)	0.01 inches
168 hours	421 (24.0%)	0.01 inches
720 hours	391 (28.6%)	0.007 inches

Table 7: Solvent Vertrel MCA Polymer Results

VERTREL MCA		
Sample	**Avg Weight Change (mg)**	**Thickness Change (%)**
Teflon		
24 hours	12.9	-5.50
168 hours	12.1	-2.60
720 hours	22.8	0.47
Viton		
24 hours	247 (14.6%)	0.003 inches
168 hours	122 (7.5%)	0.003 inches
720 hours	115 (7.1%)	0.001 inches

Table 8: Reference Solvent Polymer Results

REFERENCE SOLVENT (Distilled Water)		
Sample	**Avg Weight Change (mg)**	**Thickness Change (%)**
Teflon		
24 hours	-2.50	0.80
168 hours	0.40	0.80
720 hours	0.00	0.00
Vespel SP-1		
24 hours	1.88	0.00
168 hours	2.35	0.00
720 hours	5.28	3.70
Vespel SP-21		
24 hours	2.05	0.80
168 hours	4.33	0.00
720 hours	3.87	3.30
Vespel SP-211		
24 hours	-0.23	-0.27
168 hours	4.31	-0.53
720 hours	4.26	2.47
Viton		
24 hours	6.5 (0.40%)	0.00 inches
168 hours	9.7 (0.60%)	0.00 inches
720 hours	15.8 (1.00%)	0.01 inches

Table 9: Solvent HFE A 7100 Polymer Results

HFE A 7100		
Sample	**Avg Weight Change** (mg)	**Thickness Change** (%)
Vespel SP-1		
24 hours	-0.10	0.00
168 hours	0.10	0.00
720 hours	0.30	1.20
Vespel SP-21		
24 hours	0.00	-0.80
168 hours	0.20	0.00
720 hours	0.40	2.50
Vespel SP-211		
24 hours	0.00	-0.80
168 hours	0.20	0.00
720 hours	0.30	2.60
Viton		
24 hours	8.30	6.40
168 hours	9.40	6.50
720 hours	11.0	8.30

USE OF VARIABLE ANGLE SPECTROSCOPIC ELLIPSOMETRY IN ORDER TO DETERMINE CONTAMINANT OPTICAL PROPERTIES.

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Abstract

In order to measure contaminant levels found in the manufacture of the Redesigned Solid Rocket Motor (RSRM) optical properties of the contaminants are needed to develop standards for calibration purposes. Specific to our efforts is the determination of the complex index of refraction for a hydrocarbon mixture and a commercial methyl siloxane. Using ellipsometric measurements with multiple angles of incident and a range of wavelengths in the near infrared a determination of the index of refraction <n> and the extinction coefficient <k> were made for the contaminants. This paper will present the optical techniques and modeling approach used to determine these optical constants of the hydrocarbon mixture and the methyl siloxane studied.

Introduction

The need to ensure clean surfaces in the manufacture of aerospace hardware has stimulated a need to develop new techniques and to apply old technologies in new ways. For the characterization of contaminants on surfaces it is necessary to insure proper calibration of the inspection instruments. To achieve this calibration it is necessary to develop calibration standards with known contaminant levels. The very low contaminant levels which can cause failures for aerospace hardware require special techniques to qualify and quantify these contaminants adequately.

One of the efforts by the Surface Contamination Analysis Team (SCAT) at Marshal Space Flight Center in Huntsville, Alabama was to develop a set of standards of very low levels of contamination for two contaminants found in the manufacture of the redesigned solid rocket motor (RSRM). Ellipsometry was one of the tools chosen to identify the quantity of each of these contaminants on the set of calibration standards.

The approach was to produce a set of calibration standards for both of the contaminants, an organic mixture Conoco HD2 grease and a methyl siloxane mold release agent (silicone). The contaminant levels would then be measured by both a gravimetric method and by ellipsometry. A correlation between the two methods use for determining the levels of contaminants would yield the predictive capabilities of the eillipsometric method to within the error capabilities of the gravimetric method.

Ellipsometry

Ellipsometry is the measurement of elliptically polarized light due to a reflection at a surface. The elements which control the change in polarization are the optical constants index of refraction <n> and the extinction coefficient <k> of the surface. The thickness and optical constants of any film on the surface also affect the polarization change.[?] In Figure 1, if an electric field with mutually perpendicular and equal components S and P are incident on a surface, then upon refection by that surface the reflected electric field becomes elliptically polarized due to the unequal reflection of the S and P components.

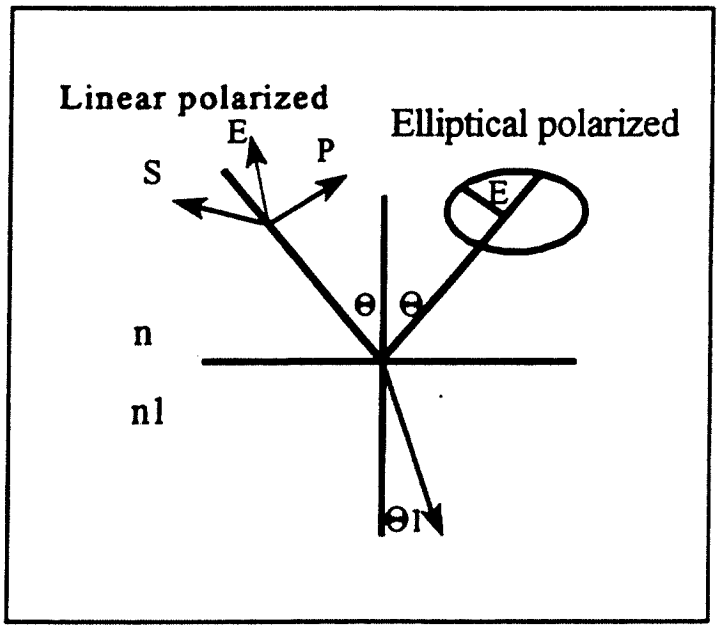


Figure 1 - Reflection of linear polarized light on a single surface.

The changes of the S and P components are not directly measurable, however, the ratio of these changes are measurable and are the familiar psi (ψ) and del (Δ) where

$$\tan \psi = (Rp/Rs)/(Ep/Es)$$
$$\Delta = \beta - \alpha$$

β and α are the phase differences between the P and S components after and before reflection.[?] Combining these definitions with the expression for the ratio of the incident and reflected electric field the basic equation becomes

$$\rho = \tan \psi \, e^{i\Delta}$$

Combining this equation with expressions for Fresnel coefficients Rp and Rs

$$Rp = (n1*\cos\theta - n*\cos\theta 1)/(n1*\cos\theta + n*\cos\theta 1)$$

$$Rs = (n*\cos\theta - n1*\cos\theta 1)/(n*\cos\theta + n1*\cos\theta 1)$$

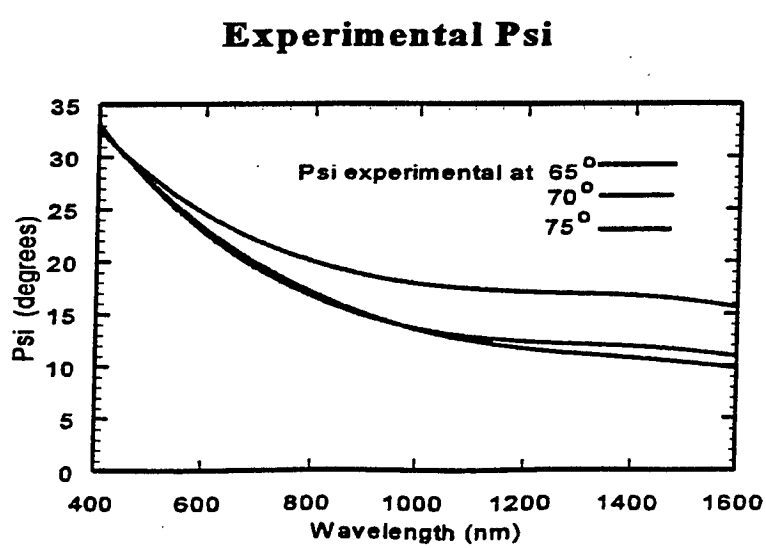
and Snell's law

$$n*\sin\theta = n1*\sin\theta 1$$

solutions for optical constants can be obtained for reflective layers of films on surfaces.[?]

For multiple layers it is necessary to establish a parameter based model of the surface. The ψ and Δ are then calculated using the Fresnel equations. Data is then collected on rotating analyzer ellipsometer for ψ' and Δ' as a function of wavelength and angle of incidence θ. The parameters for <n>, <k>, and film thickness d are then varied to achieve a best iterative nonlinear fit of the data to the Fresnel equations.

A sample of the data for the measured experimental ψ and Δ are given respectively



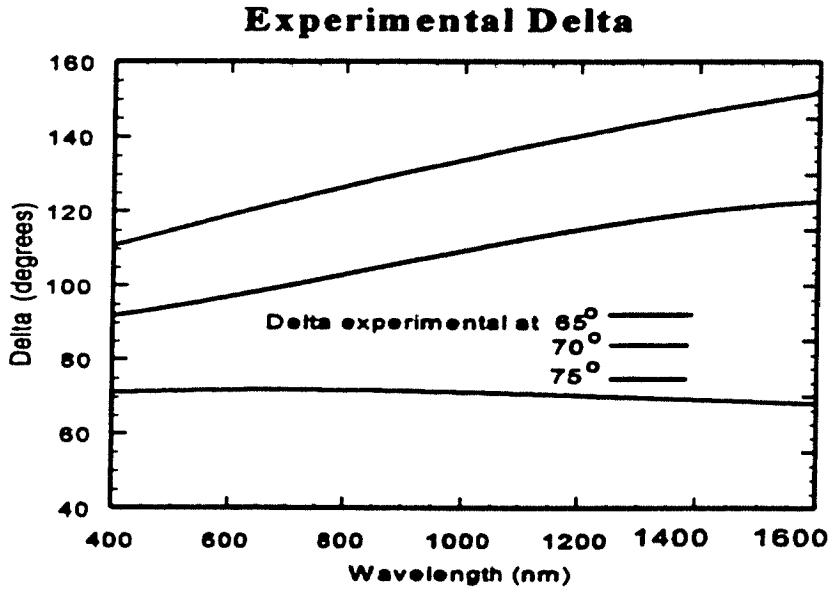


Figure 3 - Experimental delta for three angles of incidence.

Results

The optical constants for the two contaminants were found by using a model of each contaminant as a film of varying thicknesses on a silicone wafer substrate. Each thickness representing a different level of contamination. AVariable Angle of Incidence Ellipsometer (VASE®) was used to collect the data on the unknown films. The optical constants were then used to predict levels of the two contaminants on the same Si wafer substrate. Figures 4 and figures 5 show the results for the optical constants.

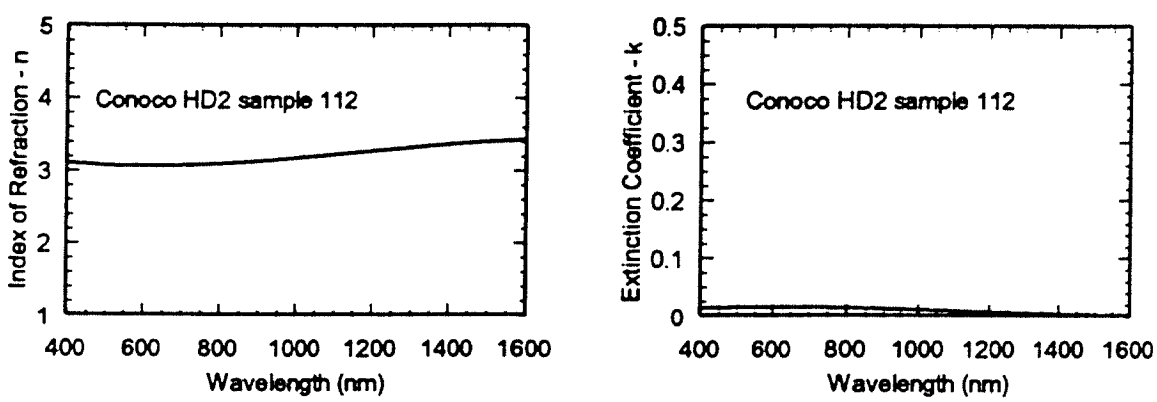


Figure 4 - Conoco HD2 grease optical constants.

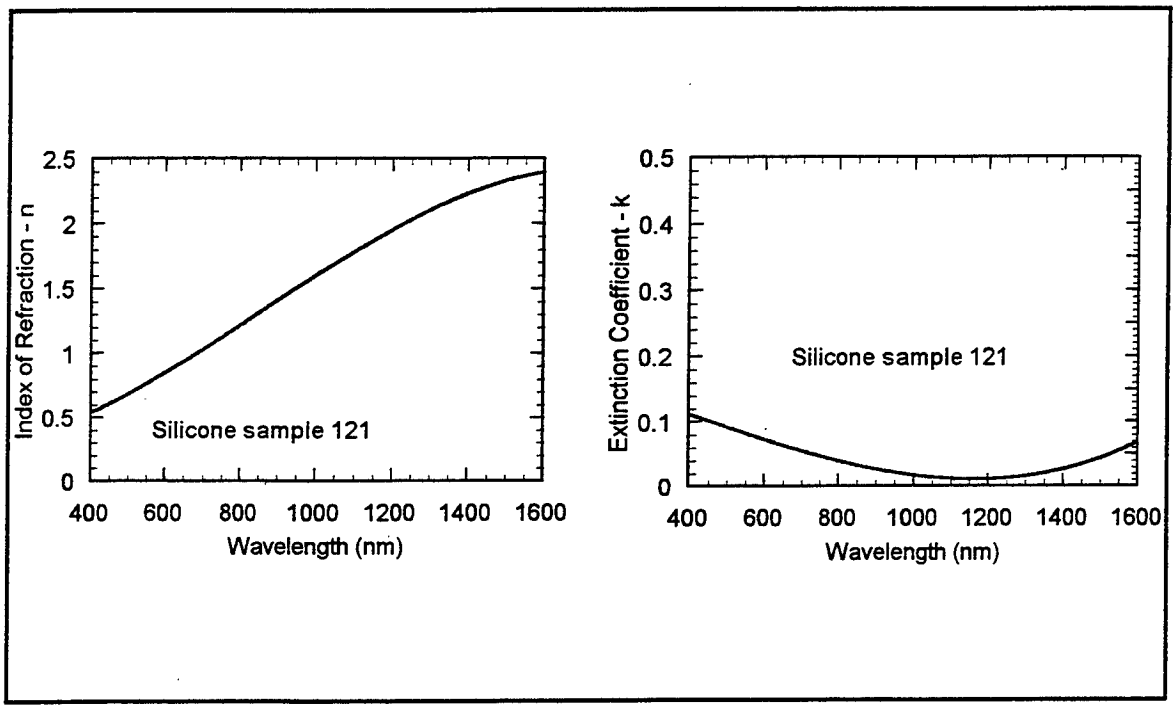


Figure 5 - Silicone mold release optical constants.

Figures 6 and figures 7 show the predicted versus gravimetric thickness of the two contaminants for the unknown contaminant levels.

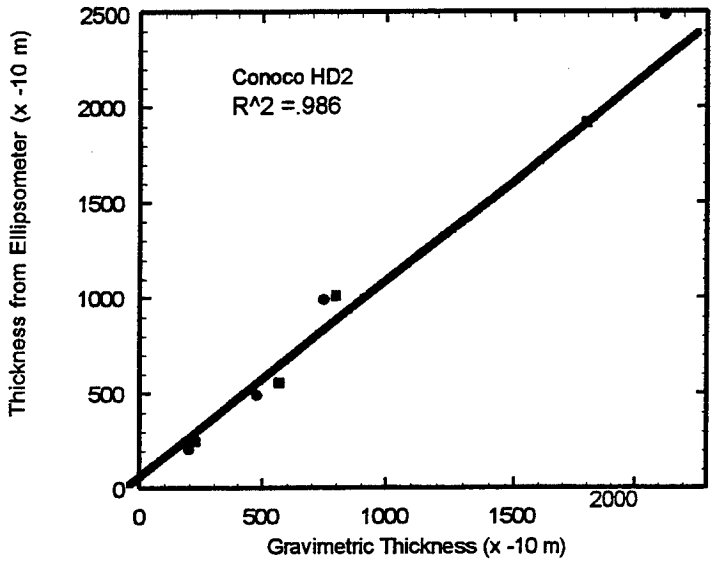


Figure 6 - Predicted by ellipsometer versus the gravimetric thickness for Conoco HD2 grease.

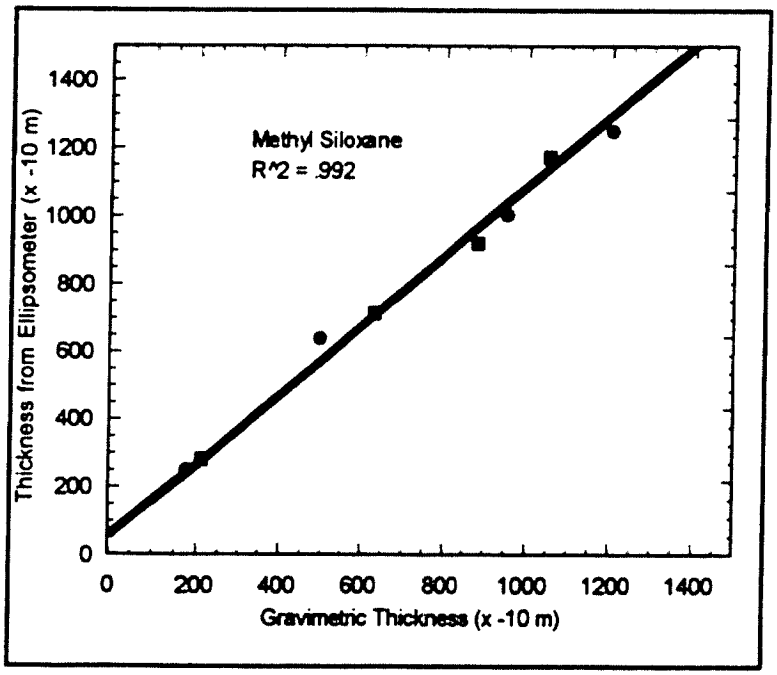


Figure 7 - Predicted by ellipsometer versus the gravimetric thickness for mold release silicone.

Conclusions

The optical constants were found for the two contaminants, Conoco HD2 grease and the mold release agent silicone. The predictive results of the unknown contaminant levels were in good agreement with the gravimetric thicknesses for both contaminants. The substrates that were used were highly specular and it is a restriction on the ellipsometric method. As long as the contaminant is deposited on a specular surface single films of the two contaminants studied here can be quantified.

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REPLACEMENT MATERIALS AND PROCESSES—II

ENVIRONMENTALLY COMPLIANT ADHESIVE JOINING TECHNOLOGY

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Abstract- Adhesive joining offers one method of assembling products. The advantages of adhesive joining and assembly are many and include the distribution of applied forces, lighter weight, and appealing appearance, just to name a few. Selecting environmentally safe adhesive materials and accompanying processes is paramount in today's business climate if a company wants to be environmentally conscious and stay in business. Four areas of adhesive joining — (1) adhesive formulation and selection, (2) surface preparation, (3) the adhesive bonding process, and (4) waste and pollution generation, clean-up, and management — all need to be carefully evaluated before adhesive joining is selected for commercial as well as military products. Designing for six sigma quality must also be addressed in today's global economy. This requires material suppliers and product manufacturers to work even closer together.

INTRODUCTION

With few exceptions, everything that is designed must be attached in some way to something else. Adhesives offer one method of joining materials and assembling products. The advantages of adhesive joining include the distribution of any stresses, appealing appearance, and lighter weight compared to mechanical joining. Adhesive joining has been used in the wood products industry for some time, and the aerospace and commercial airplane industry have used it extensively. Adhesives are also used extensively in the electronics industry. Now the automotive and transportation industries are using adhesives to assemble their vehicle bodies and components.

Adhesive joining can roughly be divided into two segments: assembly joining and structural joining. Assembly joining uses an adhesive to hold two parts (materials) together. There is little or no load applied to the joint area other than the weight of the two materials or forces created by differences in thermal expansion. The joint may be temporary, have little or no durability requirement, or later be encapsulated. Structural joining is the formation of a load-carrying joint, usually between two high strength members. Elaborate surface preparation is performed on each adherent to obtain optimum strength and performance (environmental durability, fatigue resistance, and/or chemical resistance).

Adhesives, primarily organic in chemistry, and their associated processes have certain worker health, safety, and environmental issues associated with them. These issues must be addressed during the design phase of product conception along with pollution and waste generation from the manufacturing process. "Design is the mother of all factors." "Decisions made at the design stage determine the composition of the 'waste stream' and determine environmental costs including any disposal costs."(1)

This paper will discuss the adhesive joining process and many of the decisions the designer must address in selecting environmentally compliant adhesive joining.

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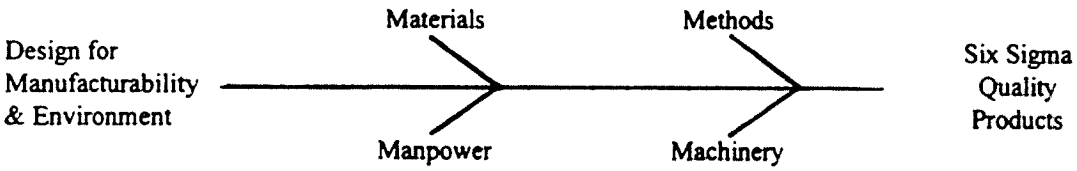
THE FOUR M's OF ADHESIVE JOINING TECHNOLOGY

All manufactured goods are produced with the 4 M's of manufacturing (materials, methods, machinery, and manpower). Figure 1 is a fishbone of the 4 M's which also applies to adhesive joining technology. Manufacturers not only have to select the correct adhesive (material) and its accompanying members (methods, machinery, and manpower) to do the job, but also must evaluate the overall impact on the environment (waste generation, amount and where it goes, employee health, and employee safety). Product design will have an impact on the adhesive assembly materials and process selection.

Figure 1
Manufacturing Fishbone



ADHESIVE SELECTION

Today, manufacturers are fortunate to have a filled arsenal of adhesives to tackle some very interesting and challenging joining requirements. Not only are there many different types and forms of adhesives, but most can be used in ways that minimize waste, reduce pollution, and meet performance. In addition to favorable chemistry, adhesive manufacturers have identified the importance of packaging and dispensing as participants to environmentally conscious manufacturing. Table 1 is a listing of traditional versus replacement adhesives.

:ble 1
Traditional versus Replacement Adhesives

TRADITIONAL ADHESIVES	REPLACEMENT ADHESIVES
Solvent Based (one and two part)	Water-based 100 % Solids Hot Melts Reactive Hot Melts Pressure Sensitive Adhesives (PSA)
Brittle Epoxies	Flexibilized Epoxies Acrylics Urethanes
Solvent Cements, Cellulose and Gums	Cyanoacrylates UV Cured (urethanes, epoxies, acrylates)

CLEANING AND SOIL (CONTAMINANT) REMOVAL

For years companies have relied upon chlorinated solvents such as trichloroethylene (TCE) and trichloroethane (TCA) to do any soil or contaminant removal from metals, plastics, and rubber parts. These solvents were used in hand-wiping operations (usually for assembly joining) as well as vapor degreasing operations (most often used for structural joining). These solvents removed a broad spectrum of organic soils and were rapid drying, non-flammable, widely available, and reasonably priced. An extra benefit was that although many plastic and rubber materials absorbed them and swelled, they readily gave up the solvent and returned to their original dimensions and shape without affecting the material and its

subsequent performance. These solvents were broad ranged cleaners and removed a wide spectrum of contaminants. Unfortunately, the availability and use of TCE and TCA are now long gone.

Today, a more methodical approach to cleaning must be taken. The author's experience working with numerous companies through the Department of Energy's Technology Transfer Program has been that many companies don't know what soils and contaminants they have on their substrates or parts. Therefore, the first two steps in establishing a cleaning process are identifying what the contaminants are and asking the question, How clean is clean? Once the contaminants have been identified and/or categorized, finding a replacement cleaning agent is much easier. The following equation is used as a general rule for cleaning.

(Cleaning Agent Concentration) x (Temperature) x (Time)
x (Mechanics) x (Fixturing) = Clean

CLEANING--HAND WIPING

Hand wiping consists of using a solvent-laden cloth to wipe the surfaces of substrates to be adhesive joined. Usually after several passes the worker looks at the cloth to see if there is any discoloration on it. If it is "clean," then he/she stops wiping. For metals (high surface energy materials), a contact angle measurement can be used to test the cleanliness of the surface. A low contact angle indicates good wetting, which is absolutely necessary for adhesive joining. A water-break-free test can also be used. Individual beads of water on the surface are an indication of soils or contaminants.

Evaluating cleanliness on plastics and rubber surfaces is more difficult because they are low surface energy materials. They are sometimes difficult to wet, even when clean. Many rubber and plastic materials must be abraded, coated with a primer, or treated by corona or plasma to obtain sufficient wetting and ultimate adhesive bonding. Because there are so many different plastic and rubber formulations, it is difficult to make one general statement to cover all of them. Each material must be evaluated separately. A good place to start is the *Processing Handbook on Surface Preparations for Adhesive Bonding* (2).

Numerous alternative wiping solvents are available. Some are a blend of several different solvents to create a range of solvency and cleaning efficacy. A company must decide what it is comfortable using in its facility — a high vapor pressure (HVP) cleaning agent versus a low vapor pressure (LVP) cleaning agent. HVP cleaners are high volatile organic chemicals (HVOCs) and are characterized as having low flash points and rapid evaporation: LVP cleaners are low volatile organic chemicals (LVOCs) and are characterized as having high flash points and slower evaporation. Each company must address the issue of what hand-wipe cleaning agent they should use, both from a standpoint of cleaning efficacy as well as worker health, safety, and environmental concerns.

CLEANING--STRUCTURAL JOINING APPLICATIONS

With the reduction in use of TCE and TCA in vapor degreasers, alternate cleaning agents and methods had to be found. Fortunately, the metal plating and conversion coating industry has extensive experience with detergent cleaners and water. Many of these cleaners are alkaline, and much of the knowledge is being transferred to industries doing structural bonding. However, some precautions are necessary. Steel and magnesium are very resistant to alkaline cleaners. Aluminum is easily attacked by alkaline cleaners, and silicates must be added to the cleaning bath to protect the aluminum from excessive etching. More thorough rinsing is also necessary to remove the silicates. Ultrasonic cleaning equipment is an excellent mechanical means of assisting the detergent and water cleaner. Some ultrasonic cleaners have heaters that raise the cleaning agent temperature and thus improve cleaning efficacy.

CHEMICAL ETCHING FOR ALUMINUM BONDING

For years the standard for aluminum alloy structural bonding was the Forest Products Laboratory (FPL) sulfuric acid/sodium dichromate etch formulation. However, the formulation is not acceptable by today's environmental standards because of sodium dichromate. The Boeing Company developed the phosphoric acid anodizing (PAA) process which is much better because it produces a deeper and more stable aluminum oxide skeleton for adhesive attachment. This improved etching results in improved structural joint durability. It is used extensively in the aircraft industry. However, for many other aluminum applications it is not necessary, and therefore the additional expense is not justified. Such an example of reduced need for the PAA etch process is in the Department of Energy (DOE) weapons program, which for years used the FPL etch process. An alternate to the FPL etch process was needed for environmental reasons. Most DOE weapons program needs are for adhesive joining of small aluminum parts and assembles that do not require high durability performance.

An alternate aluminum etching formulation was developed at Picatinny Arsenal, NJ (3). It has been identified as the P-2 etch and contains sulfuric acid and ferric sulfate. Aluminum parts are processed (etched) in a similar manner as they would be processed with FPL etch. The P-2 etch is more environmentally acceptable because it does not contain chrome. For adhesive producers who must test their products with aluminum alloys or manufacturers who do routine aluminum bonding, P-2 etch has been found to be an acceptable replacement (4). Today, FPL and P-2 etch formulations can be found in ASTM-D-2651, *Preparation of Metal Surfaces for Adhesive Bonding*. The FPL and P-2 formulations are listed in Table 2.

Table 2
FPL and P-2 Etch Compositions

COMPONENTS	FPL COMPOSITION	P-2 COMPOSITION
Sulfuric Acid	333 grams	370 grams
Sodium Dichromate	33 grams	----
Ferric Sulfate	----	150 grams
DI water to make	1 liter	1 liter

EVALUATION OF P-2 ETCHANT

Eight different adhesives (seven epoxies and one urethane) were evaluated with the P-2 etchant to see how they would perform. Many of the production joining operations used at Federal Manufacturing & Technologies (FM&T) involve materials other than aluminum. However, the facility does use 2024-T3 Alclad aluminum for all of its receiving inspection testing. Table 3 is a listing of the important information about the adhesives used in the evaluation. All test specimens were prepared and tested to meet the requirements of ASTM-D-1002, *Strength Properties of Adhesives in Shear by Tension Loading*.

Other materials and processing parameters comparing included (1) cleaning efficacy of trichloroethane (TCA) vapor degreasing versus alkaline cleaning in an ultrasonic cleaner versus acetone wipe followed by an isopropyl alcohol (IPA) wipe, (2) etch time, and (3) time between etching and bonding. Table 4 is a summary of the results.

Table 3
Candidate Adhesives

ADHESIVE	DESCRIPTION	CURE SCHEDULE
Epon 828 & Versamid 140	Two part flexible epoxy (50/50)	24 hr @ RT + 2 hr @ 160°F
EC 2216 B/A	Two part flexible epoxy	16 hr @ RT + 16 hr @ 160°F
Epibond 104 A/B	Two part, highly filled, high modulus epoxy	3 hr @ 160°F
EA 934 NA	Two part, high temp. resistant epoxy	2 hr @ 200°F
FM-123-5	Nitrile-epoxy film	2 hr @ 250°F with 25-30 psi pressure
Ablefilm 501	General purpose epoxy film	2 hr @ 200°F
Halthane 88/61002	Two part urethane adhesive	4 hr @ RT+2 hr @ 150°F+2 hr @ 200°F
Hysol 608	Two part fast cure epoxy	2 hr @ 140°F

Table 4
Materials and Processes
Comparison

PROCESS PARAMETER	OPTIMUM RESULTS
General soil removal	No difference between TCA vapor degreasing vs. alkaline cleaning in an ultrasonic cleaner. Both are better than hand wiping with acetone and IPA.
Etch time	Ten minutes appears optimum for both etch systems. All specimens resulted in cohesive bond failure.
Time between etching and adhesive bonding	Bond strength and cohesive failure mode appear to degrade after several days for both etch materials.

In conclusion, it was determined that using an alkaline cleaner and water in an ultrasonic bath followed with the P-2 etch process for 10 minutes was an acceptable alternative to using trichloroethane in a vapor degreaser followed by FPL etch for 10 minutes. Both processes produced test results having cohesive failure. Cohesive failure is defined as a failure in the adhesive material as compared to adhesive failure, which is a failure in the adhesive/substrate interface. Cohesive failure is more desirable.

GUIDELINES FOR GOOD ADHESIVE JOINING

There are some good adhesive joining assembly guidelines that this author has established which are carried to any new product design and assembly meeting. The author feels these rules establish the foundation for using adhesive joining as a method of assembling materials and parts. These rules are listed in Table 5.

CHALLENGE THE ADHESIVE SUPPLIER

There are challenges that the designer must place upon adhesive suppliers who supply the materials used to join materials together. Some simple points to keep in mind when talking to an adhesive supplier are listed in Table 6.

Table 5
Guidelines for Good Adhesive Joining

- Design sufficient joint area to handle the expected loads.
- Use surface preparation techniques to optimize the joint strength.
- The adhesive must wet both surfaces to be joined.
- Use a sufficient amount of adhesive.
- Have a match between the modulus of elasticity of the adhesive and substrates.
- Anticipate thermal expansion.
- Parts must fit well together.
- Read the cleaning, surface preparation, and adhesive material safety data sheets and understand any chemical dangers.

Table 6
Selecting an
Adhesive Joining System

Select an adhesive joining system for your application that is
- Easy to use
- Uses environmentally safe adhesives
- Requires minimal surface preparation
- Uses on-demand joining whenever possible
- Produces no or minimal waste
- Meets environmental regulations

DESIGNING FOR SIX SIGMA QUALITY

Whether building boats, airplanes, automobiles, or furniture, there are certain steps one should take in order to produce quality products. These items should be addressed early in the design phase and are true for adhesive joining assembly or any other assembly methods. First, design is the weapon of choice in producing quality products. Design determines the limits of product quality and determines the type and size of a manufacturing waste stream. Any changes and/or modifications must be made during the design phase. Changes or modifications made once the product has gone into production will most likely maintain product quality, not improve product quality. Therefore, sufficient time must be spent in the design phase of a new product. Table 7 lists several other suggestions for attaining six sigma quality using adhesive joining technology.

Table 7
Attaining Six Sigma Quality
Using Adhesive Joining Technology

- Reduce the number of manufacturing steps.
- Specify manufacturing processes which do not require numerous secondary operations.
- Avoid variable processes:
  - skill intensive
  - difficult to monitor
  - use highly variable materials
- Use prepackaged materials.
- Automate as much of the assembly process as possible.
- Know the workers' capabilities.
- Don't try to implement several new processes simultaneously.

CONCLUSION

P-2 etchant has been found to be an acceptable replacement for FPL etchant for verifying the strength of adhesives purchased from numerous adhesive suppliers. In addition, it is an acceptable aluminum surface preparation treatment for applications that do not require joint durability. Each company must decide what cleaning material(s) they can accept and use in their manufacturing facility. In order to help make this determination, they must first identify what are the contaminants that must be removed. Second, they must answer the question, How clean is clean? In many cases, trade-offs must be made to select cleaning materials that will do the job and meet today's environmental regulations.

In conclusion, using adhesive joining in today's manufacturing climate is a challenge. Companies must not only consider Design for Manufacturing but also Design for the Environment. In the past, waste generation and pollution at the end of the manufacturing pipeline was a concern. Today, using the Environmental Protection Agency's definition of pollution prevention, the manufacturer must consider waste and pollution streams as part of the product design process. In order to achieve high quality products using adhesive joining to assemble products, companies must minimize the number of manufacturing steps, especially those requiring secondary operations, and avoid variable processes that require judgments and/or decisions by their workers. Elimination of on-the-line decisions can be made by using prepackaged adhesives and automated application and assembly operations.

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(3) Wegman, R. F., Surface Preparation Techniques for Adhesive Bonding, Noyes Publications.

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NICKEL STRIKE ELIMINATION

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1. INTRODUCTION

Nickel is one of seventeen materials targeted by the EPA for regulation. In fact a recent Boeing Safety, Health, and Environmental Affairs (SHEA) toxicology report declared that "nickel may present the same degree of carcinogenic risk as does cadmium and chromium." In anticipation of potential regulation, Boeing has voluntarily committed to reduce its use by 50% by 1995.

Elimination of nickel within the company would target three current processes: electroless nickel plating (Boeing corporate process specification BAC 5728), electrolytic nickel plating and nickel striking (BAC 5746). Of these three processes, nickel strike, which is covered in BAC 5746, is the most widely used; consequently its elimination carries a significant benefit for the Boeing Company. The present report summarizes an investigative effort made by Boeing Defense & Space Group Materials & Processes group to reduce Boeing nickel use by substitution of iron strike.

2. BACKGROUND

A fast forming oxide film on an active alloy is beneficial from a general corrosion resistance standpoint because the alloy is thereby rendered relatively inert to many environments. However, when an electroplate is called out as a finish on such an alloy in order to meet some other engineering requirements, the oxide film impedes adhesion of the electroplate. In such cases, nickel striking the part, in a bath separate from the plating bath, is done prior to plating to promote plate adhesion. As a clean and previously activated part is energized as the cathode in a strike bath, hydrogen is co-deposited along with a thin layer of nickel. Because of strike bath inefficiency (only about 10%), massive amount of hydrogen gas bubbles evolve which scrub the part surface while nickel is being deposited. A nickel strike bath while very effective at providing a very thin substrate for plating also gives off harmful airborne nickel mist which raises environmental concerns.

2.1 Processes Requiring Nickel Strike

Presently, several Boeing process specifications callout nickel strike (per BAC 5746) as a surface preparation prior to further processing. These are:

BAC 5701, Cadmium Plating
BAC 5722, Copper Plating
BAC 5709, Hard Chromium Plating
BAC 5746, Nickel Plating (Electrolytic)
BAC 5728, Electroless Nickel Plating
BAC 5715, Silver Plating
BAC 5700, Zinc Plating.

Almost 90% of all drawing callouts are followed by cadmium plating (BAC 5701). For other widely used processes, such as chrome plating (BAC 5709), the strike is only an option and not the preferred process.

2.2 Nickel Strike Use at the Boeing Company

A breakdown of nickel strike callouts on design drawings, by alloy type, is presented for both Boeing Commercial Airplanes Group (BCAG) (Figure 1) and Boeing Defense & Space Group (BD&SG) (Figure 2). By far the main application is on precipitation hardened (PH) steels. This breakdown by major Boeing group is significant insofar as it shows that nickel strike has also been used to improve plate adhesion on alloy steels as well. Most of this use occurs only on the KC-135 Program.

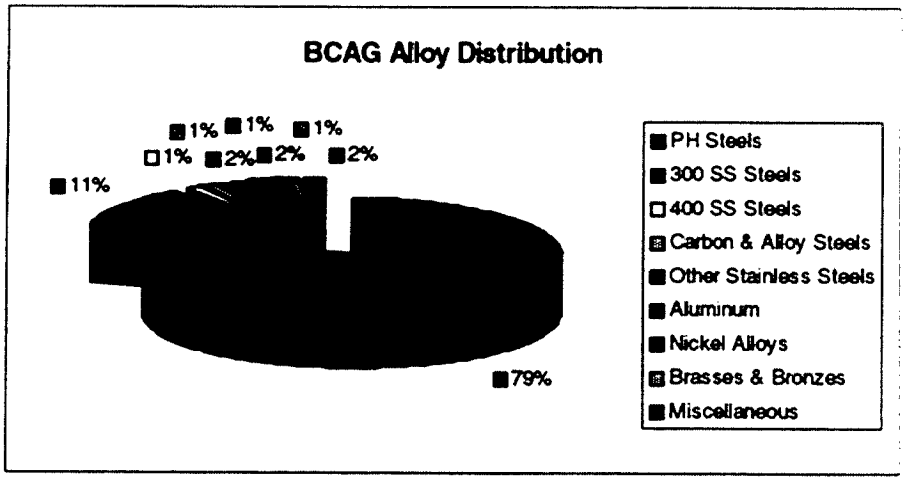


Figure 1: Use of nickel strike prior to plating in the Commercial Airplane Group

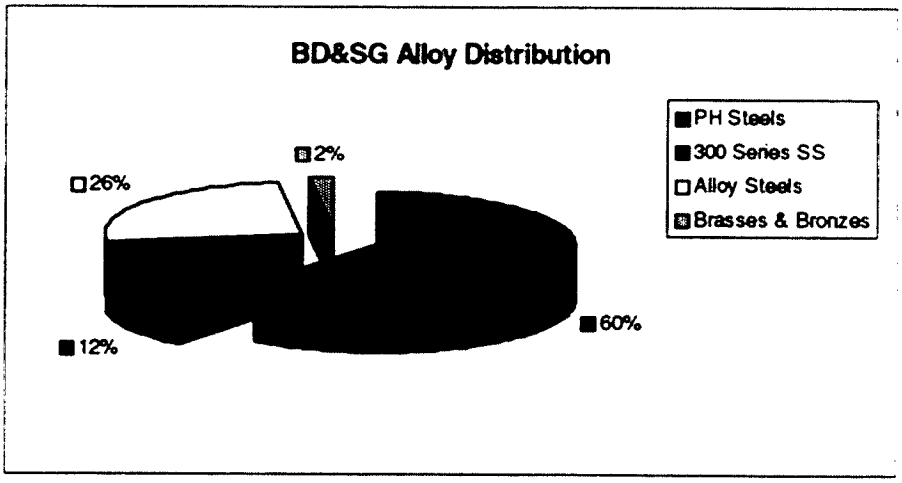


Figure 2: Use of nickel strike in the Defense and Space Group

2.3 Boeing Tank Capacity

The total nickel strike tank capacity in the U.S. Boeing facilities is about 7000 gals. Although this quantity is not large, it represents well over 60% of our use of nickel. An obvious advantage to a successful implementation of this nickel reduction approach is that it allows us to exceed our 50% reduction target. The detail breakdown of our nickel strike capacity by facility is the following:

- **Puget Sound** (4800 gals): Kent (850 gals); Auburn Machine Shop (1,900 gals); Auburn Emergent Manufacturing (1,100 gals), Everett (550 gals), Renton (400 gals);
- **Portland** (550 gals);
- **Wichita** (1000 gals);
- **Philadelphia** (100 gals);
- **Chicago** (550 gals).

3. EXPERIMENTAL PROCEDURE

3.1 Approach

Several issues had to be resolved at the outset before the experimental program was started.

3.1.1 Choice of a Strike Bath

The initial choice of a strike bath was an iron chloride/hydrochloric acid bath, patterned after the nickel strike bath of BAC 5746, Section 9.3. Concerns over flash oxidation of the thin iron deposit on the surface, oxidation of the iron anode in the tank, release of iron oxide impurities in the bath, pitting of the overplate, and the high acidity of the solution (pH< 1.0) led us to consider other solutions, including: ferrous sulfate/ascorbic acid and ferrous sulfate/citric acid. A mixed bath of nickel sulfate and iron sulfate was also considered (see Section 3.2). Either citric acid or ascorbic acid were added on an equimolar basis with iron to prevent oxidation of Fe^{2+} to Fe^{3+}[1]. Later in the investigation (Section 3.3) only the iron chloride/hydrochloric acid and the iron sulfate/citric acid baths were considered.

3.1.2 Evaluation Criteria

It was clear that a strike layer alone would be impossible to evaluate on the basis of general electroplate evaluation criteria of appearance, corrosion, adhesion. Thus, rather than directly comparing iron strike to nickel strike, we evaluated the properties of the overplate as a way of verifying that the plated specimen suffered no performance debit. Since the majority of nickel struck parts are cadmium plated, cadmium or its known electroplate alternatives (Sn-Zn and Zn-Ni) were evaluated.

3.2 Corrosion Testing of Cadmium Plated Panels

Verification of the corrosion properties of iron struck and cadmium plated specimens were made using the following materials and processes:

Materials

- Type 416 Stainless Steel
- Nickel Alloy 625
- 15-5PH Steel

Martensitic type 416 stainless steel was chosen for its inferior corrosion resistance among the stainless steels. Precipitation hardening type 15-5 PH was chosen because it is the most widely used. Nickel Alloy 625 was chosen because adhesion is most difficult to achieve using the conventional nickel strike/cadmium plate process (BAC 5701). Two specimens of each type were iron struck and plated.

Processing parameters:

- Process C (Control: nickel strike process)
  1. 170-400 grit glass bead blast (BAC 5748, Type II, Class 1)
  2. Inhibited hydrochloric (2 min)
  3. Double rinse (2 min)
  4. Nickel Strike per BAC 5746 (cathodic strike for 5 min at 25 ASF)
  5. Double rinse (flash double rinse)
  6. Cadmium plate and chromate post-treatment per BAC 5701.

- Process I, II, III or IV (Iron Strike processes)
  1. 170-400 grit glass bead blast (BAC 5748, Type II, Class 1)
  2. Inhibited hydrochloric (2min)
  3. Double rinse (2 min)
  4. Iron strike in solution I, II, III or IV** (cathodic strike for 5 min at 25 ASF)
  5. Double rinse
  6. Cadmium plate and chromate post-treatment per BAC 5701.

**Note: Iron strike I = Ferrous sulfate/Ascorbic acid; II = Ferrous sulfate/Citric acid; III = Ferrous sulfate/Citric acid/Nickelous sulfate; IV = Ferric chloride/Hydrochloric acid;

Evaluation:

Diagonal scribes were marked with a knife edge prior to exposure in a salt spray environment, where they were inspected at the end of 96 hrs, then every week until 996 hrs elapsed.

3.3 Adhesion Testing

3.3.1 Overall Process for Better Adhesion

A 16-run full factorial Design Of Experiments (DOE) was set up with plate adhesion as the evaluation criterion.

Materials

- 15-5PH
- Ni alloy 625 panels.

Processing parameters:

Panels of the above materials were Sn-Zn plated after the following surface preparation:

- glass beads vs. aluminum oxide blasting;
- inhibited hydrochloric (BAC 5751), 2 minutes immersion activation vs. sulfuric/HF (per BAC 5709) 2 minutes anodic activation;

Strike:

- anodic-cathodic strike vs. cathodic strike (40ASF);
- 30 s vs. 90 s rinse and delay time prior to plating.

Evaluation

Once plated, adhesion was tested per BSS 7225 Type I Class 4 (90° crosshatch scribes, dry tape adhesion test) . Attempts were made initially to test per BSS 7235 (bend test for plate adhesion); however, hardened 15-5PH strips proved to be too hard to bend.

3.3.2 Current Density for Better Adhesion

Once the optimum process was established through the DOE, a Hull cell was used to study the effect of strike current density on adhesion of the overplate.

Materials

- 15-5PH
- Ni Alloy 625

These panels were cut to fit a 500 ml Hull Cell.

Processing parameters:

The side of the panel facing the Hull Cell anode was masked as shown in Figure 3. The back side was entirely masked except the electrical contact area. One or two strike solutions were used: Iron chloride/hydrochloric acid and iron sulfate/citric acid. Figure 3 also gives an indication of the strike current densities obtained across the length of the panel

Panels of the above materials were either Sn-Zn or Zn-Ni or cadmium plated following the surface preparation, iron strike given below.

1. H_2SO_4/HF activation, Anodic @ 60 to 100 ASF for 60 sec.
2. Rinse for 1 min or less.
3. Strike for 5 min @ 1A, 2A, or 3A. (Rinse)
4. Plating
   - Tin-Zinc Plating (Dipsol-Gumm, Draft specification)
     Sn-Zn plate at 20 ASF for 20 minutes

Rinse and dry

- Zinc-nickel plating (per BAC 5637)
  Zinc-nickel strike, cathodic 90 ASF for 60 sec.
  Zinc-nickel plate, 20 ASF for 39 minutes
  Rinse and dry.
- Cadmium plating (per BAC 5701)
  Cadmium strike, cathodic 90 ASF (5A) for 30 sec.
  Cadmium plate, 20 ASF (1.1A) for 17 min.
  Rinse and dry.

Evaluation

All panels were primed with BMS 10-11 (chemical and solvent-resistant epoxy primer) followed by a seven day cure. Adhesion was first tested per BSS 7225 Type I or III Class 5 (1 day or 7 day soak in deionized water, 45° cross-hatch scribes), then followed by a 160 in.lb impact on the scribed area. The impact area was further tape tested.

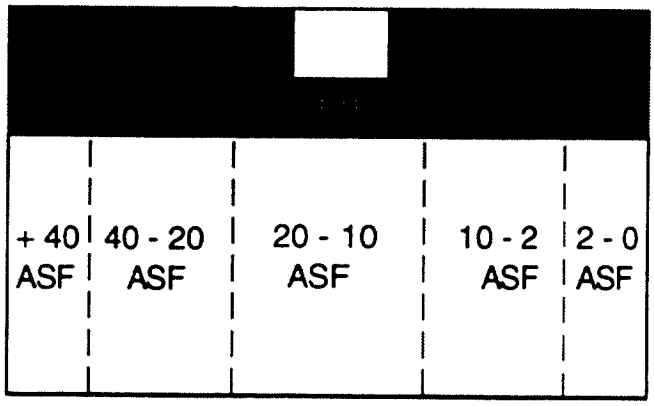


Figure 3: Sketch of iron-struck then normally plated 15-5PH or Ni 625 panels

4. RESULTS

4.1 Evaluation for Corrosion

With the exception of nickel struck panels (control), which had a consistently smooth and adherent cadmium overplate, the appearance of the iron struck panels varied considerably. Most had a blistered cadmium overplate. Nickel 625 panel surfaces were the worst. The iron sulfate/citric acid solution gave more consistent results on all materials. Here however, only corrosion results after 96 hours exposure in neutral salt spray, then weekly until 996 hrs were considered relevant to this evaluation. All panels passed the inspection for "white corrosion products of cadmium [or] basis metal at the end of 96 hrs" (BAC 5701, Sec 11.5.a). The results, with particular attention paid to the scribe area, appears in Table 1.

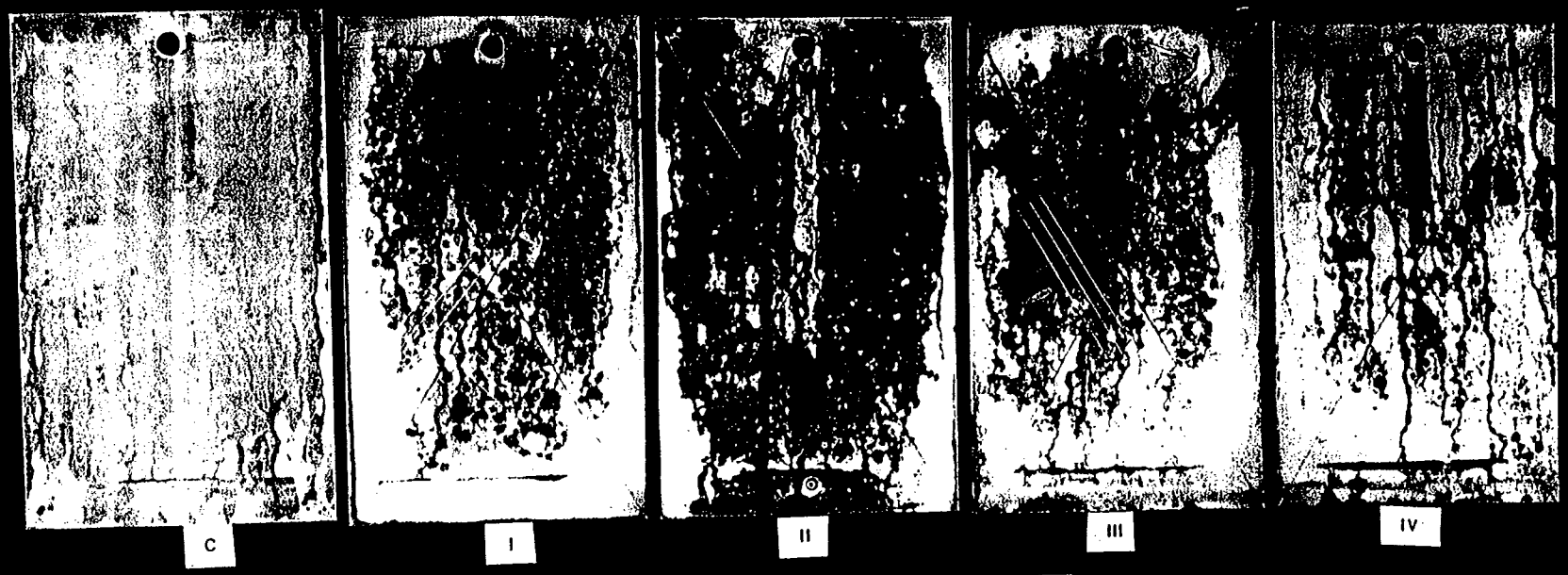
At the end of 996 hrs, none of the panels showed signs of corrosion. Neither red-rust for steel panels nor greenish white for the Ni 625 panels. As a result they were, again, rated as "pass". At this stage, however, all the panels, including the controls, had a dark and dull appearance with small areas where the irridesence of the original chromate treatment still showed. See Figures 4, 5 and 6.

Table 1: Results of Corrosion Test In Neutral Salt Spray

Specimen IDs	*96 hrs SS*	*996hrs SS*	*Comments After 996 hrs SS*
15-5PH Specimens			
15-5-C	P	P	
15-5-C	P	P	
15-5-B-I	P	P	Some black discolor (?) in scribe
15-5-Y-I	P	P	Some black discolor (?) in scribe
15-5-B-II	P	P	
15-5-Y-II	P	P	
15-5-B-III	P	P	
15-5-Y-III	P	P	
15-5-B-IV	P	P	Slight loss of metal luster in scribe
15-5-Y-IV	P	P	Slight loss of metal luster in scribe
Ni 625 Specimens			
I-C	P	P	
I-C	P	P	
I-B-I	P	P	
I-Y-I	P	P	4 tiny black spots on scribe
I-B-II	P	P	
I-Y-II	P	P	
I-B-III			
I-B-III			
I-B-IV	P	P	Black discolor. (?) in scribe
I-B-IV	P	P	
416 CRES Specimens			
B-C	P	P	
B-C	P	P	
Y-I	P	P	Black discolor. (?) on scribe
B-I	P	P	3 discolored spots (pits?)
B-II	P	P	
Y-II	P	P	
B-III	P	P	
Y-III	P	P	4 small black spots on scribe
Y-IV	P	P	
B-IV	P	P	

C = Control
I = Ferrous Chloride/Hydrochloric Acid
II = Ferrous Sulfate/Ascorbic Acid
III = Ferrous Sulfate/Citric Acid
IV = Ferrous Sulfate/Citric Acid/Nickelous Sulfate

Figure 5 Appearance of iron-struck and cadmium plated 15-5PH following 996 hours exposure to neutral salt spray (ASTM B117)



C = Control
I = Ferrous Chloride/Hydrochloric Acid
II = Ferrous Sulfate/Ascorbic Acid
III = Ferrous Sulfate/Citric Acid
IV = Ferrous Sulfate/Citric Acid/Nickelous Sulfate

Figure 4 Appearance of iron-struck and cadmium plated Ni 625 following 996 hours exposure to neutral salt spray (ASTM B117)

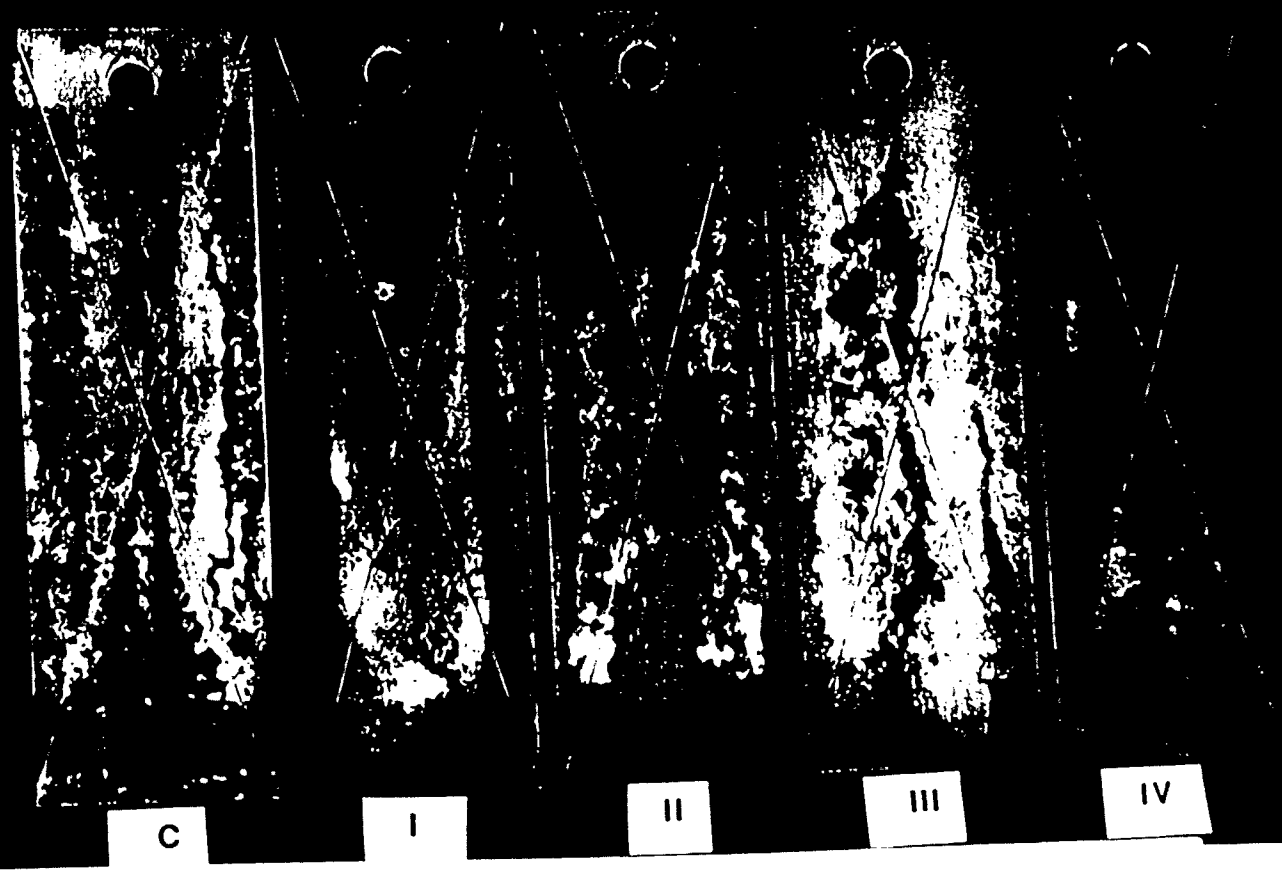


Figure 6 Appearance of iron-struck and cadmium plated 416 CRES following 996 hours exposure to neutral salt spray (ASTM B117)

C = Control
I = Ferrous Chloride/Hydrochloric Acid
II = Ferrous Sulfate/Ascorbic Acid
III = Ferrous Sulfate/Citric Acid
IV = Ferrous Sulfate/Citric Acid/Nickelous Sulfate

4.2 Evaluation For Plate Adhesion

4.2.1 Tin-Zinc Plate Adhesion

4.2.1.1 Preparation for Better Adhesion

Results were obtained on both 15-5PH and Ni Alloy 625.

15-5PH

The results of the DOE established early on that all panels immersion cleaned in inhibited HCl prior to being struck in $FeSO_4$/Citric acid bath failed the tape adhesion test. The DOE was then modified to include two current density settings (60 vs 100 ASF) of an electrolytic activation in a sulfuric/HF solution (Section 9.5, BAC 5709). The results, as evidenced in Table 2, clearly show that all aluminum oxide blasted specimens, except those that received an anodic striking prior to a cathodic strike, passed the BSS 7225 Type I Class 5 test (45° scribes, dry tape adhesion test). All other panels failed along the edges of the panels.

Table 2: Results of DOE: Sn-Zn adhesion on iron struck 15-5PH panels

Run	*Abrasive Blast*	*Sulfuric/HF Current Density*	*Anodic*	*Time Prior To Plating*	*Adhesion Test*
1	AlOx	100	No	90	Pass
2	GlassB	60	Yes	90	Fail
3	AlOx	100	No	30	Pass
4	AlOx	60	No	30	Pass
5	GlassB	60	Yes	30	Pass/Edge Fail
6	GlassB	60	No	30	Pass/Edge Fail
7	AlOx	60	No	90	Pass
8	GlassB	100	No	30	Pass/Edge Fail
9	GlassB	100	Yes	90	Pass/Edge Fail
10	AlOx	100	Yes	90	Pass/Edge Fail
11	AlOx	60	Yes	30	Pass/Edge Fail
12	GlassB	100	Yes	30	Pass/Edge Fail
13	GlassB	100	No	90	Pass/Edge Fail
14	AlOx	100	Yes	30	Pass/Edge Fail
15	AlOx	60	Yes	90	Pass/Edge Fail
16	GlassB	60	No	90	Pass/Edge Fail

Ni Alloy 625

It was surmized that an anodic strike of the specimens in a mildly oxidizing solution (iron sulfate/citric acid) would not help adhesion since this would only cause the formation of an oxide film. Consequently, anodic striking in iron sulfate/citric acid was eliminated from the process. Results of the same set of tests on Ni Alloy 625 proved that all glass bead blasted panels failed

the dry tape adhesion test. This is illustrated in Figure 7. Table 3 summarizes these results of tin-zinc adhesion.

Table 3: Results of DOE: Sn-Zn adhesion on iron struck Ni Alloy 625 panels

Run	*Abrasive Blast*	*Sulfuric/HF Current Density*	*Time Prior To Plating*	*Adhesion Test*
1	AlOx	100	90	Pass
3	AlOx	100	30	Pass
4	AlOx	60	30	Pass
6	GlassB	60	30	Fail
7	AlOx	60	90	Pass
8	GlassB	100	30	Fail
13	GlassB	100	90	Fail
16	GlassB	60	90	Fail

Aluminum oxide blasting followed by a 60 to 100 ASF sulfuric/HF activation were found to be excellent methods of preparing the surface of both 15-5PH and Ni Alloy 625 for striking and Sn-Zn plating. This became the preferred method of surface preparation for the rest of the program. In addition, the combined rinse and travel time of 30 to 90 seconds into the Sn-Zn plating bath did not have an impact on adhesion. A 90 seconds rinse and travel time became part of our preferred process for the rest of the investigation.

4.2.1.2 Adhesion Testing: Effect of Strike Current Density

4.2.1.2.1 Adhesion Testing: with iron strike

Following the preferred surface preparation, panels of 15-5PH struck in a Hull cell at a total current of 1A, 2A and 3A and Sn-Zn plated were cut in strips matching current density regions shown in Figure 3. Each individually tested strip passed the scribed, 160 impact and dry tape test, suggesting that even areas of zero current density (no iron strike) might pass the adhesion test.

4.2.1.2.2 Adhesion testing: without iron strike

Following the preferred surface preparation, panels of 15-5PH and Ni Alloy 625 were plated without iron striking. These panels were primed with BMS 10-11 Type 1. All panels passed 45% angle scribe wet and dry tape adhesion test. They passed the tape adhesion test following 160 in.lb impact on the scribed region. Figure 8 illustrates the appearance of the Ni Alloy 625 and 15-5PH panels following the adhesion and impact testing.

4.2.1.3 Verification testing on Bushings

Concerns over how "real parts" might behave were addressed with three 15-5PH bushings Sn-Zn plated following the preferred surface preparation. The excellent adhesion was verified by scraping the plate with a knife edge and checking for separation of the plate from the basis metal.

These bushings are shown in Figure 9. It is of interest to note we could not produce cadmium plate free of blisters on these bushings in spite of our repeated attempts to do so.

4.2.2 Zinc-Nickel Plate Adhesion -

4.2.2.1 Effect of Strike Current Density

The results of the evaluation of Zn-Ni plated 15-5PH and Ni Alloy 625 previously iron struck in $FeSO_4$/citric acid or $FeCl_2$/HCl appear in Table 4

Table 4: Zn-Ni adhesion on iron struck 15-5PH and Ni 625 panels

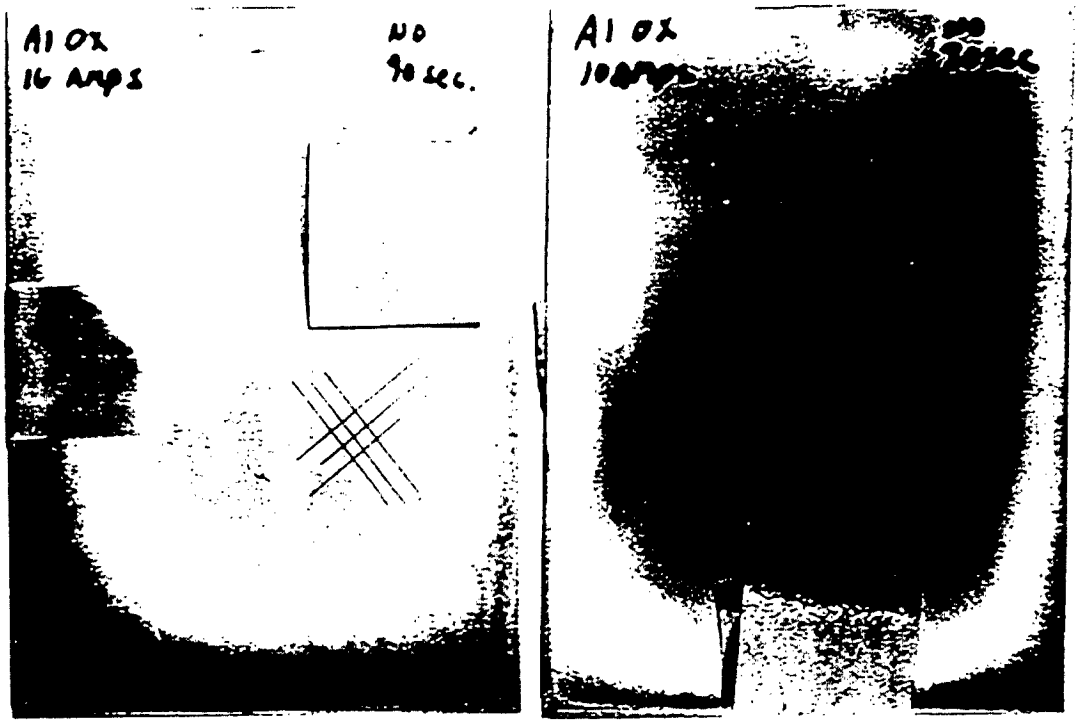
Panel #	*Substrate*	*Strike bath*	*Tape Test*		*Impact Test*		*Comments*
			24-hr	*7-day*	*24-hr*	*7-day*	
1	15-5PH	$FeSO_4$ (1A)	9	10	Fail	Fail	Med. removal
2	15-5PH	$FeSO_4$ (2A)	10	10	Good	Good	Small Amt
3	15-5PH	$FeSO_4$ (3A)	10	10	Good	Good	Small Amt
4	Inconel	$FeSO_4$ (1A)	--	--	--	--	Not painted
5	Inconel	$FeSO_4$ (2A)	10	10	Fail	Good	Fail-low cd area
6	Inconel	$FeSO_4$ (3A)	10	10	Fail	Good	Fail-low cd area
7	Inconel	$FeCl_2$ (1A)	10	10	Fail	Fail	Large removal
8	Inconel	$FeCl_2$ (2A)	10	10	Fail	Fail	Large removal
9	Inconel	$FeCl_2$ (3A)	10	10	Good	Fail	Fail-low cd area
10	15-5PH	$FeCl_2$ (1A)	10	10	Fail	Fail	Med. removal
11	15-5PH	$FeCl_2$ (2A)	10	10	Good	Good	Small Amt
12	15-5PH	$FeCl_2$ (3A)	--	--	--	--	Not painted
13	Inconel	No strike	10	10	Fail	Fail	Large removal
14	15-5PH	No strike	10	10	Fail	Fail	Large removal

cd: current density

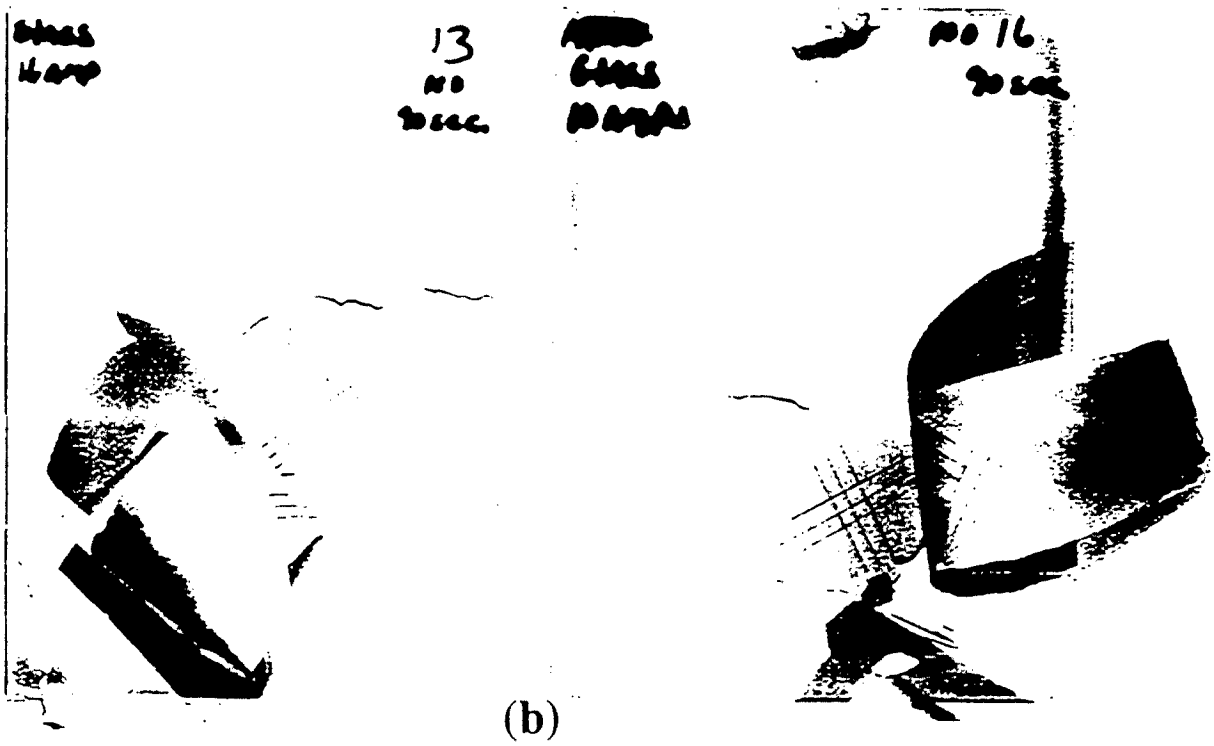
Paint adhesion results are good for zinc-nickel as seen from Table 5. A better measure of plate adhesion is provided by the impact test, as it is the case with Sn-Zn plated specimens. Two main conclusions are readily apparent from the results. First, the $FeSO_4$/citric acid strike solution has an edge over the $FeCl_2$/HCl as there are no large removal of Zn-Ni plate following impact test. Second, adhesion failures recorded on runs 13 and 14, when specimens did not receive a strike, and consistent failure in low density areas for runs 5 and 6 indicate that a strike is an absolute necessity when Zn-Ni plating difficult stainless steels and nickel alloys and the higher the iron strike current the better (> 30ASF).

4.2.2.2 Verification Testing on Bushings

Verification testing of an iron strike Zn-Ni plate combination on 15-5PH bushings confirms that iron striking is a necessity. Figure 10 shows the Zn-Ni plated bushings. The bushings plated following iron strike had better adhesion.

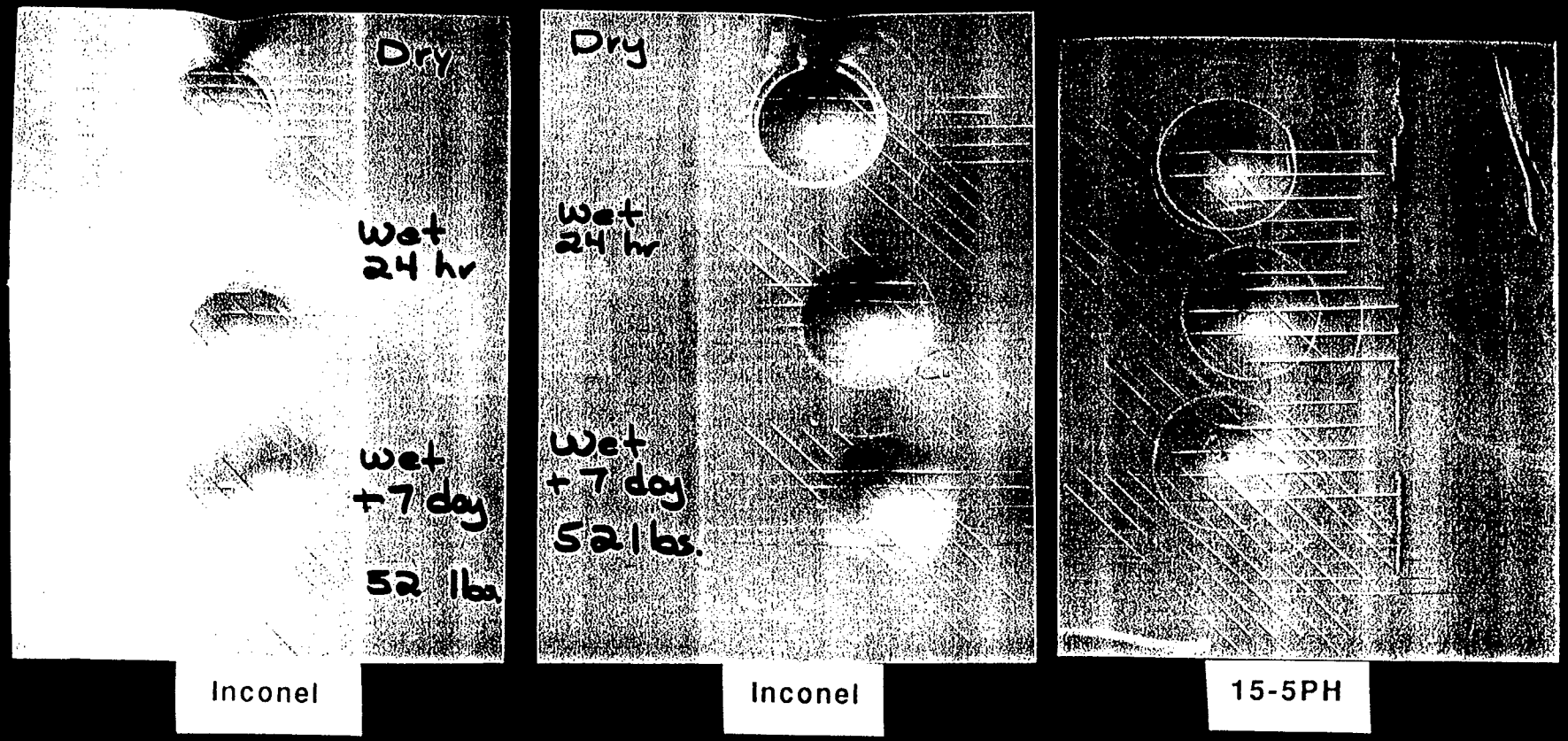


(a)



(b)

Figure 7 Appearance of iron-struck, Sn-Zn plated panels: (a) Al_2O_3 blasted . (b) glass bead blasted



Adhesion Test: Tin-Zinc Plate over Sulfuric-Hydrofluoric Acid Anodic Activation, No Strike

Figure 8 Appearance of impact and tape adhesion tested primed panels

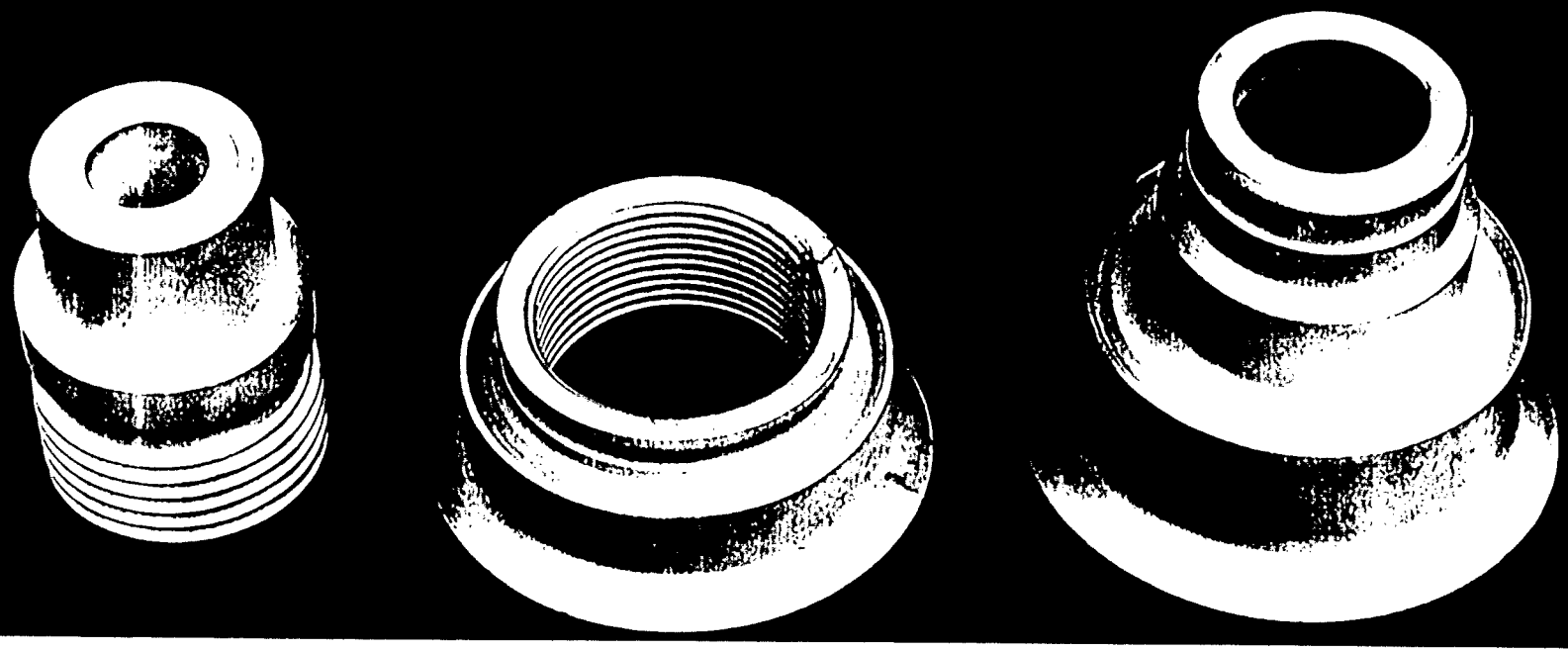


Figure 9 Appearance of Sn-Zn plated bushings - No iron strike

Figure 10 Appearance of Zn-Ni plated bushings

4.2.3 Cadmium Plate Adhesion

4.2.3.1 Effect of Strike Current Density

The results of adhesion tests on cadmium plated panels appear in Table 5. All panels that were not struck appeared blistered. Inspection of these panels reveals that the iron strike must be conducted above a current density of 30 ASF, as areas that fall below that range failed the impact test. The Improved appearance and better adhesion of the cadmium plate obtained here, when compared with panels iron-struck then plated for the earlier corrosion test (see Section 4.1), results from energizing the panels before immersion into the cyanide cadmium plating solution.

Table 5: Cadmium adhesion on iron-struck 15-5PH and Ni 625 panels

Panel #	*Substrate*	*Strike bath*	*Tape Test*		*Impact Test*		*Comments*
			24-hr	*7-day*	*24-hr*	*7-day*	
C1	15-5PH	$FeCl_2$ (2A)	10	10	Pass	Pass	
C2	15-5PH	$FeCl_2$ (2A)	10	9	Pass	Pass	
C4B	15-5PH	$FeSO_4$ (2A)	10	2[1]	Pass	M[1]	Adhesion tested below 12 ASF
C9	15-5PH	$FeSO_4$ (2A)	10	9	Pass	Pass	
C8	15-5PH	None	10	10	Pass	Pass	
C17	15-5PH	None	10	8	Fail	M	Covered with blisters
C10	Inconel	$FeCl_2$ (2A)	10	10	M	Pass	Adhesion tested below 20 ASF
C11	Inconel	$FeCl_2$ (2A)	10	10	Pass	Pass	
C12	Inconel	$FeSO_4$ (2A)	10	10	Pass	M	Adhesion tested above 100 ASF
C12A	Inconel	$FeSO_4$ (2A)	10	10	Fail	Pass	Adhesion tested below 20 ASF
C16	Inconel	None	9	7	Fail	Fail	Covered with fine blisters
C7	Inconel	None	9	9	Fail	Fail	Covered with fine blisters

4.2.3.2 Verification Testing on Bushings

Figure 11 shows bushings, cadmium plated following H_2SO_4/HF activation and iron strike. These appear along with one bushing that was not iron struck. The cadmium plate obtained is smooth and adherent to the 15-5PH substrate material.

Figure 11: Appearance of Cd plated bushings

5. CONCLUSION

Striking stainless steels or nickel alloys with an iron strike solution prior to Sn-Zn or Zn-Ni plating offers an alternative to the conventional nickel strike without sacrificing the corrosion or adhesion properties of the overplate. While a dry abrasive blast (per BAC 5748 Type I) followed by a H_2SO_4/HF activation (per BAC 5709) will ensure an excellent surface preparation overall, optimum adhesion can only be achieved with attention paid to the specific overplate for the determination of appropriate strike parameters. Specifically:

- Sn-Zn coatings can be sucessfully applied to surfaces struck from $FeSO_4$/Citric acid or $FeCl_2$/HCl at any current density and even on surfaces plated directly without a strike, after $FeSO_4$/HF activation.
- Zn-Ni coatings are best applied to surfaces struck from $FeSO_4$/Citric acid solution at current densities greater than 30 ASF
- Cadmium plating can be applied to surfaces struck from $FeSO_4$/Citric acid or $FeCl_2$/HCl solution at current densities greater than 30 ASF provided that the part is energized prior to immersion in the cadmium plating solution.

Validation of the results on bushings indicates that applicability to actual parts can be assured during scale-up. Scale-up of this technology is greatly recommended.

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CHROME-FREE CONVERSION COATING PROCESS EVALUATION

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ABSTRACT

The purpose of this US EPA project was to perform a full-scale evaluation of a chromium-free chemical conversion coating process. The metal substrate selected for screening purposes was 6061-T6 aluminum alloy. The chromium-free conversion coating, a fluotitanic acid modified organic chemistry from a commercial supplier, was demonstrated using the variable screening portion of a sequential experimental design and analysis strategy. The technique of analysis of variance, and the associated significance tests was applied. The approach consisted of using realistic manufacturing conditions to conversion coat aluminum followed by powder coating or cathodic electrocoating. Critical process operating parameters of the conversion coating baths, including the composition of discharges to the environment, were monitored and reported. Further, the quality of the coating properties, when compared to the customer's requirements, were tested and reported.

INTRODUCTION

Chromate conversion coating has been used to take advantage of aluminum's affinity for oxygen to transform aluminum oxide into a thickened and strengthened, chemically stable film that can readily accept other finishes. As with most surface finishing processes, the surface to be conversion coated must be particularly clean, deoxidized and active. The dichromate ion is the typical oxidizer in the oxidation-reduction chemical reactions that chemically convert the aluminum alloy substrate surface to this adhesive and corrosion resistant film.

$$2Al + Cr_2O_7^{2-} + 2H^+ + 6HF \rightarrow 2AlF_{3(aq)} + 2CrOOH_{(s)} + 3H_2O$$
$$2Al + Cr_2O_7^{2-} + 2H^+ \rightarrow Cr_2O_3 + Al_2O_3 + H_2O$$

Since chromates have been identified as hazardous to human health, chromium-free conversion coating technologies have been proposed. This would help reduce the quantities of F006 solid wastes generated from conventional chromate conversion coating operations, help reduce discharges of hexavalent chromium containing acid over-spray into the atmosphere, help prevent hexavalent chromium from entering the water system, and additionally increase worker health and safety.

The chromium-free conversion coating, a fluoacid-modified organic chemistry, was selected based primarily upon its results from the Chrome Alternatives Project conducted under the auspices of

the National Center for Manufacturing Sciences (NCMS). When compared to chromate conversion coating, the Material Safety Data Sheets for this chromium-free conversion coating indicates that it has less restrictive human exposure limitations, based upon the chemicals' respective threshold limit values (TLV), and permissible exposure levels (PEL).

This conversion coating is manufactured in a way that orients the "modified" end of the organic molecule towards the aluminum substrate (see Figure 1). The substrate surface should be generally free of oils to assist this. The fluotitanic acid component oxidizes a portion of the aluminum substrate, incorporates it into the film, and, therefore, forms a conversion coating.

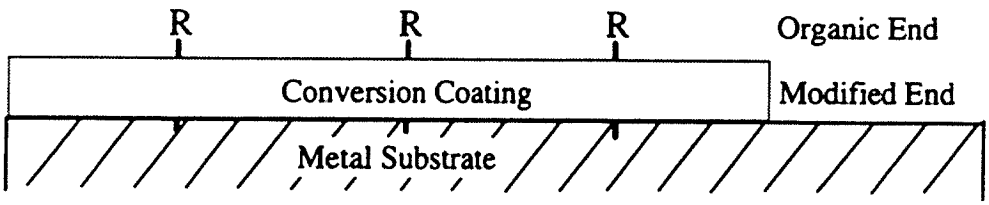

Figure 1. Desired Orientation of Conversion Coating on Substrate.

This chrome-free alternative to conventional chromate conversion coatings was demonstrated by varying process conditions systematically, and thereby:

1. Measuring the physical and mechanical properties of the conversion coating.
2. Measuring the composition of the liquid discharge to the environment from the conversion coating process.

This objective was accomplished by the full-scale processing of coupons (Phase 1), and of parts (Phase 2) through a selected process, under varying conditions, to measure controlling factors. This processing and testing was conducted at Concurrent Technology Corporation (*CTC*) Demonstration Factory in Johnstown, Pennsylvania.

EXPERIMENTAL PROCEDURE

Materials

Coupons of 6061-T6 aluminum alloy obtained from Alcoa in Pittsburgh, Pennsylvania, were used throughout the bench tests and full-scale demonstration. Commercial parts, of varying aluminum alloy composition, were obtained from United Technologies Carrier Transcold in Syracuse, New York, and from Westinghouse Air Brake Company in Pittsburgh, Pennsylvania.

Solutions were obtained from Brent-America in Lake Bluff, Illinois. The cleaner contained potassium hydroxide (5 - 10 wt. %), and potassium silicate (5 - 10 wt. %). The deoxidizer, used during

bench tests only, contained ferric sulfate (25 - 30 wt. %), and mixed mineral acids. The conversion coating solution contained an organic component, and a hexafluotitanic acid component (5 - 10 wt. %).

The material of construction of the immersion baths was polypropylene. Bench testing used a polyethylene container for the conversion coating, and glass beakers for the cleaner and for the deoxidizer, when used. Glass was not used with the conversion coating because it embrittled glass. The panels were threaded through a PVC-coated, wooden dowel rod, and separated from one another with Tygon® tubing as spacers. Aluminum wire suspended the assembly of panels, and of commercial parts as pictured in Figure 2 below.

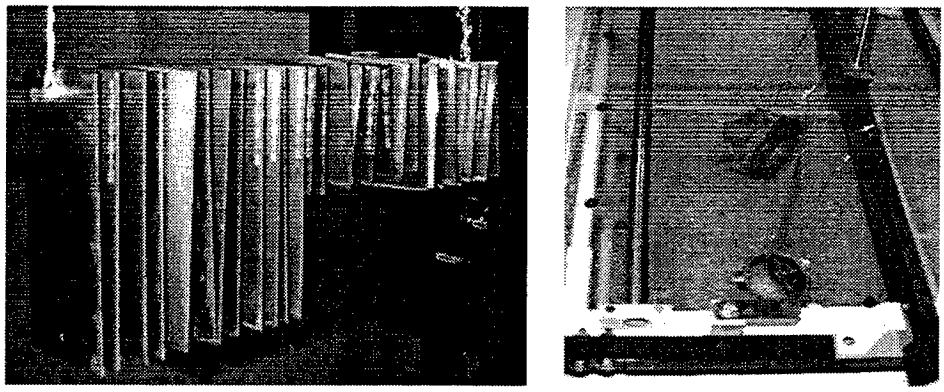

Figure 2. Configuration of racked aluminum alloy coupons and parts

Some conversion coated panels were epoxy coated with either Morton Corvel Cloud Grey powder coating (10-7010), or BASF Gray Cathogaurd® 300 electrodeposition coating. During the project's Phase 2 (parts demonstration phase), 5052 aluminum alloy panels were acrylic cathodic electrodeposition coated with PPG 830/504 at the PPG Industries, Inc., Springdale, Pennsylvania facility.

Project Quality Assurance (QA) Objectives

Conversion coatings were tested during Phase 1 (coupon trial phase), according to the provisions of MIL-C-5541E (Chemical Conversion Coatings on Aluminum and Aluminum Alloys). Deviations from this specification were the absence of chromates, and the application of cathodic electrocoating and powder coating as the final surface finish because they have emerged as viable, low volatile organic coatings, and because they are particularly sensitive to the quality of the conversion coating.

Also, discharges from the process were sampled and analyzed for potential environmental hazards. Analytical methods are selcted, based upon what was known about the chrome-free conversion coating chemistry. For example, Chemical Oxygen Demand (COD), is used to screen for significant organic concentrations. Table 1 summarizes the quantitative QA objectives for the critical-only measurements relevant to this project.

Table 1. QA Objectives for Quantitation Limits, (Critical-only Measurements).

Critical Measurement	Matrix	Method	Units	Quantitation Limit	Precision[1]	Accuracy[2]	Completeness
Physical Measurements							
Adhesion -- Wet Tape	Coupon	Fed. Test 6301.2	Pass/Fail 0-5[3]	Complete to no failure	All pass or all fail	Not applicable	Not applicable
Bare Coating Corrosion Resistance	Coupon	ASTM B 117-94	Quantity & size of pits	0 spots, > 1/32" dia.	All pass or all fail	Not applicable	Not applicable
Chemical Measurements							
Al, Cu, Fe, Ti	Conversion Coat & its Rinse Water	EPA 200.7	mg/L	0.05	20%	80-120%	95%
COD		EPA 410.4	mg/L	5.0	20%	80-120%	95%
Total Suspended Solids		EPA 160.3	mg/L	2.5	20%	Not applicable	95%
Process Measurements							
Temperature	Conversion Coating	Mfg. Instructions (Love 2500)	°F	0.1 °F	1.5%	Not applicable	NA

[1] As relative percent difference of two replicates unless specified otherwise.
[2] As percent recovery of a matrix spike (carried through same sample preparation stages as samples).
[3] In addition to the pass/fail evaluation, the 0-5 rating scale of ASTM 3359 was applied.

Site Selection and Sample Handling Procedures

The processing site was within the *CTC* Demonstration Factory with chemical analysis being performed adjacent to the process and also within the *CTC* Testing Laboratory. Coupons were kept from being wetted or soiled while in the Demonstration Factory. Following written demonstration plans for each test run, coupons and parts were stamped with an identification number, and then processed through the inorganic and organic finishing line equipment. Laboratory personnel maintained control of the coupons after processing. Grab samples of process discharges were obtained from their drain points, and maintained through a chain of custody by laboratory personnel. The process set-up, as it relates to this equipment, is diagrammed in Figure 3, and documented in Table 2.

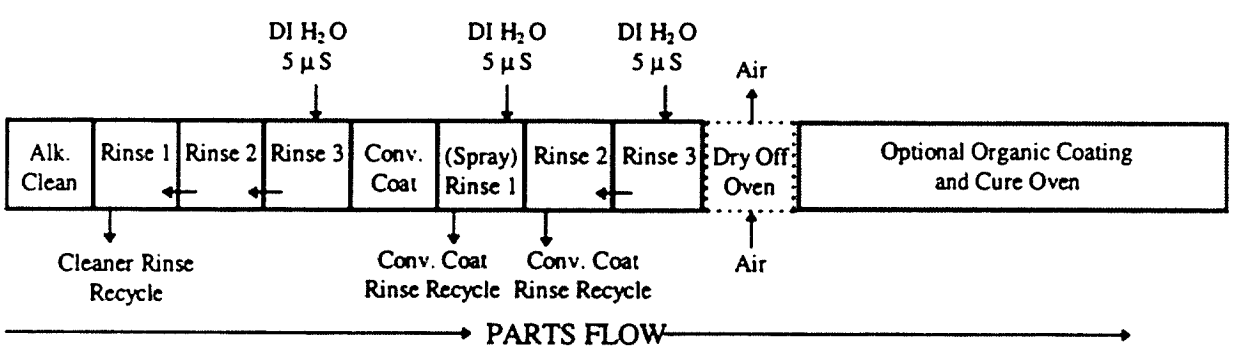

Figure 3. Process Flow Scheme for 6061-T6 Aluminum Alloy

Table 2. Process Evaluation Set-Up, Mid-Point Conditions

	Alkaline Clean	Rinse 1 (Clean)	Rinse 2 (Clean)	Rinse 3 (Clean)	Conv. Coat[1]	Rinse 1 (NCCC)	Rinse 2 (NCCC)	Rinse 3 (NCCC)	DryOff Oven[1]	Cathodic E-Coat[2]	Rinse 1 (E-Coat)	Rinse 2 (E-Coat)	Rinse 3 (E-Coat)	Cure Oven
Material	CHEM CLEAN 1220	Water from Rinse 2	Water from Rinse 3	Water @½ gpm feed	CHEM COAT	Water @½ gpm feed	Water from Rinse 3	Water @½ gpm feed	Air	Epoxy	Water	Water	Water	Air
Volume	81 Gal.	60 Gal.	60 Gal.	60 Gal.	93 Gal.	74 Gal.	60 Gal.	60 Gal.	——	2800 G.	900 G.	2800 G.	2800 G.	——
Time	60 s.	20 s.	20 s.	20 s.	2½ min.	20 s.	20 s.	20 s.	2 min.	210 s.	22 s.	32 s.	30 s.	22 min.
Temp.	120 °F	Ambient Room Temperature (70 - 75 °F)							150 °F	80 °F	Ambient			425 °F
Conc.	5 %	Rinse 2	Rinse 3	5µS	2 Parts[3]	5µS	Rinse 3	5µS	Forced	80 Volts	Rinse 2	Rinse 3	5µS	Forced
Discharge	None	Surface	None	None	Dumps	Bottom	Surface	None	——	N/A	N/A	N/A	N/A	N/A

[1]See Table 3 below for adjustments to the these process settings for the designed experiment.
[2]Alternative finish, powder coating, were: 80 kV, 22 psi fluidizing air, 12 psi atomizing air, (no rinses), cure @ 425 °F for 15 minutes.
[3]Brent "CHEMCOAT" = 2 Parts: L497260A (Coating) @5.25 g/l + L494190 (pH Adjuster) @ 2.5 g/l.

After bench tests, and one full-scale demonstration at the mid-point conditions, a designed experiment was executed. It consisted of twelve test conditions for a seven (7) independent variable Plackett-Burman pattern given in Table 3. The reason for selecting these variables are as follows:

1. Pot life impacts raw material costs.
2. Solution temperature could fluctuate, depending on a factory building's ambient conditions.
3. Solution's pH effect on outputs needed investigation.
4. Organic concentration, relative to pH, showed the effect of an over-charged or depleted bath.
5. Dry-off time before painting may be important for some manufacturing operations.
6. Dry-off temperature affect factories that do no have a dry-off oven.
7. Pre-paint storage time affects manufacturing operations with work-in-process.

These ranges for the process settings were set wide enough that an important effect — if one existed — could be detected, but not so wide as to be impractical.

Table 3. Test Conditions and Input Variables for Conversion Coating Experiment

Test Condition Number	Input Variable ("RT" = Room Temperature @70-75°F)						
	Conversion coating				Dry Off Oven		Pre-Paint
	Pot–life	Temp. (°F)	pH Adj. (%)	Organic (%)	Time(min.)	Temp. (°F)	Time(days)
1	0 days	RT	0.10	0.40	2	RT	0 (immediate)
2	0 days	100	0.10	0.40	2	180	7
3	2 days	RT	0.10	0.40	30	180	7
4	0 days	100	0.30	0.40	30	RT	0 (immediate)
5	2 days	RT	0.30	0.40	2	RT	7
6	2 days	100	0.30	0.40	30	180	0 (immediate)
7	0 days	RT	0.10	1.00	30	180	0 (immediate)
8	2 days	100	0.10	1.00	2	RT	0 (immediate)
9	2 days	100	0.10	1.00	30	RT	7
10	0 days	RT	0.30	1.00	30	RT	7
11	0 days	100	0.30	1.00	2	180	7
12	2 days	RT	0.30	1.00	2	180	0 (immediate)

RESULTS AND DISCUSSION

Mid-Point Test Results Satisfy Requirements after Second Bench Test

The 6061-T6 aluminum alloy coupons were analyzed with a scanning electron microscope, energy dispersive spectroscopy, at 10 KeV. They appeared generally clean, and free of corrosion products.

Processing 6061-T6 aluminum alloy coupons at the mid-point conditions (Table 2, above), gave satisfactory results after the second bench test. The results from initial bench scale processing satisfied paint adhesion requirements (no failure under both ASTM D 1308 and ASTM D 3359), but gave only marginal painted neutral, 5% salt spray corrosion resistance (ASTM B 117-94), and marginal bare salt spray corrosion resistance. The second bench test employed overflow rinsing rather than stagnant rinsing, and resulted with no corrosion products within the 336 salt spray exposure period. Suprisingly, panels whose pretreatment process included deoxidation immediately before conversion coating fared worse, with numerous pit corrosion products developed within approximately 24 hours. Microscopy at 1500× magnification (Figure 4), indicated that the conversion coating process that omitted deoxidation had more void area. Overflow rinsing was desirable for product quality, and omitting deoxidation was best for product quality — and it reduced the oveall discharges from the aluminum pretreatment process.

Although the pot life for this conversion coating chemistry was only a couple days, chemical additions were made to bring the chemistry back to acceptable processing levels. A seven-day old bath did not produce a conversion coating that satisfied the bare corrosion resistance requirement, but, when this bath was chemically recharged, the conversion coating satisfied corrosion resistance requirements.

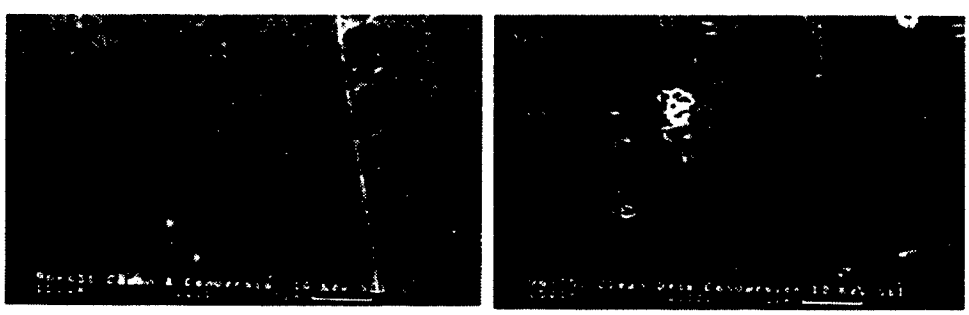

Figure 4. Conversion Coated 6061-T6 Aluminum Alloy, omitting deoxidizer (left), versus including deoxidizer (right) 10 KeV Scanning Electron Secondary Mode, 1500×

Samples of conversion coating and its rinses were analyzed for metals, organics, and other characteristics. They are summarized in Table 4. The Chemical Oxygen Demand results for the rinse waters indicate dilute solutions, that necessitate testing for neither Biological Oxygen Demand nor Total Organic Carbon. To measure how concentrated the rinse waters could become before further testing would be warranted, a Microtox Acute Toxicity test was conducted on the rinse waters. This test is similar to ASTM D 5660 - 95, using a toxicity test with a luminescent marine bacterium. These test

results indicated that if the rinse waters were concentrated to one percent (1%) of the conversion coating solution further waste water discharge testing would be warranted.

Table 4. Chemical Measurements of Discharges from Mid-Point Processing Conditions

Test Parameter	Conversion Coating	Spray (Rinse 1)	Dip (Rinse 2)	Reporting Limit	Test Method
Aluminum	0.17 mg/L	BDL	BDL	0.02 mg/L	EPA 200.7
Copper	BDL	BDL	BDL	0.02 mg/L	EPA 200.7
Iron	0.21	BDL	BDL	0.02 mg/L	EPA 200.7
Titanium	455.6 mg/L	0.11 mg/L	BDL	0.02 mg/L	EPA 200.7
Chemical Oxygen Demand	14,300 mg/L	55 mg/L	50 mg/L	5 mg/L	EPA 410.4
Total Suspended Solids	6 mg/L	< 1 mg/L	< 1 mg/L	1 mg/L	EPA 160.3
Total Organic Carbon	2310 mg/L	—	—	2 mg/L	EPA 415.1
Biological Oxygen Demand	5550 mg/L	—	—	2 mg/L	Std. Method 5210B
Turbidity	16 FTU	—	—	1 FTU	HACH 8237
Total Kjedahl Nitrogen (NH_3-N)	1.84 mg/L	—	—	0.5 mg/L	EPA 351.3
pH	4.4 S.U.	6.5 S.U.	6.5 S.U.	—	EPA 150.1

Table 5. Physical Measurements of Product from Mid-Point Processing Conditions

Measurement	Coupon #	Results
Adhesion, Organic Powder Coating (P-Coat)	13 to 14	No Failure
Adhesion, Organic Electro-deposition Coating (E-Coat)	18 to 19	No Failure
Bare Corrosion Resistance	1 to 5	0 pits @336 hours (Pass),
Bare Corrosion Resistance Unexposed Control Specimen	6	1st pit @ 1344-1416 hours, Discoloration
Visual Appearance	1 to 5	Clear Coating, no visible marks
Film Thickness (ASTM B 244), P-Coat Specimens	7 to 11	2.73 ± 0.33 mils
Corrosion Resistance (scribed area), P-Coat Specimens	7 to 11	1st Creepage @504-528 hours,
Corrosion Resistance, P-Coat Unexposed Control Specimen	12	No Loss in Unscribed Area (3096 hour test)
Film Thickness (ASTM B 244), E Coat Specimens	20 to 24	0.50 ± 0.01 mils
Corrosion Resistance (scribed area), E-Coat Specimens	20 to 24	1st Creepage @ 1680 - 1752 hours
Corrosion Resistance, E-Coat Unexposed Control Specimen	25	1st Loss in Unscribed Area @ 2256-2328 hours
Weight of Conversion Coating (HNO_3 soak for 15 minutes)	15 to 17	12 ± 2 mg./sq.ft.

Twelve Test Condition, Conversion Coating Experiment Shows Corrosion Resistance Variation

Coupons of 6061-T6 aluminum alloy were processed in accordance with the conversion coating experiment shown in Table 3 above, starting on April 10, 1996, and ending on May 6, 1996. The statistical significance of the estimated effects were assessed via comparison with a measure of experimental error variation, and are provided in Table 6. The organic coating adhesion requirement (no

Table 6. U.S. EPA Chrome-Free Conversion Coating Project, Analysis of Variance and Associated Significance Test

336 HOUR SALT SPRAY RANKING OF FACTORS (P-VALUE)/BEST SETTING							
	CONVERSION COATING				DRY OFF OVEN		PRE-PAINT
RESPONSE VARIABLE	POT LIFE	TEMP	pH ADJUSTER	ORGANIC	TIME	TEMP	TIME
AVERAGE NUMBER OF PITS	5(.702) LOW BEST	3 (.290) LOW BEST	1(.038) LOW BEST	2(.137) HIGH BEST	6(.905) HIGH BEST	4(.303) LOW BEST	NA
AVERAGE NUMBER OF HOURS TO FIRST PIT	1(.114) LOW BEST	3(.308) LOW BEST	2(.242) LOW BEST	4(.327) LOW BEST	5(.404) LOW BEST	6(.587) LOW BEST	NA
AVERAGE CORROSION RATING	5(.580) HIGH BEST	3 (.349) LOW BEST	1(.021) LOW BEST	2(.147) HIGH BEST	4(.402) LOW BEST	6(1.00) N/A	NA

1008 HOUR SALT SPRAY RANKING OF FACTORS (P-VALUE)/BEST SETTING							
	CONVERSION COATING				DRY OFF OVEN		PRE-PAINT
RESPONSE VARIABLE	POT LIFE	TEMP	pH ADJUSTER	ORGANIC	TIME	TEMP	TIME
P-COAT PANELS AVG. HRS. TO NOTICEABLE ADHESION LOSS	5(.792) LOW BEST	1(.017) LOW BEST	6(.800) LOW BEST	3(.332) LOW BEST	7(.826) LOW BEST	2(.323) LOW BEST	4(.535) LOW BEST
E-COAT PANELS AVG. HRS. TO NOTICEABLE ADHESION LOSS	3(.664) HIGH BEST	4(.773) LOW BEST	1(.026) HIGH BEST	5(.803) LOW BEST	2(.191) HIGH BEST	6(.816) HIGH BEST	7(.957) HIGH BEST
P-COAT AVG. CORROSION RATING	5(.748) LOW BEST	1(.031) LOW BEST	4(.518) LOW BEST	2(.180) LOW BEST	6(.748) HIGH BEST	3(.325) LOW BEST	7(1.00) NA
E-COAT AVG. CORROSION RATING	1(.200) HIGH BEST	7(1.00) NA	3(.346) HIGH BEST	6(1.00) NA	2(.200) HIGH BEST	4(.535) HIGH BEST	5(.758) LOW BEST

CHEMICAL OXYGEN DEMAND (COD) RESULTS RANKING OF FACTORS (P - VALUE)/BEST SETTING							
	CONVERSION COATING				DRY OFF OVEN		PRE-PAINT
RESPONSE VARIABLE	POT LIFE	TEMP	pH ADJUSTER	ORGANIC	TIME	TEMP	TIME
C.O.D. WATER DIP TANK NO. 9	4(.859) HIGH BEST	2(.441) HIGH BEST	3(.536) HIGH BEST	1(.004) LOW BEST	NA	NA	NA
C.O.D. SPRAY RINSE TANK NO. 13	4(.908) HIGH BEST	3(.801) HIGH BEST	2(.704) HIGH BEST	1(.000) LOW BEST	NA	NA	NA

A statistical p-value for an estimated effect ranges from 1.00 (extremely insignificant) to 0.00 (extremely significant).

loss of adhesion), was satisfied for all except test condition number 1 electrocoating. This single case of adhesion loss was not investigated further. The concentration of metals and of total suspended solids in the discharges were similarly insignificant. Bare conversion coating corrosion resistance, organic coating system corrosion resistance, and chemical oxygen demand were effected by the input variables in Table 3. This experimental plan satisfied the project objectives to determine those process input variables that are individually most important in influencing output variables. The joint, or interactive, effects of the input variables on the outputs cannot be evaluated using this experimental plan.

The bare conversion coating's average number of hours to its first pit was most effected by the conversion coating pot life. After pitting corrosion occurred, the inputs that effected its average amount of pitting was the pH adjuster concentration, followed by the organic component concentration. The powder coating's average number of hours to first noticeable creepage was most effected by the conversion coating temperature, with the lower temperature better. The electrocoating's average number of hours to first noticeable creepage was most effected by pH adjuster, with the higher pH adjuster concentration better. The chemical oxygen demand was most effected by the organic concentration.

Dry-off oven temperature did not have a large effect on the conversion coated product's corrosion resistance and wet tape adhesion. The more significant effects indicates that low dry-off temperature was individually better.

Regression analysis verified that there was no significant correlation between the organic coating thickness and each of the corrosion evaluations: R^2 ranged from 0.003 to 0.142.

Of the process conditions tested, the mid-point settings gave the best results for both bare and electrodeposition coating system corrosion resistance. The powder coating corrosion evaluation results were best from test condition numbers 1, 3, 4, and 5, because these four test conditions had no creepage within the 1008 hour test period. However, because the mid-point settings gave the best critical product measurement results, the conversion coating mid-point condition was used to process parts.

Parts Processing and Evaluation Not Completed

Parts were obtained from Westinghouse Air Brake Company and United Technologies Carrier Transcold. These parts, with various aluminum alloy composition, are still undergoing evaluation. Preliminary results indicate the following:

1. Unprotected conversion coated and sealed 356 sand cast aluminum alloy part had no pits within the inspection time period (96 hours).

2. Unprotected conversion coated 6061-T6 aluminum alloy plate (114 in.^{2}) had 2 pits within the inspection time period (168 hours). Pre-existing corrosion on the part is suspected; a deoxidizer will be inserted into the process to test this suspicion.

3. Unprotected conversion coated and sealed 380 die cast aluminum alloy (3.5% copper) had severe corrosion products within the inspection time period (48 hours).

4. Unprotected conversion coated 5052 aluminum alloy panels (18 in.^{2}) had 13 pits within 336 hours. The 6061-T6 aluminum alloy coupons, processed at the same time, had no corrosion pits. Pre-existing corrosion products on the 5052 aluminum alloy panel are suspected. For qualification, new panels are being obtained.

CONCLUSIONS

1. Overflow rinsing is desirable for improved neutral salt spray corrosion resistance. The rinse water discharges should be re-analyzed when their concentration builds to one percent (1%) of the conversion coating solution concentration.

2. For the 6061-T6 aluminum alloy coupons, omitting deoxidation is best for product quality — and it also reduces discharges from the overall aluminum pretreatment process.

3. Although the pot life for this conversion coating chemistry is only a couple days, chemical additions can be made to bring the chemistry back to acceptable processing levels. This reduces the volume of process discharges.

4. Concentration of the pH adjuster for the conversion coating bath significantly effects product corrosion resistance.

5. The thickness variation of both the powder coating and the electrodeposition coating applied to the conversion coated aluminum did not effect the ASTM D 1654 creepage rating.

6. Of the process conditions tested, the mid-point settings were the best for bare, conversion coating corrosion resistance.

ACKNOWLEDGMENT

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RAPID, QUANTITATIVE MEASUREMENT OF THE LEVEL OF CROSSLINK DENSITY BASED ON A VARIATION OF THE *SOLVENT SWELL* PRINCIPLE

Submitted by

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ABSTRACT

The three minute, analytical method known as Evaporative Rate Analysis (ERA) permits rapid, microcomputer-based measurement of the level of crosslink density in polymers based on a variation of the classic *solvent swell* method.

The ERA method involves deposition of 18 microliters of a factory preformulated test solution (a low boiling, nonradioactive solvent or solvent combination containing a high-boiling-but-volatile Carbon-14 labeled material in a ratio of ca 60,000 / 1 - solvent / radiochemical) onto a polymer surface. With a GM detector positioned directly above the surface and with metered air flowing between the surface and the detector, the tendency of the polymer surface to retain the radiochemical is monitored. The air sweeps the already evaporated, vapor phase solvent and the radioactive molecules out from under the detector. Following the initial evaporation of the lower boiling solvent, the rate at which the radiochemical evaporates is a function of the level of crosslink density--the more rapid the rate, the higher the level of crosslink and *vice versa*.

The particular solvent / radiochemical formulation employed in the method is based on tests of a representative four stage cure ladder--low cure, low specification, high specification, and overcure. The method provides unique information particularly with respect to slight undercure and slight overcure conditions.

The Montreal Protocol deadline has materially altered the composition of many solvent combinations since the solvency characteristics of trifluorotrichloroethane had earlier been used extensively. Current formulations based on cyclopentane, 2,3- dimethylbutane, and 2,2-dimethylbutane with varying percentages of chloroform, methylene chloride, or tetrahydrofuran as the low boiling solvent or solvent combinations have been shown generally to be superior substitutes for test solution formulations.

One of two USNRC license EXEMPT C-14 radiochemicals are routinely used in the several test solution formulations, namely: Tetrabromoethane-C14 and Tridecane-C14.

INTRODUCTION

In the development of polymer chemistry during the early middle of this century, much research was directed to linear polymers such as 66 nylon, polyacrylonitrile, etc. in which each high molecular weight molecule has only two ends. Even high molecular weight linear polymers are able, generally, to *dissolve* in appropriate solvents, i.e., to form true solutions.

On the other hand if linear polymers are subjected to crosslinking processes, the solubility exhibited by linear polymers rapidly decreases as the crosslinking progresses. At higher levels of crosslink density the polymers are only swelled by the same solvents that dissolve linear polymers of similar chemical composition. Hence the principle of 'solvent swell' was early used and is often still used in polymer characterization to determine the level of crosslink density: A solvent swells a highly crosslinked polymer to a low degree while one having fewer crosslinks swells to a greater degree. Employed since the early days of polymer research, the *solvent swell* method has been used as a measurement tool in which a preweighed sample of crosslinked polymer is placed in a solvent for an extended period of time depending on the polymer and the solvent. The sample is removed from the

solvent, the outwardly adherent solvent is removed by blotting and the sample is reweighed. The uptake of solvent by the sample is an inverse measure of the degree of crosslink density.

Today there are many other methods of measuring the level of crosslink density including thermal mechanical analysis (TMA) and differential scanning calorimetry (DSC), among others, as well as less elegant methods such as abrasion testing, solvent rub techniques, pencil hardness, etc. Particularly applied to thinner coatings and inks, the solvent rub and pencil hardness tests are widely used but each is subject to considerable individual variation.

The ERA method was originally discovered in the early 1960's. It has been studied, developed and improved, and employed by numerous users. Earlier literature references are available.[2,3]

BACKGROUND

In this paper a number of abbreviations, special words, and trademarks are employed:

(1) *uCi* means *microCurie*, a unit of radiation which corresponds to 3.7 E 4 (37,000) disintegrations per sec.

(2) *Carbon-14 (C-14)* refers to the radioactive isotope of the element Carbon, an isotope which emits only soft or low energy beta particles; most C-14 beta particles are stopped by a sheet of paper.

(3) USNRC *EXEMPT* means the very low level of Carbon-14 that is not regulated by the U. S Nuclear Regulatory Commission. No license is required for possession or use. Only USNRC licensed companies are permitted to distribute EXEMPT quantities not to exceed ten 100 uCi C14 (or combinations of smaller quantities that added up to 100 uCi C14) at one time. Multiple quantities may be stored by the user.. Shipments may be made to anyone in the US under USDOT *excepted package* rules. For foreign shipments IATA rules apply.

(4) u*L* means microliter (1 millionth of a liter).

(5) *ca* is the abbreviation for the Latin *circa* which means 'approximately'.

(6) GM detector refers to a thin end-window Geiger Mueller detector tube which detects the C-14 beta emissions which penetrate through the 1.4 - 2.0 mg/cm^2 mica window.

(7) *MESERAN, MICRO-SOLVENT-SWELL, CROSS#LINK, XLNK* and *.LNK* are trademarks licensed to E R A Systems, Inc.

The current microcomputer-based ERA (or MESERAN) technology involves deposition using a precision microsyringe onto a flat or concave surface of 18 ul of a test solution comprising a low boiling solvent or solvent combination and a high-boiling-but-volatile Carbon-14 labeled compound (in a ratio of ca 60,000:1). The amount of radiochemical per single test (less than 0.06 uCi) corresponds to ca 6 E 14 molecules which equates to the *equivalent* of ca one molecular layer over one sq cm. Metered air or gaseous nitrogen is then permitted to flow between the surface and a GM detector positioned directly above the surface in order to sweep away and to remove vapor phase solvent and radiochemical molecules. The evaporation of the low boiling solvent and then the radiochemical is observed as a function of time by recording the detected emissions per second *arising from the radiochemical molecules remaining on, or retained by, the surface*. Figure 1 illustrates the GM detector / test surface configuration.

Figure 2 illustrates the log-count-per-second versus time for typical responses observed for undercure, cure, and overcure measurements. The initial increase in count is caused by absorption of the soft beta emissions by the solvent during its evaporation. The peak of each curve represents the final evaporation of liquid solvent while the post peak curve provides the meaningful evaporative response used for quantifying the level of crosslink density discussed in detail below. The postpeak evaporative process is best described as a somewhat complex second order process.

For effective selection of optimal test solution for a given polymeric formulation, it is necessary to examine a cure ladder (low cure, low and high specification cures, and overcure) and to select the test solution formulation which provides optimal differentiation for the crosslink levels of interest. If the solvent system selected has no significant swelling of the test surface at any level of cure, the radiochemical evaporates completely within ten to 20 seconds. Excessive swelling and radiochemical invasion resulting from too strong a solvent exhibits almost complete retention and a slope approaching zero. In both cases virtually no differentiation of cure levels results.

Each test takes only 3 minutes; the amount of radiochemical employed is EXEMPT under U S Nuclear Regulatory Commission and/or 'Agreement State' licensing regulations due to the very low level of C-14 involved.

The ERA method has one other major application: The quantification of micro-organic residues on surfaces and NVR (NVOR) in solvents. This application is described in a paper presented in another section of this conference.

Two radiochemicals are routinely used for analyzing the level of crosslink density in polymeric substrates, namely:

(*A*) 1,1,2,2-Tetrabromoethane-1,2-C14 and (*B*) Tridecane-1,13-C14

The '*A*' and '*B*' designations are used in naming and coding the particular test solution formulations.

One or two of a number of low boiling non-radioactive solvents are employed in the several formulations to permit optimized differentiation during the invasive and evaporative portions of each test, namely:

(*H*)	Methylene chloride	(*K*)	Cyclopentane
(*L*)	Chloroform	(*M*)	Methanol
(*P*)	Tetrahydrofuran	(*V*)	2,2-Dimethylbutane
(*W*)	2,3-Dimethylbutane		

In days past (*J*) Trifluorotrichloroethane was extensively employed for solvency purposes but test solutions containing ***J*, *a CDC,*** are no longer distributed. A number of other low boiling solvents have also been studied but none are currently available in test solution formulations. (*M*) Methanol is available as a solvent but is rarely used.

A typical, somewhat invasive formulation for acrylics is ***BW20H*** which is tridecane-C14 in 2,3-dimethylbutane / methylene chloride in a solvent ratio by volume of 80 parts W and 20 parts H. This cited formulation is part of the series ***BW, BW05H, BW10H, BW20H, BW40H, BH*** with increasing solvency caused by increasing proportions of (*H*).

From the standpoint of invasion or swellability, tridecane-C14 (*B*) tends both to invade and to reemerge and evaporate more readily than the somewhat polar tetrabromoethane-C14 (*A*). Neither invade if the low boiling solvent or solvent combination fails to swell the polymer surface. Conversely both invade excessively when the solvent system swells excessively.

The solvent characteristic employed is the primary key to the success of the test procedure. The order of increasing solvency of the primary hydrocarbon solvents are $V << W < K$. *V* (2,2-dimethyl- butane) is the weakest solvent by virtue of the quaternary carbon at position 2 due to the three methyl groups and one ethyl group attached to that carbon atom--*V* is the most sterically hindered and has the largest cross-section of the several solvents. Solvents ***H***, ***L***, and ***P*** are more powerful in swelling but not necessarily in that order depending on the polymeric substrate chemistry.

From a safety standpoint, the levels of vapor phase radiochemical and solvent encountered by a user are orders of magnitude below those permitted by USNRC, OSHA, and/or EPA regulations when used in accord with recommended procedures. See comments below.

EXPERIMENTAL

A MESERAN CROSS#LINK Analyzer Model 800 XLNK was used to obtain all data in Figures 3 to 7. This instrument is linked to a PC DOS through an insertable printed wiring card and umbilical connection. A software program designed for determining the level of crosslink density is used in the computer to access and to operate the instrument and to store and analyze the evaporative rate data.

Each test is carried out by depositing the preselected test solution formulation onto the leveled polymer surface when the computer program is in the proper position for testing so that pressing the START button after deposition automatically turns on the metered air flow and initiates data acquisition. Following data acquisition, the data is saved, the several CURE INDICES calculated and the vapors are exhausted to the rear (and properly to the outside with separately exhausted air of at least 100 cfm.)

The accumulating data are automatically plotted on the monitor in real time on a log-count-per-nine-seconds basis and plotted as a function of time. In addition four separate CURE INDICES as well as TOTAL COUNT (i.e. area) under each evaporative curve are calculated automatically at the conclusion of the data acquisition and the INDEX values are displayed on the monitor. These four INDICES represent differing parameters of the evaporation process which are individually and separately useful for measuring the level of cure and in comparing the process based on counts per second less recorded background as follows:

INDEX I is an integer form of the mantissa derived from the total count of the highest 30 second expressed as a log value divided by the total count of the final 30 second period expressed as a log value.

INDEX II is an integer form of the mantissa derived from the total count in the first half of the postpeak period expressed as a log value divided by the total count of the second half of the postpeak period expressed as a log value.

INDEX III is a positive integer form of the statistical slope of the first forty second post peak period calculated on the basis of log count vs the square root of time using smoothed one second counts.

INDEX IV is a positive integer form of the statistical slope of the first twenty second post peak period calculated on the basis of log count vs time using smoothed one second counts.

Figure 3 illustrates a ladder of six levels of crosslink density using a proprietary solder mask involving 1, 2, 3, 4, 5, and 6 joules of appropriate uv energy tested with test solution ***AH2X*** (double strength tetrabromoethane-C14 in methylene chloride). The recommended cure level is represented by the 4 joule curve. It should be noted that the evaporative curve at the 6 joule level is somewhat similar to the 4 joule level but also has a materially differing shape than any of the other five. This condition at 6 joules represents a marked change in evaporative behavior due to overcure and presumably relates to degradative effects. Table 3a shows the several CURE INDICES which also indicate this backwards movement at 6 joules. The marked differences in all INDICES and particularly in III and IV between 3 joules and 4 joules is indicative of the achievement of a reasonable level of cure.

Figures 4, 5, and 6 and corresponding Tables 4a, 5a, and 6a show the effects of increasing solvency on a thermally cured solder mask using a five step cure ladder of 15, 30, 60, 90, and 120 minutes at 150 C. The test solution used in the Figure 4 test series is ***AJ40H2X***; in Figure 5 it is ***AL2X***; in Figure 6 it is ***AH2X***. The cure at 60 minutes is the manufacturer's recommended cure. In these cases again the large differences between 30 and 60 minutes particularly in Figures 5a and 6a are apparent. The ***AJ40H*** test solution based on trifluorotrichloroethane, a CFC, is no longer available.

Figure 7 illustrates an acrylic ink coating the full cure of which is defined only by very pure ***BV***.(tridecane-C14 in 2,2-dimethylbutane), the weakest solvent system presently available. When less than 1.5% of cyclopentane (***K***) is added to ***BV*** it fails to differentiate the cure adequately--that is the test solution swells excessively and is very similar to the undercure level which is not shown.

DISCUSSION

The ERA method permits the quantitative and highly reproducible measurement of the degree of crosslink density in polymeric applications and particularly in relatively thin coatings and inks. As currently used, the method is a comparison one requiring a suitable cure ladder for calibration and preselection of optimal test solution formulation. Within those limitations, however, the method permits highly definitive measures of the near cure, cure, and slight overcure conditions in a rapid and sensitive manner. Many industrial users have found the method to be very valuable for production control applications.

Whenever possible the reference cure ladder should be prepared using production equipment to reduce the possibility of inadvertent errors. For example laboratory ovens used for test curing are notoriously variable with respect to temperatures across the oven and door openings to remove samples cause large variations in curing conditions.

Cleanliness of syringes to prevent inadvertent contamination of test solutions must be maintained. Proper storage of test solutions after opening of the sealed-in-glass shipping tubes is required to reduce to a minimum premature evaporation of the low boiling solvent or solvents with respect to the higher boiling radiochemical.

SAFETY AND ENVIRONMENTAL ASPECTS

The Material Safety Data Sheet provided with the each preformulated and precalibrated test solution provides --in addition to the conventional information--comprehensive surveys of the use of the materials with respect to release to the atmosphere and the actual levels of exposure of individuals. These levels are compared to OSHA and EPA recommended limits of both solvents and radiochemicals as well as the USNRC limits of release based on the limit to unrestricted areas of ***3 E - 9 uCi / ml***, a value which is, strictly speaking, applicable only to USNRC and/or 'Agreement State' licensed activities whereas the radiochemicals distributed as *EXEMPT* from such licensing have no such limit.

In all cases the release to the environment of vapor phase solvent and the chemical aspect of the radiochemicals are invariably many orders of magnitude less than the applicable OSHA and/or EPA limits. Even in the event of accidental breakage or spillage of a standard 1.6 ml quantity of test solution, no limits are exceeded with respect to the exposure of an individual.

One calculation shows that release to the atmosphere of the vapor phase radiochemical during maximal testing of ten tests per hour with exhausting to the outside atmosphere at only 100 CFM never exceeds the 3 E - 9 uCi / ml level at the release point. Another calculation shows that release of all the vapor phase material directly into a working area of 6 m x 5 m x 4 m with only six air changes per hour never exceeds any of the applicable limits of either solvent or radiochemical although release of the vapor phase constituents to the outside using a small hood is recommended.

CONCLUSIONS

The microcomputer-based ERA (or MESERAN) method for the quantitative determination of the level of crosslink density in polymeric compositions provides rapid and reproducible, numerical measures of the degree of cure. Particularly at cure levels immediately above and below the desired cure, the definition achieved is without parallel among all methods of measurement.

REFERENCES

1. Mark G. Benkovich is a Consultant for The MESERAN Company. He is currently employed by Allied-Signal Inc. Federal Manufacturing and Technology as a Staff Engineer.

2. Anderson, J.L., *Evaporative Rate Analysis: Its First Decade*. A chapter in CHARACTERIZATION OF METAL AND POLYMER SURFACES. L.H. Lee, Editor, Vol 2, Academic Press, Inc., New York, 1977, pp 409-427. This paper summarizes all known references prior to 1975.

3. Anderson, J. L., Russell, R. F., and Slover, C. C., *Measurement of Crosslink Density in UV Cured Materials by Evaporative Rate Analysis*, JOURNAL OF RADIATION CURING, April 1985, pp 10-17.

Figure 1

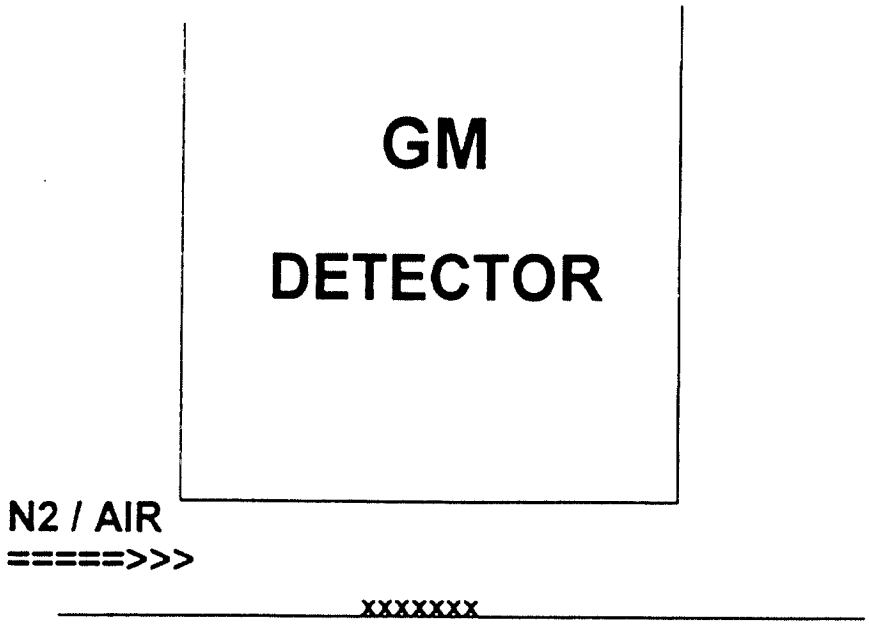


Figure 2
Plot of Counts Per 9 Seconds vs Time
Showing Low, Medium, and High Levels of Cure

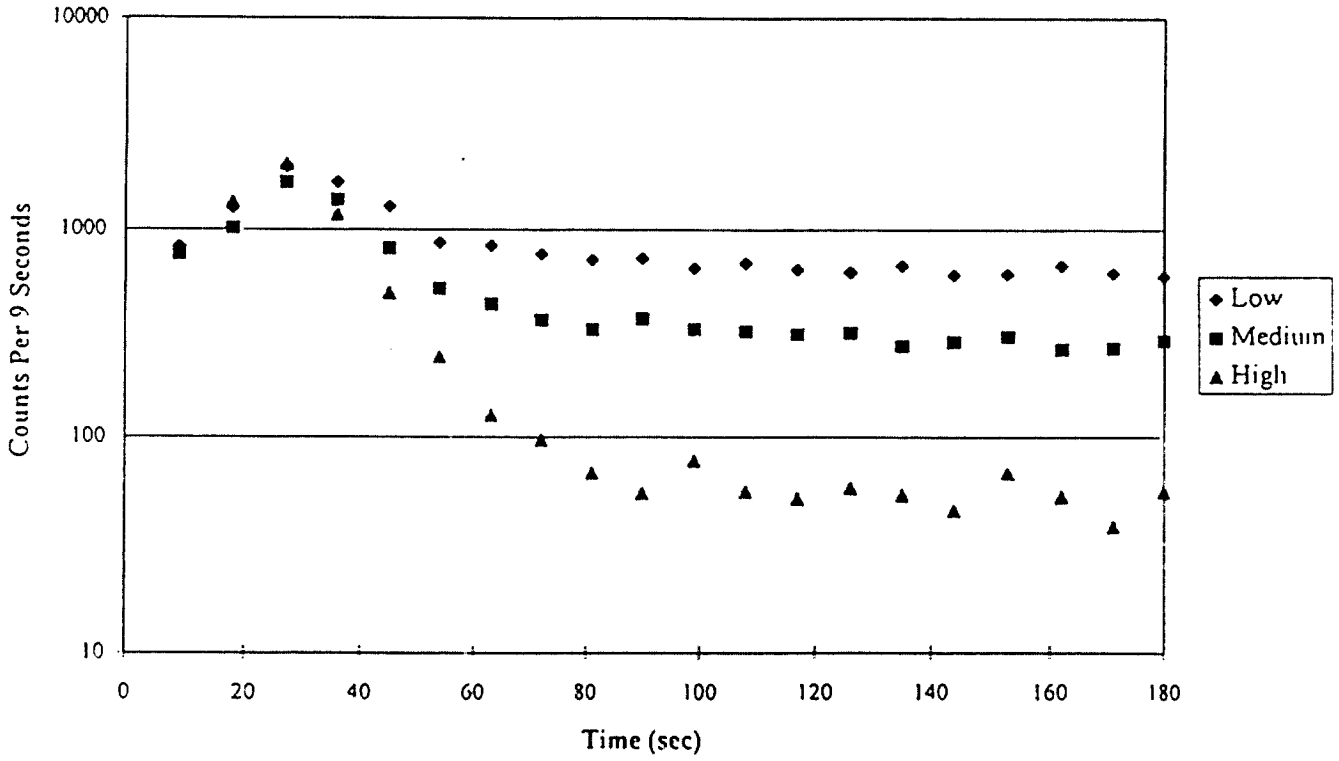


Figure 3
Plot of Counts Per 9 Seconds vs Time
Showing Various Degrees of UV Cure on Solder Mask

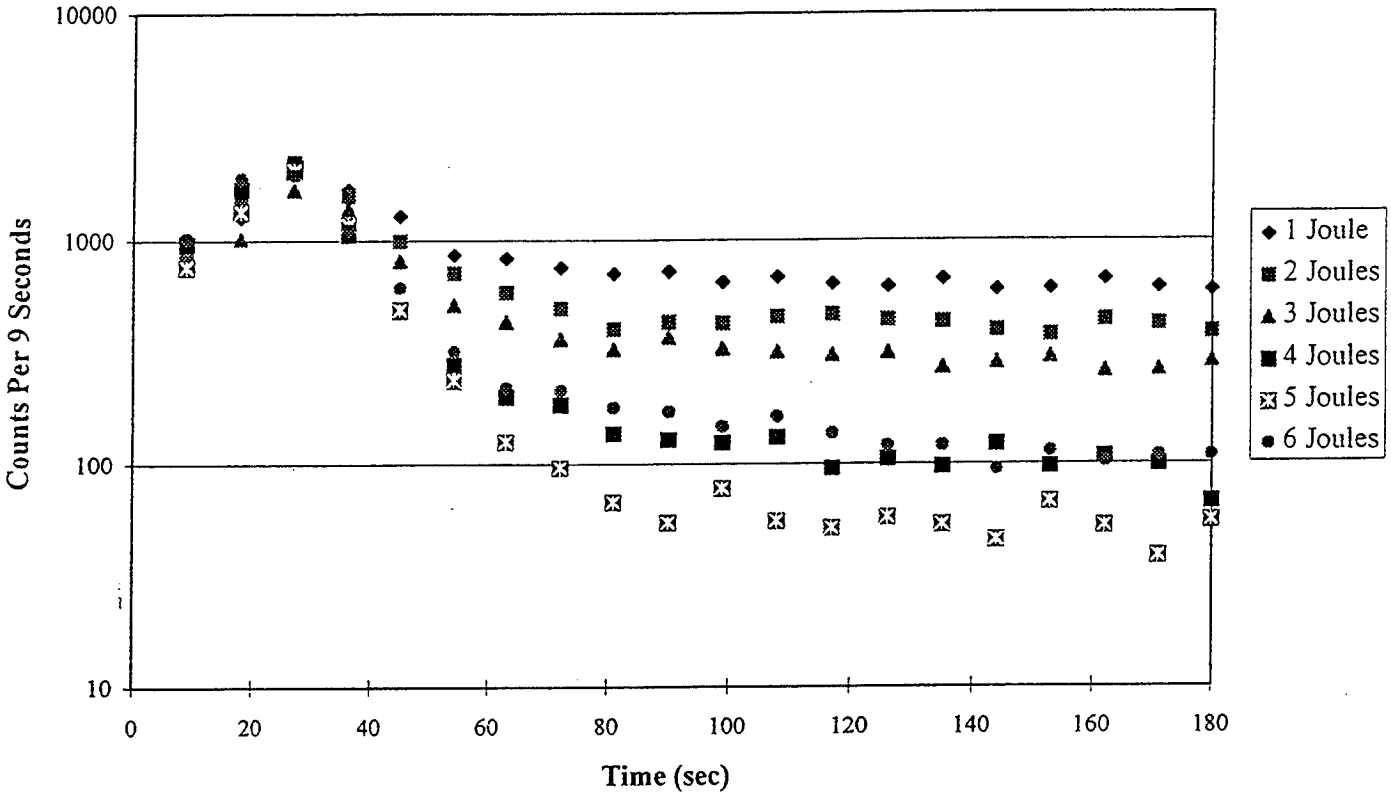


TABLE 3a

SOLDER MASK 'A' CURE INDICES USING AH2X - CURED USING UV

JOULES	CURE INDICES				TOTAL
	I	II	III	IV	COUNTS
1	136	84	220	292	17175
2	202	104	308	506	13971
3	234	121	334	572	10593
4	494	234	540	884	8323
5	665	357	649	897	6942
6	471	246	508	659	8950

Figure 4
Plot of Counts Per 9 Seconds vs Time Showing
Various Degrees of Thermal Cure at 150°C on Solder Mask Using
Radiochemical (A) in a 40% Methylene Chloride Solution

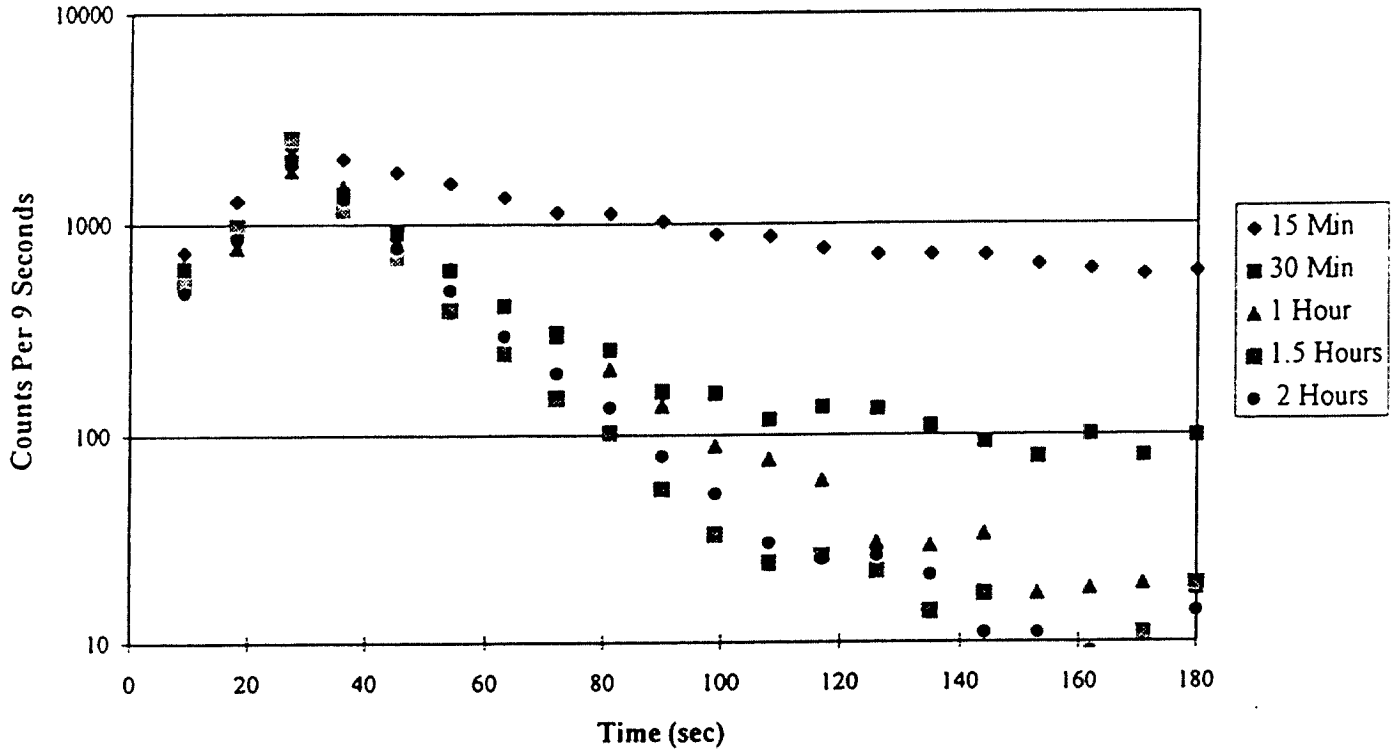


TABLE 4a

SOLDER MASK 'B' CURE INDICES USING AJ40H2X - HEATED AT 150 C

TIME (min)	CURE INDICES I	II	III	IV	TOTAL COUNTS
15	162	113	123	179	21203
30	484	285	357	470	8697
60	1037	557	371	513	7532
90	1453	857	507	729	6997
120	1516	784	441	577	6725

Figure 5
Plot of Counts Per 9 Seconds vs Time Showing
Various Degrees of Thermal Cure at 150°C on Solder Mask
Using Radiochemical (A) in 'Pure' Chloroform

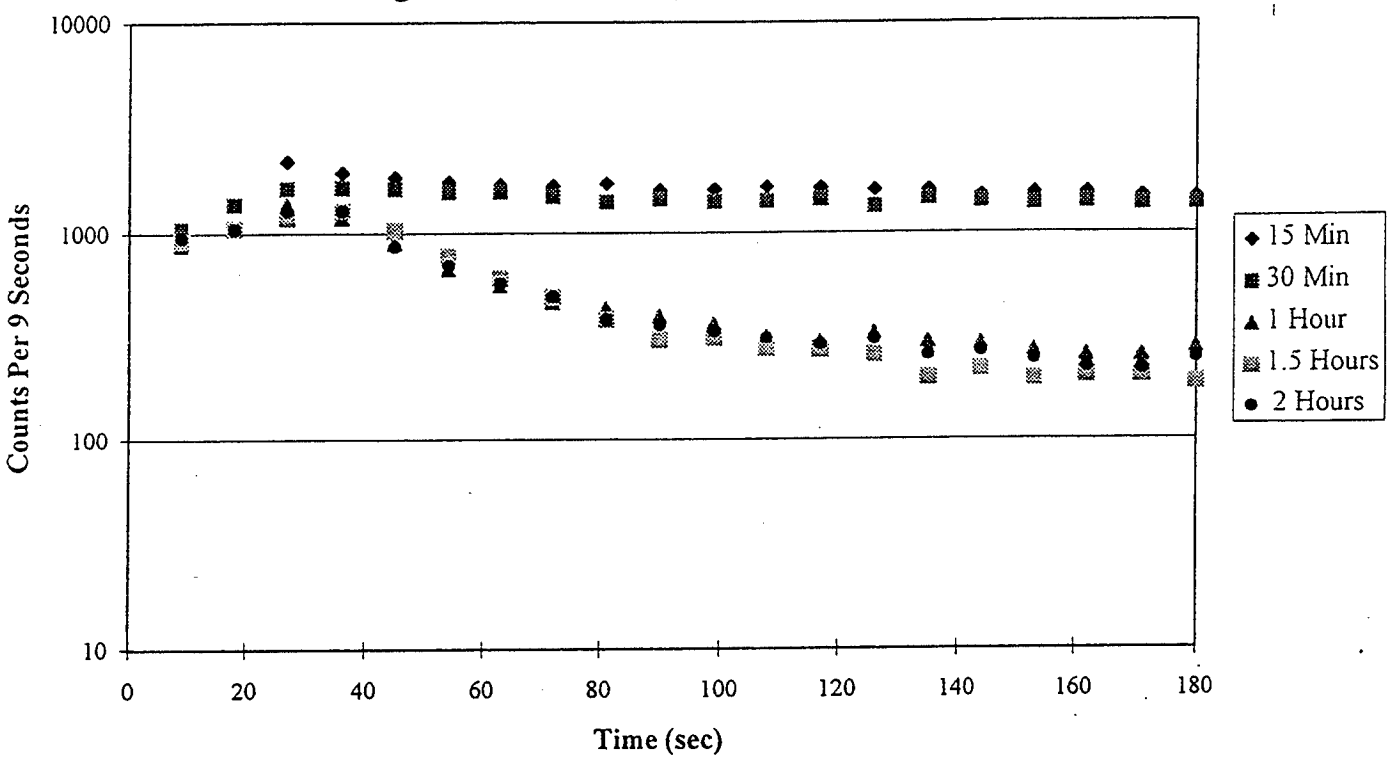


TABLE 5a

SOLDER MASK 'B' CURE INDICES USING AL2X - HEATED AT 150 C

TIME (min)	CURE INDICES I	II	III	IV	TOTAL COUNTS
15	40	43	28	5	32608
30	31	44	21	51	28954
60	222	139	222	281	10943
90	267	166	225	316	10446
120	245	142	214	357	10719

Figure 6
Plot of Counts Per 9 Seconds vs Time Showing
Various Degrees of Thermal Cure at 150°C on Solder Mask
Using Radiochemical (A) in 'Pure' Methylene Chloride

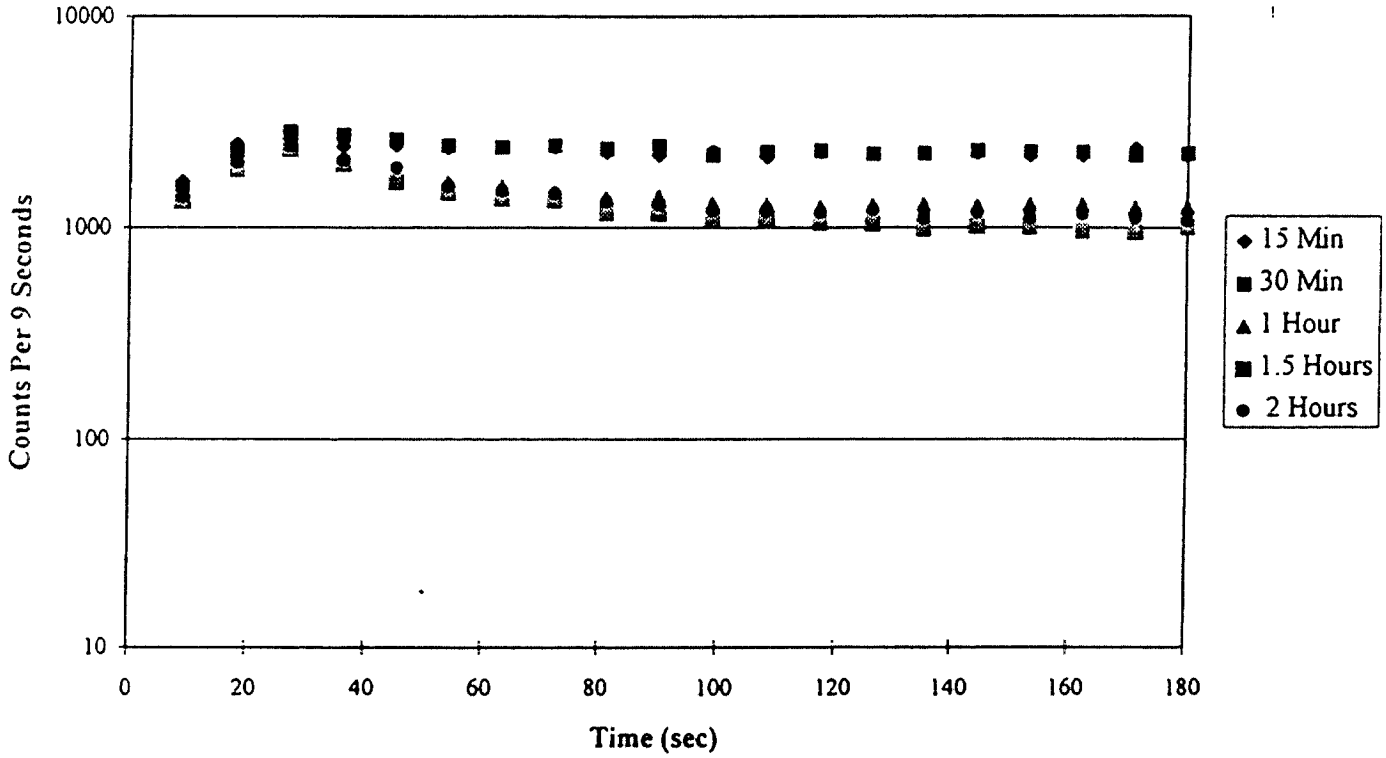
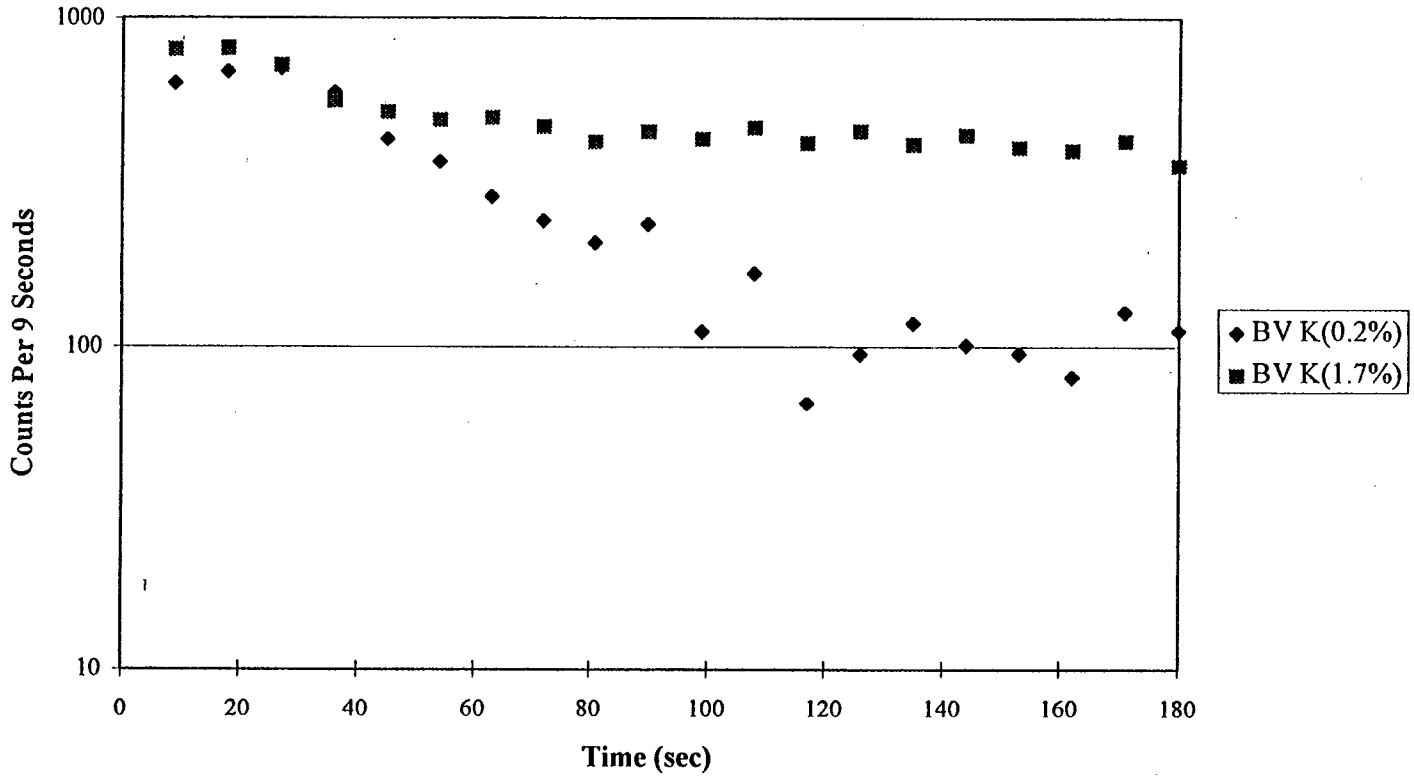


TABLE 6a

SOLDER MASK 'B' CURE INDICES USING AH2X - HEATED AT 150 C

TIME (min)	CURE INDICES I	II	III	IV	TOTAL COUNTS
15	20	36	16	59	45519
30	27	41	37	53	46612
60	70	58	97	205	30044
90	93	72	114	210	26068
120	84	67	108	130	28695

Figure 7
Plot of Counts Per 9 Seconds vs Time Showing Differences Obtained with 1.5% More Cyclopentane in BV on Cured Ink



Supercritical Carbon Dioxide Processing of a Pyrotechnic

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ABSTRACT

The magnesium, Teflon and Viton (MTV) pyrotechnic ignition material has been produced at NSWC/IHD since the early 1950's using the Shock-Gel process. MTV crumb was prepared by slurrying magnesium and Teflon in an acetone solution of Viton, followed by drowning the mixture with hexane. Residual acetone was extracted from the MTV crumb with additional hexane washes. The hexane wet MTV crumb was oven dried, extruded and cut to length. The Shock-Gel process generates ten pounds of hazardous waste per pound of MTV produced.

The new and improved method for MTV preparation was designated the Super-Shock process. In this process carbon dioxide replaces hexane as the antisolvent. The MTV crumb was extracted with SC-CO_2 to remove trace amounts of acetone thereby eliminating the need for drying prior to extrusion. The Super-Shock process generates essentially no hazardous waste because carbon dioxide, acetone and out of specification crumb were recycled.

INTRODUCTION

The magnesium, Teflon and Viton (MTV) pyrotechnic ignition material has been produced in 200 pound batches at NSWC/IHD since the early 1950's using the Shock-Gel process. MTV is used for rocket motor igniters and flare decoys. MTV meets the requirements of a class 1.3 explosive. Figure 1. is the Shock-Gel MTV flow diagram. MTV

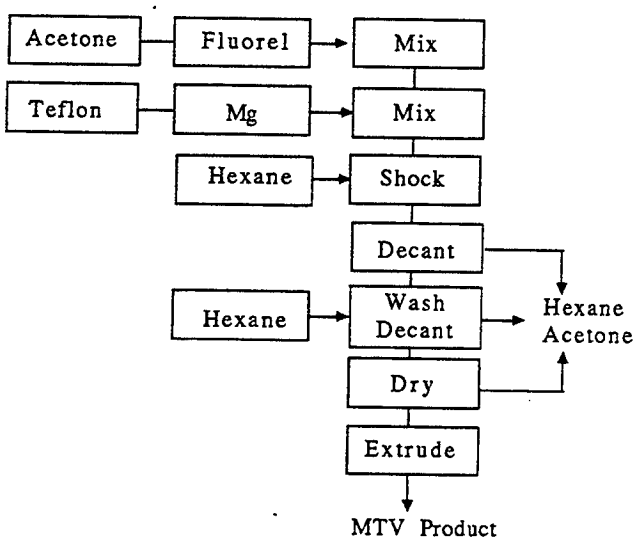

Figure 1. Shock-Gel MTV flow diagram

crumb was prepared by slurrying magnesium and Teflon in an acetone solution of Viton or Fluorel, followed by drowning the mixture with hexane. The resulting crumb was washed with additional hexane to remove the residual acetone. The hexane wet MTV crumb was oven dried, extruded and cut to length. The Shock-Gel process generates about ten pounds of liquid (hexane and acetone) hazardous waste per pound of MTV produced with a disposal cost of about $600 per drum. The Super-Shock process eliminates the probability of electrostatic ignition of hexane, and the release of volatile organic compounds (VOCs) on drying, which is encountered with the Shock-Gel's MTV process.

The supercritical carbon dioxide (SC-CO_2) MTV process was designated the Super-Shock process. The MTV formulation investigated contained 54% magnesium, 30% Teflon and 16% Viton[1]. In this process carbon dioxide replaces hexane as the antisolvent[2]. The MTV crumb was extracted with SC-CO_2 to remove trace amounts of acetone thereby eliminating the need for drying prior to extrusion. Batches of MTV of various sizes (50 to 375 grams) were processed using a 500 and a 2,500-mL heated pressure vessel equipped with an agitator. Shown in Figure 2. is a flow diagram of the Super-Shock process. Off specification MTV was mixed with acetone and the proper amount of starting materials and added to subsequent batches of MTV, which resulted in high quality MTV.

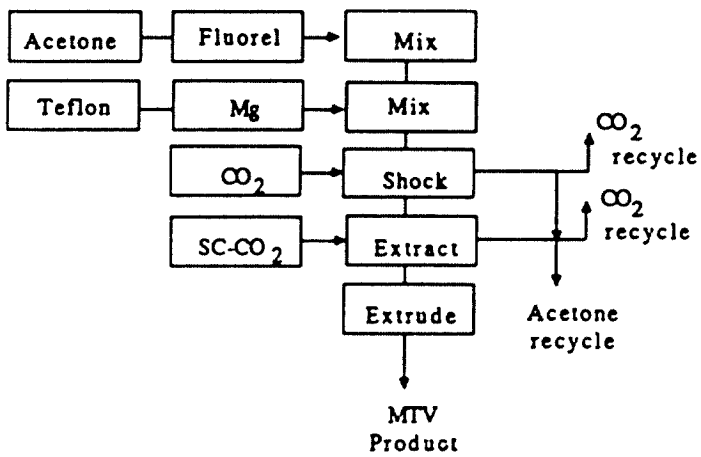

Figure 2. Super-Shock MTV flow diagram

Results of the Super-Shock MTV hazardous analysis

Extensive hazard analyses were performed to assure the Super-Shock process was safe. All metal equipment must be grounded. As a safety precaution the magnesium and MTV crumb was weighed using conductive containers and conductive spatulas and the worker must be grounded. The air in the room was monitored for carbon dioxide. The TWA (time weighted average) for carbon dioxide is 5,000 ppm. The work area was entered only when the concentration of carbon dioxide was less than 3,000 ppm. A thermal conductivity meter (Leak Hunter from Cole-Parmer) with a sensitivity of 3×10^{-5} cc/sec of carbon dioxide was used to detect leaks in the system.

The Super-Shock MTV equipment was operated remotely. The vessels used had spring loaded Teflon primary pressure seals. This reduces metal to metal contact. The valves that may accidently contain MTV were air operated valves. The air operated valves were normally open and thus will fail in the open position. If the porous metal filter in the top of the processing vessel accidently becomes plugged, the pressure can be released by opening the air operated valve at bottom of the vessel and releasing pressure through the bottom of vessel. The threads on the vessels and fittings were inspected and cleaned before assembly. The equipment was tested with inert batches of MTV (the magnesium replaced with alumina). Shown in Table 1. are the results of inert batches run to test the equipment. Automation was installed on the 2.5-liter processing unit which unscrews the bottom cap and and lower the cap and the basket containing the MTV remotely.

Table 1. Inert MTV batches using 500-mL pressure vessel

2,000 psi and 60 ° C

Batch #	Batch size (g)	% Acetone in paste	CO_2:acetone ratio at start	CO_2 used (g)	CO_2 flow (L/min)
27-96[1]	50	40	6.57	962	6
30-101	75	39	3.77	1216	7

[1]Newport compressors used - inline filter plugged and the last the 300 psi of pressure released from bottom.

A computer controlled high pressure pump maintains the pressure at the predetermined set point. If the high pressure alarm setting is reached or a sudden loss of pressure the computer stops the pump (the pump must be reset before it will restarted). Rupture disks were used as secondary safety devices.

The MTV produced from the Super shock and Shock-Gel process had the same range of sensitivity tests values. The sensitivity tests results from 50 gram MTV batch (31-102) were: impact 350 mm (3+ 5 kg weight), electrostatic 8.33 joules, and friction 135 psi.

DISCUSSION OF RESULTS

A Jerguson Gauge was used for the initial experiments. The Jerguson Gauge is a 80-mL glass tube encased in steel and is rated for 5,000 psi at 100 ° F. It was designed for visual observation of water level in steam boilers. This Gauge was useful for visual observation of MTV during processing. Three types of addition were investigated:

1. addition of Viton/acetone solution to the magnesium and Teflon suspended in an upward flow of carbon dioxide.
2. addition of MTV paste (a mixture of acetone, magnesium, Teflon and Viton) to the Jerguson Gauge downward flow carbon dioxide (2,000 psi and 60 ° C).
3. addition of MTV paste to the Jerguson Gauge and upward flow of carbon dioxide 2,000 psi and 60 ° C).

The results of the MTV batches prepared in the Jerguson Gauge are:

- Upward flow of carbon dioxide was best (downward flow 3% Viton carry over in the collected acetone).
- Addition of MTV paste to pressure vessel and extracting the acetone was best type of processing
- Agitation was needed during MTV processing.
- A 15 cm/minute upward flow carbon dioxide does not fluidize the MTV
- The Teflon needs to be delumped (mixed for 30 seconds in a blender at medium speed).

All processing of MTV was essentially performed remotely. Shown in Figure 3. is an illustration of the equipment used to process MTV. A detailed description of the MTV Super-Shock equipment is shown in Table 2.

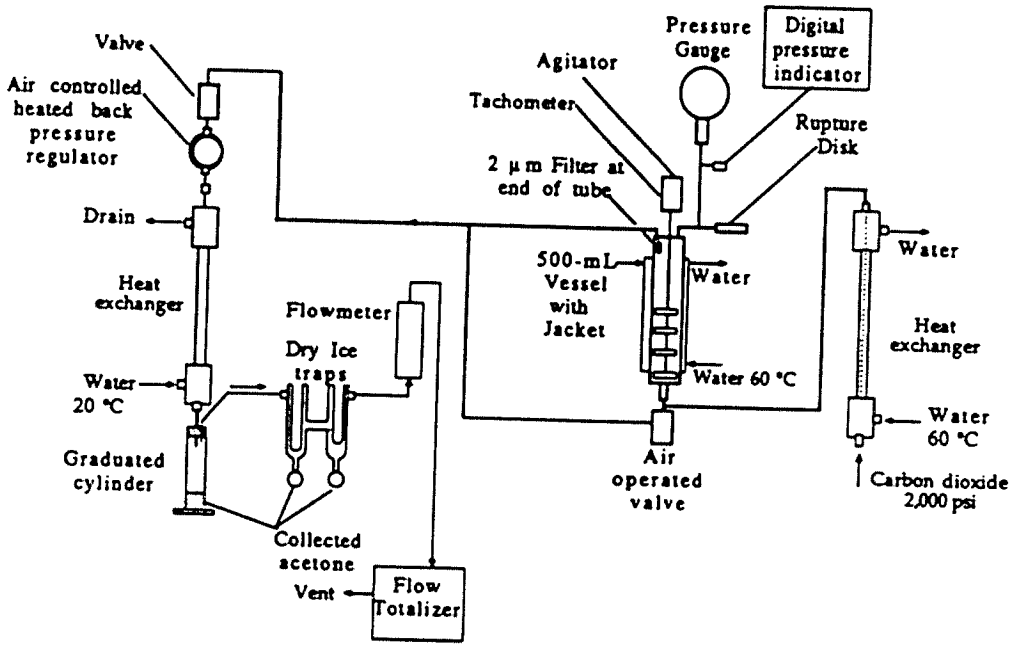

Figure 3. MTV processing equipment

Table 2. MTV Super-Shock equipment

- A heat exchanger with a refrigerated cold water recirculating system chills the carbon dioxide to 0 °C. This prevents cavitation in the pump.
- For carbon dioxide addition a Thar Design computer controlled high pressure pump (HPP-350) was used. This pump controlled the pressure to ± 10 atm at a flow of 50 grams of liquid carbon dioxide a minute (25 L/minute STP). A Newport air operated diaphragm-type compressor (46-14021-2) was also used.
- A heat exchanger heated the carbon dioxide to 60 °C (the operating temperature).
- A Thar Design 500-mL vessel (HPV-500 ML-PH) with a jacket (HJ-500-mL) and agitator (500-mL-STS). The agitator had four high shear impellers. The vessel also had a tachometer and an internal thermocouple.

- For improved safety, an additional air operated valve (HIPCO-30-11H-F6) was installed for venting the system from the bottom. The bottom valve can be opened if the top exit became plugged.
- A Tescon air controlled back pressure regulator (54231D4-12-A) remotely controlled the exit pressure.
- Associated Design stainless steel dry ice traps collected acetone.
- King Gauge flow totalizer (DTM 200A-1). This gauge measured total liters at STP of carbon dioxide used.

Experimental Super-Shock process MTV process

MTV paste was prepared in a two step process. First the acetone solution of Fluorel-2175 (Viton-A replacement) was prepared by standing overnight in a stainless steel beaker. Secondly, the magnesium (Type II) and Teflon 7C were slurried into the solution. The paste was added to a 500-mL pressure vessel equipped with with a thermocouple, agitator and tachometer. An upward flow of carbon dioxide at 60 °C at 136 atm (2,000 psi) quenched the mixture under agitation (400 ± 50 RPM). The MTV crumb was continuously extracted with SC-CO_2 until acetone no longer built up in the traps. Dry free flowing gray MTV was poured out of the vessel and about 10 to 15% of MTV stuck to the agitator and vessel.

Table 3. contains a summary of the MTV batches. The Viton-A was replaced with Fluorel-2175 which has the same CAS number and is used as a direct replacement in MTV production.

Table 3. Summary of Super-Shock MTV batches using 500-mL pressure vessel

2,000 psi and 60 °C (except as noted)

Batch #	Batch size (g)	Acetone in paste[a] %	CO_2:acetone ratio at start	CO_2 used (g)	% Acetone collected	% Fluorel collected in acetone	CO_2 flow (L/min)	Yield %	Fluorel in MTV %
31-102	50	44	4.94	1825	40	0	10	84	16
33-103	50	32	8.61	897	25	0	20	86	17
36-106[b]	100	50	1.45	800+	-	-	10	96	-
37-107[c]	150	54	0.46	3015	45	3	15	95	-
40-110	200	41	0.66	3830	23	>0.1	30	96	12
41-111	200	51.6	0.20	2583	22	36.4	15	95	11.9
43-112	100	52	1.20	1852	42	2[d]	15	94	11
44-113	100	40	3.82	1794	53	>0.1	14	83	14 to 16
46-114[e]	175	40	1.54	1367	41	>0.1	15	92	16

[a]Fluorel-2175 (lot FC2175), Mg Type II (lot 92-M-066B), Teflon 7C (lot 970209)
[b] The 45% of the MTV near agitator, was good crumb, the rest was a solid piece - (Need multiple impeller) - There was also a leak in the collection system
[c]Four radial flow high shear impeller blades 1 inch apart in this and subsequent batches
[d]The 2% Fluorel mostly likely is from residual material in the system
[e]Batch conditions; 300 atm (4,410 psi) and 60°C

The results of the Super-Shock processed MTV in the 500-mL vessel are:

Efficient agitation was found to be very important in the preparation of free flowing crumb similar to that produced by the Shock-Gel process. Batches of up to 75 grams produced free flowing crumb with one impeller blade for agitation. At the 100 gram batch level using one impeller blade, only 45 % of the MTV was free flowing, the remainder of the MTV was agglomerated into a soft solid mass. The need for efficient agitation was demonstrated when four impeller blades were used. All the 100 to 200 grams batches of MTV crumb produced using four impeller blades were free flowing.

A parameter study was performed to determine the effects of acetone content on the Super-Shock MTV process. The amount of carbon dioxide needed to extract the acetone from the MTV was also investigated. The ratio of carbon dioxide to acetone at the start of each batch is shown in Table 1. At ratios higher than 1.5 a negligible amount of Fluorel was collected with the acetone. At a ratio of 0.20, 36.4% of the Fluorel was collected in the acetone. Fluorel is insoluble in carbon dioxide with low acetone content. Fluorel proved to be very soluble in a mixture containing 20% carbon dioxide and 80% acetone.

FUTURE PLANS

Install a total hydrocarbon analyzer to indicate when acetone extraction was complete, make other pyrotechnic compositions, and use a gear pump to slowly add MTV paste to the pressure vessel with an upward flow of carbon dioxide.

CONCLUSIONS

Preparation of high quality MTV crumb by the Super-Shock process require efficient agitation and an upward flow of carbon dioxide. The process generated essentially no hazardous waste. Acetone, carbon dioxide and off specification crumb was recycled. The amount of carbon dioxide at the start of the processing cycle should be greater than 1.5 times the amount of acetone used.

The advantages of the Super-Shock process include; it will help the Navy meet the 75% reduction in air toxic emissions required by the 1990 Clean Air Act Amendments, eliminates the labor intensive drying of MTV crumb (hexane moist MTV crumb from Shock-Gel process), and the acetone and carbon dioxide can be recycled. It also improves safety because the nonflammable carbon dioxide is present instead of hydrocarbons.

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[1]Military Specification "Ignition Pellets Magnesium-Fluorocarbon",MIL-I82736A9(OS) 16 November 1988

[2]McHugh, M.A.; Krukonis, V.J., Supercritical Fluid Extraction; Butterworth-Heinemann, 1994.

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Comparison of Environmentally Friendly Space Compatible Grease to its Predecessor in a Space Mechanism Bearing Test Rig

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Perfluoroakylpolyether (PFPE) greases are used extensively in critical flight hardware in a space environment. In the past, these greases have been processed using chlorofluorocarbon (CFC) based solvents. In response to the recent ban of CFC's, new formulations of environmentally friendly PFPE greases that are not processed with CFC based solvents were developed. The purpose of this study was to compare the performance of a new environmentally friendly formulation PFPE grease to a previously proven space compatible formulation PFPE grease. A one year test using 20 small electrical motors (two bearings per motor) was conducted in a high vacuum environment($2.0*10^{-6}$) Torr at a temperature of 90 ° C. Twenty bearings were lubricated with a new environmentally friendly formulation, and twenty bearings were lubricated with an old formulation. The mass of each lubricated bearing was measured both pre and post test. Along with mass loss measurements a profilometer trace was taken to measure post test wear of the bearings. In addition the bearings were visually examined and analyzed using an optical microscope.

Introduction

Perfluoroakylpolyether (PFPE) lubricants have been used extensively in critical flight hardware in space environment for many years. PFPE based lubricants have been the lubricant of choice for space applications because of their low gassing properties, wide range of operating temperature and chemical stability. In the past, PFPE greases have been processed using chlorofluorocarbon (CFC) based solvents. However, due to a recent ban on the production of CFC's some lubricant manufacturers had to change their processes to eliminate the use of any CFC solvent. This change lead to the production of new "environmentally friendly" formulation of PFPE greases that have been processed without use of any CFC based solvent. This process change raises the question whether these new environmentally friendly formulations have the same lubricating properties of their predecessor.

The purpose of this study was to compare a new environmentally friendly PFPE grease to its predecessor using a space mechanism test rig. This study is a continuation of the work done by E.L. McMurtrey [1] on grease-lubricated bearings operating in a vacuum environment. The test conditions for this study were chosen to closely simulate the space environment. An elevated test temperature was used to increase the severity of the test. Two lubricants were evaluated. One lubricant was Braycote 601EF, which is a new environmentally friendly PFPE grease that is process without a CFC solvent. The second lubricant evaluated was Braycote 601EP, which is a PFPE grease that was processed with a CFC based solvent. These greases are chemically equivalent with the exception that Braycote 601EP has a molybdenum disulfide additive. Molybdenum disulfide is an extreme pressure additive added to improve the grease performance in a boundary lubrication condition. The lubricants were evaluated using forty AISI 440c R-4 instrument bearings.

Test Equipment

The tests were conducted at the Marshall Space Flight Center using a High Vacuum Test Manifold. This manifold is connected to two 10 inch diffusion pumps that are capable of maintaining pressures in the 1E-6 torr range during test operation. This manifold has twelve workstations that can be individually valved off. A typical workstation is shown in Figure 1. It consists of a glass bell jar and a temperature conntrolled aluminum mounting plate. Twenty electrical motors were installed on the plate.

In this study a total of twenty electric motors, each containing two test bearings, were tested. Ten motors(twenty bearings) were lubricated with the new environmentally friendly PFPE formulation and ten motors were lubricated with the old PFPE formulation. The bearings used for testing were R-4 size, 0.635 cm I.D. by 1.59 cm O.D., AISI 440c with ribbon type stainless steel cages. Each bearing was lubricated with a 25 to 30 percent fill of the candidate grease.

The motors used for the test had the following characteristics:

1) Type - ac hysteresis, single phase, 60 cycles

2) Speed - 3600 rpm, synchronous

3) Current - 0.22 Amp.

These motors are brushless so no problems with brush dust contamination were encountered. Also the motors used approximately the same current when stalled as when operating so a bearing failure did not cause motor damage due to overheating. A disassembled motor with the R-4 bearing is shown in

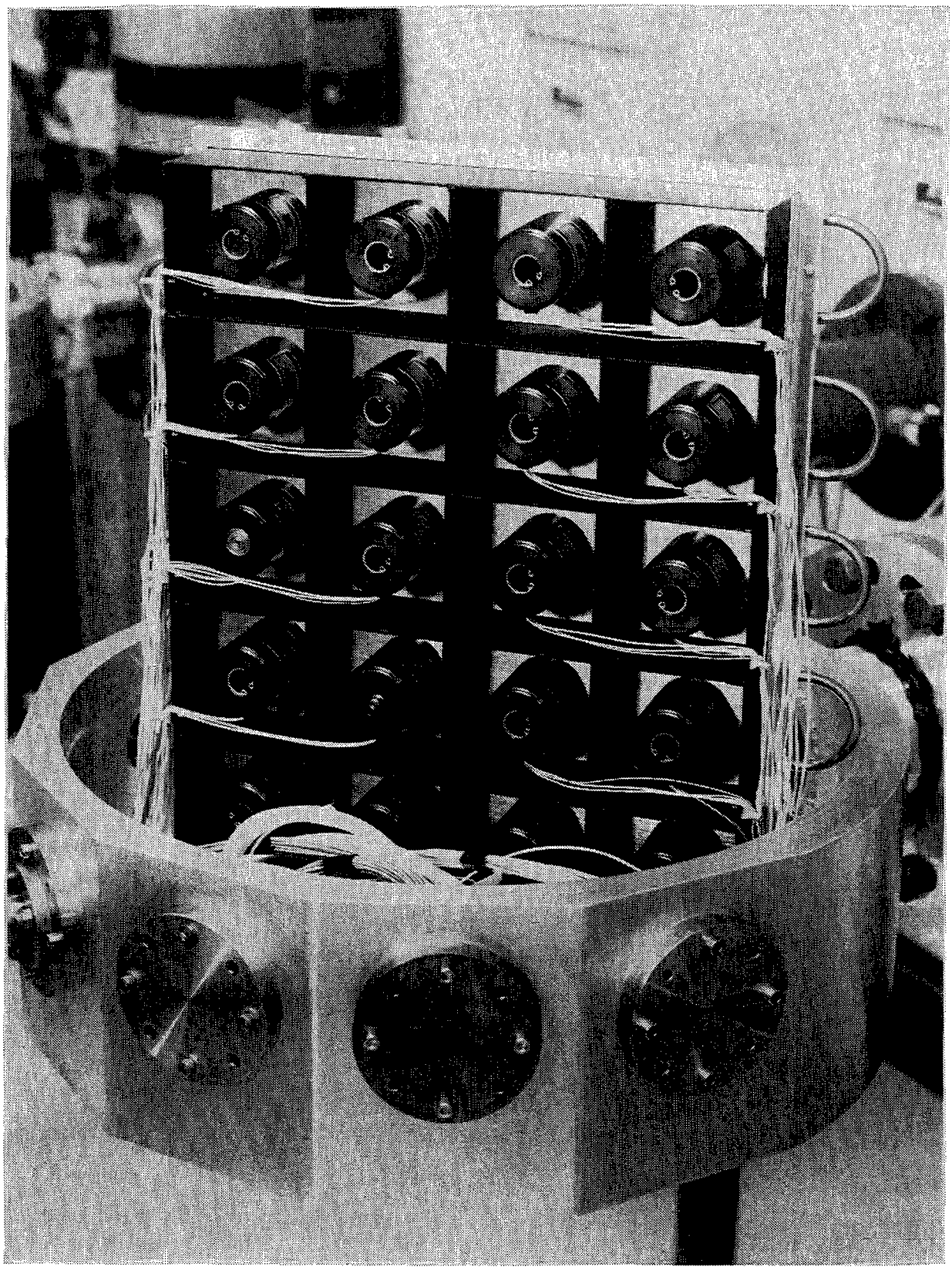


Figure 1. Test motors in vacuum chamber with bell jar removed.

Figure 2. For this test the motors were operated at an elevated temperature(90 °C) in order to increase the severity of the test. To control this temperature, the motors were mounted in an aluminum plate that included cooling passages so a thermal control fluid (ethylene glycol) could be used to control the motor temperatures. A recirculating heated bath was used to circulate and control the fluid temperature and control the bearing operating temperatures.

Test Procedure

The purpose of this study was to compare a new environmentally friendly grease to its predecessor in a space environment. For this test twenty bearings were cleaned, and then lubricated with Braycote 601EF, and twenty bearings were cleaned and then lubricated with Braycote 601EP. All bearings were ultrasonically cleaned with CFC 113 before being lubricated. After lubrication the bearings were mounted on amartures and placed in the motors. Ten motors had bearings lubricated with Braycote 601EF, and ten motors had bearings lubricate Braycote 601EP.

The motors were installed in the aluminum mounting plate which was held at a constant 90 °C temperature. The motors ran continuously for one year in bell jar vacuum system at approximately 1E-6 torr pressure. The load to the test bearing was a thrust load applied by a wave washer. The motors were loaded to maintain a 2.3 (5lb) thrust load on both bearings. This load results in a maximum hertzian contact stress of 1.69 GPa(246,000 psi) on the inner race. The bearings are operating continuously at 3600 rpm. This speed and load condition result in a full elastohydrodyamic film being form in the contact area. Each bearing that survives for the full test completed 1,892,000,000 revolutions.

The evaluation criteria for the test was based primarily on a go/no-go system. The motor torque was low and the inertia of the system was also low. As a result if a bearing drag torque increase due to a lubricant or bearing failure then the motor stops without further damage to the bearing. The following data was monitored during the test.

1. Total test time
2. Vacuum
3. Temperature

The bearings were weighed before and after testing on a high precision balance, and the percent of lubricant weight loss was calculated. After testing the bearings were visually examined under an optical microscope to determine the condition of the bearings and grease. In addition grease samples, both, new and used , were sent for chemical analysis. The greases were chemically analyzed using an infra red spectrometer and an Environmental Scanning Electron Microscope (ESEM). A Rank Talyor Hobson Taly-Surf profilometer was used to measure depth of the inner race wear track inner race.

Test Results

The results of the testing are shown in Table 1. The twenty bearings lubricated with the new environmental friendly grease were labeled test samples A1 through A20. The twenty bearings lubricated with the old formulation were labeled A21 through A40. The ten motors that were lubricated with the new environmentally friendly had two failures. Failure occurred when the motor stalled during the testing. Post test evaluation showed these failures to be motor failures and not lubricant failures. The ten

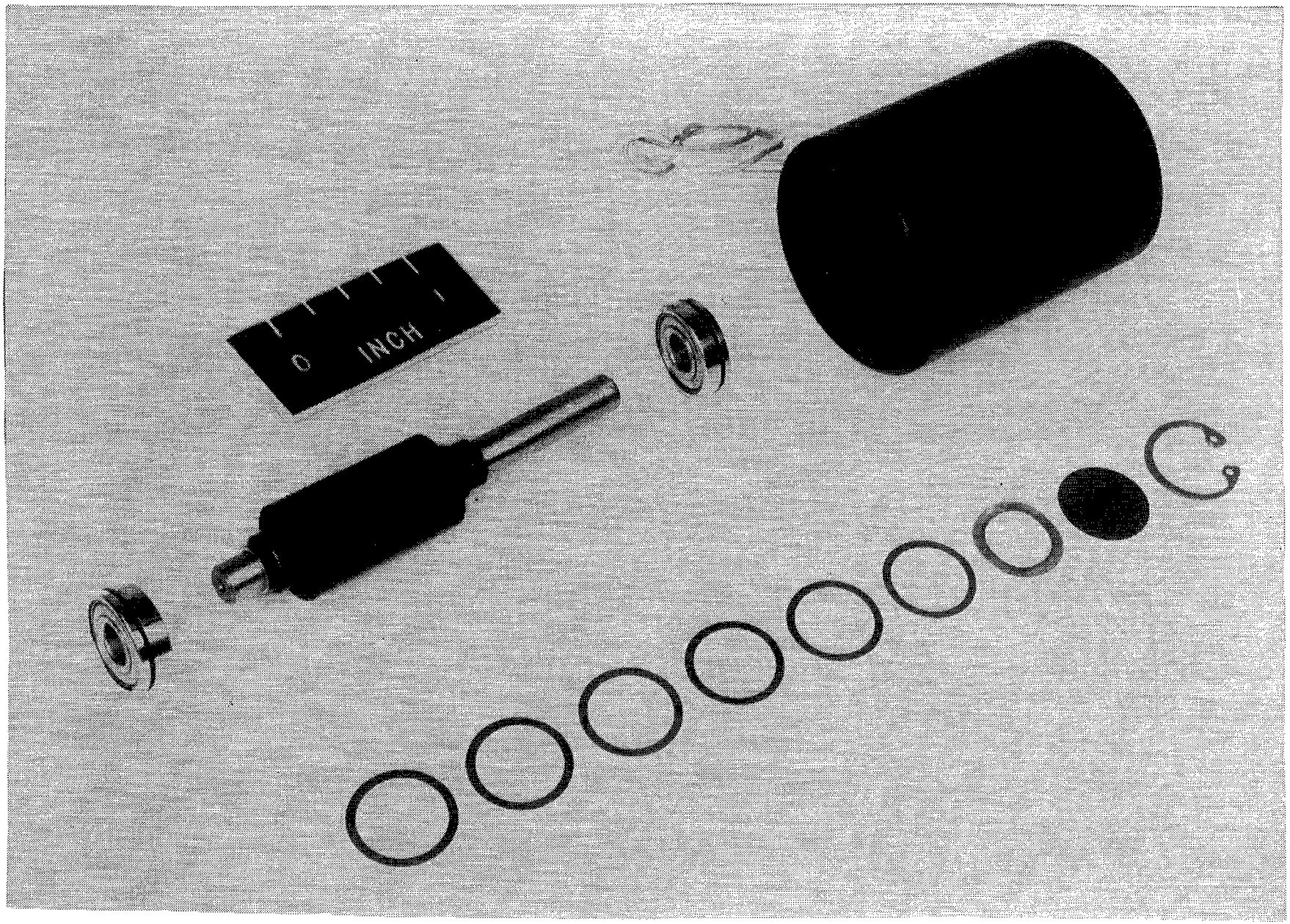


Figure 2. Disassembled ac motor with R-4 bearings.

Table 1. Summary of Testing Results

Bearing	Lubricant	Hours to Failure	Weight loss (%)	Wear track depth (microns)
A1	BRAYCOTE 601 EF	motor failure	3.4	1.8
A2	BRAYCOTE 601 EF	motor failure	4.5	1.3
A3	BRAYCOTE 601 EF	8760	11.5	4.3
A4	BRAYCOTE 601 EF	8760	2.6	3.2
A5	BRAYCOTE 601 EF	8760	9.4	2.4
A6	BRAYCOTE 601 EF	8760	22.9	2.2
A7	BRAYCOTE 601 EF	8760	13.4	5.2
A8	BRAYCOTE 601 EF	8760	9.8	4.7
A9	BRAYCOTE 601 EF	8760	21.8	6
A10	BRAYCOTE 601 EF	8760	31.5	6.4
A11	BRAYCOTE 601 EF	motor faillure	7.8	4.4
A12	BRAYCOTE 601 EF	motor failure	6.5	5.2
A13	BRAYCOTE 601 EF	8760	17.6	1.8
A14	BRAYCOTE 601 EF	8760	17.7	2.5
A15	BRAYCOTE 601 EF	8760	20.5	5.1
A16	BRAYCOTE 601 EF	8760	19.5	6.3
A17	BRAYCOTE 601 EF	8760	17.9	6.2
A18	BRAYCOTE 601 EF	8760	21	3.8
A19	BRAYCOTE 601 EF	8760	16.2	1.8
A20	BRAYCOTE 601 EF	8760	13.2	2.4
AVERAGE		8760	14.7	3.8
A21	Braycote 601 EP	8760	no data	2.1
A22	Braycote 601 EP	8760	9.44	2.5
A23	Braycote 601 EP	8760	15.16	6.9
A24	Braycote 601 EP	8760	28.2	7.2
A25	Braycote 601 EP	8760	11.3	1.8
A26	Braycote 601 EP	8760	no data	7.3
A27	Braycote 601 EP	8760	17.7	3.9
A28	Braycote 601 EP	8760	14.4	4.5
A29	Braycote 601 EP	motor failure	15.5	5.9
A30	Braycote 601 EP	motor failure	no data	2.3
A31	Braycote 601 EP	8760	10	2.9
A32	Braycote 601 EP	8760	16.4	4.6
A33	Braycote 601 EP	8760	no data	6.6
A34	Braycote 601 EP	8760	10.9	4.5
A35	Braycote 601 EP	motor failure	14.29	10.8
A36	Braycote 601 EP	motor failure	no data	6.9
A37	Braycote 601 EP	8760	6.29	2.5
A38	Braycote 601 EP	8760	10.29	3.2
A39	Braycote 601 EP	8760	35.7	3.8
A40	Braycote 601 EP	8760	10.6	3.5
Average		8760	15.1	4.7

motors that were lubricated with the old formulation also had two failures, both of which were also motor failures. Of the twenty motors evaluated in this test no failures were attributed to lubricant degradation. This failure rate agrees with previous test data produced by E.L. McMurtrey[1] using the same test equipment. In his testing, Braycote 601(formerly Bray 3L-38RP) had no failures in a year of continuous vacuum bearing testing under almost identical test condition. These results indicate that the new environmentally friendly formulation has no difference in performance when compared to either the old formulation that contain molybdenum disulfide or to the old formulation (Braycote 601) that did not contain molybdenum disulfide.

After testing each bearing was weighed, and the lubricant weight loss was calculated. These results are shown in Table 1. An average weight loss for the twenty bearings lubricated with the new environmentally friendly formulation was 14.7 %, and the average weight loss for the old formulation was 15.1 %. Some weight loss data for the old formulation was questionable so data points that were obvious outliers were not used. The average weight loss for the two formulations are essentially equal. This data agrees well with previous weight loss data on Braycote 601 produced at MSFC[1].

Each bearing was disassembled and visually inspected under an optical microscope to determine the condition of the grease and the bearings. Post test inspection of the bearings lubricated with the new environmentally grease showed them to be in good condition. Under the microscope there was a visible wear track on both races but no surface distress was observed. Post test inspection of the used grease showed that the grease had turned black in all but two bearings. These two bearings were A1 and A2 which ran for only a few weeks before the motor failed. Grease in these bearings looked new and was slightly tan in color with no signs of degradation. Initially, the environmentally friendly formulation was white in color, and the old formulation grease was a grayish black. The old formulation was this color was due to the presence of the extreme pressure additive, molybdenum disulfide.. The grease in the remaining bearings visually appeared to be somewhat degraded and slightly dry. However, the grease was still be very lubricious and the bearings were still operating very smooth.

Post test inspection of the bearings lubricated with old formulation showed similar results. All of the bearings were in good condition with a visible wear track on both, the inner and outer raceways. No sign of surface distress was observed. The used grease appeared to have turned a darker black color. The grease appear to somewhat dry but again the bearings were still operating very smooth. The conditions of this tested grease appeared consistent with previous testing at MSFC.

A profilometer was used to measured the depth of the inner race wear track. All forty bearings were measured, and the results are shown in Table 1. A typical profilometer trace of an inner race is shown in Figure 3. The results of this analysis shows the wear to be slight, however, on average the old formulation demonstrated slightly more wear (4.7 microns) than the new formulation(3.8 microns). The results indicated that inclusion of molybdenum disulfide did not reduced wear; however as mention previously, this test operated in the EHD regime. Molybdenum disulfide may be more beneficial for bearings operating in the boundary lubrication regime.

After testing grease samples, both new and tested, were sent for chemical analysis. The results of this analysis is shown in the appendix. The results of the ESEM shows that both grease formulations had pick up bearing wear debris during testing. This is shown by the presence of iron, chrome, and nickel in the spectrum of the tested grease but not the control grease sample. The ESEM results showed that the two formulations have very similar chemical composition with the exception of the molybdenum and sulfur that is present in the old formulation. Infra Red Spectroscopy shows that the two formulations have a similar IR signature. The new formulation shows the presence of additional hydrocarbons (CH groups)

in the new grease, but these CH groups are greatly reduced after testing. The presence of these hydrocarbons could be due to contamination or residue from the new solvent used to process the grease's thickener. These groups appear to evaporate off during this vacuum testing and from the test results did not effect the grease's performance. It has been reported in the literature that PFPE grease can be degraded and break down during long term vacuum applications. The reported mechanism for this break down is that fresh iron wear products react with liberated fluorine to form iron fluoride. This iron fluoride reacts with PFPE molecules and causing it to break down.[2] IR analysis was done in an effort to detect iron fluoride in the tested grease. However, from the analysis it could not be determine whether iron fluoride was present. No significant difference was observed between the spectrums of the used or new grease. This does not mean that iron fluoride is not present in the used grease; it could mean that the IR analysis is not sensitive enough to make that determination. Additional analysis using the ESCA procedure needs to be performed to make this determination.

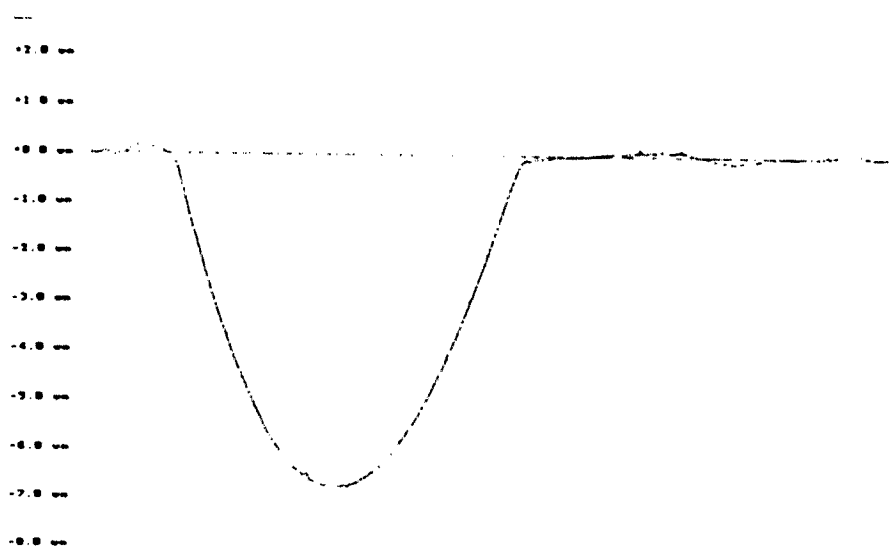


Figure 3. Typical profilometer wear trace of tested bearing inner race

Conclusions

1) In a one year continuous high vacuum and high temperature bearing test the failure rate for the new environmentally friendly PFPE was identical to the failure rate of the old formulation. In fact no lubricant failures were observed for either formulation.

2) The average lubricant mass loss for the two grease formulations were essentially equal.

3.) Both grease formulations provide adequate lubrication in this space mechanism bearing test rig.

4) The new environmentally friendly formulation yielded slightly less bearing wear than the old formulation that contained molybdenum disulfide.

5) Chemical analysis shows the new and old formulation have very similar chemical compositions.

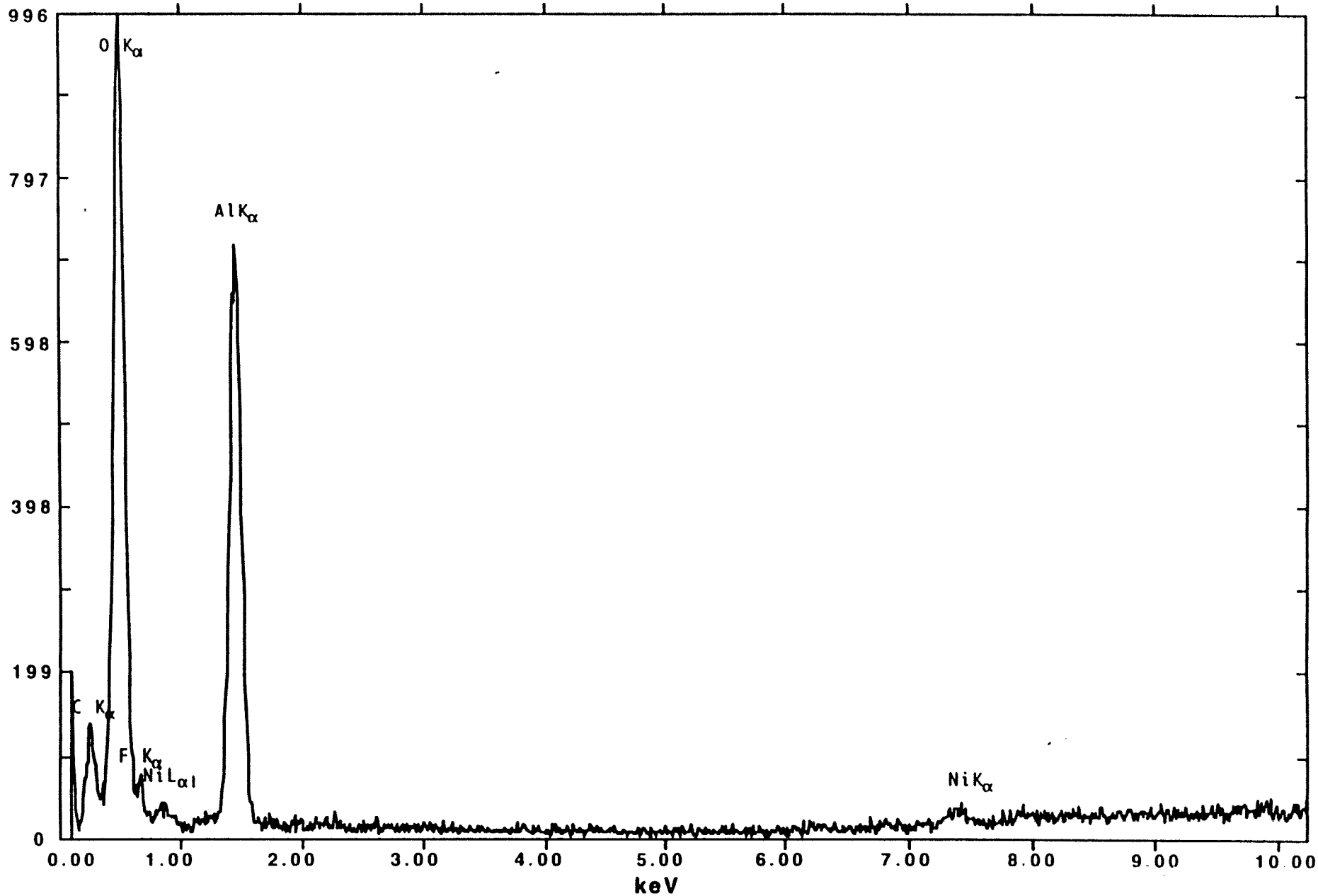
6) After one year of testing, PFPE greases darkened in color and contain ferrous wear debris, but were still lubricious. IR sprectoscopy indicates no change in the PFPE grease chemical structure after one year of continuous testing in a simulated space environment.

References

1)McMurtrey, E. L.: An Evaluation of Grease-Type Ball Bearing Lubricants Operating in Various Environments(Final Status Report No. 8). NASA/Marshall Space Flight Center, Al, NASA TM-86480.

2)Carre, D.J., "Perfluoropolyalkylether Lubricants Under Boundary Conditions: Iron Catalysis of Lubricant Degradation", Report No. SD-TR-88-27, March 1988.

Appendix



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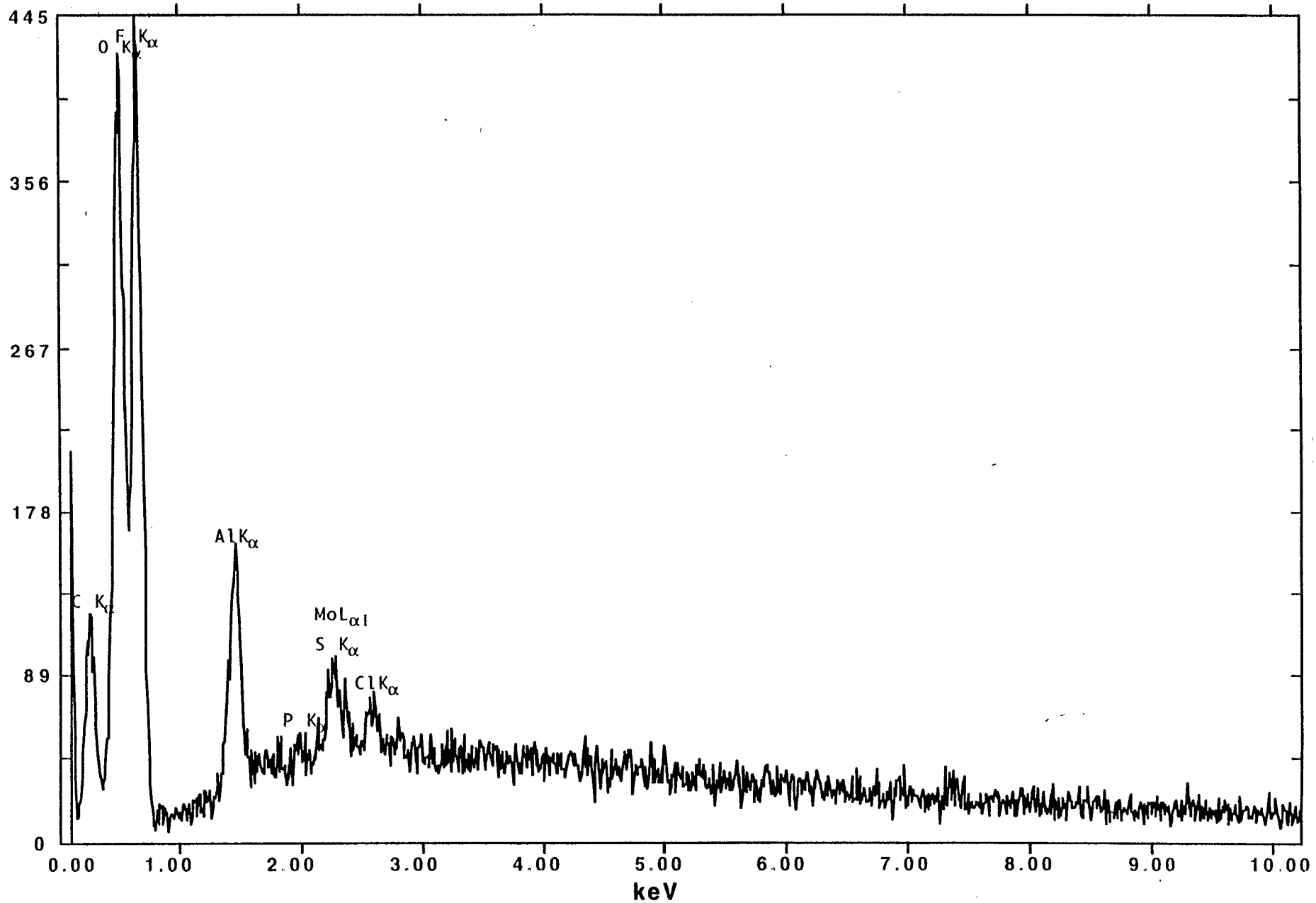

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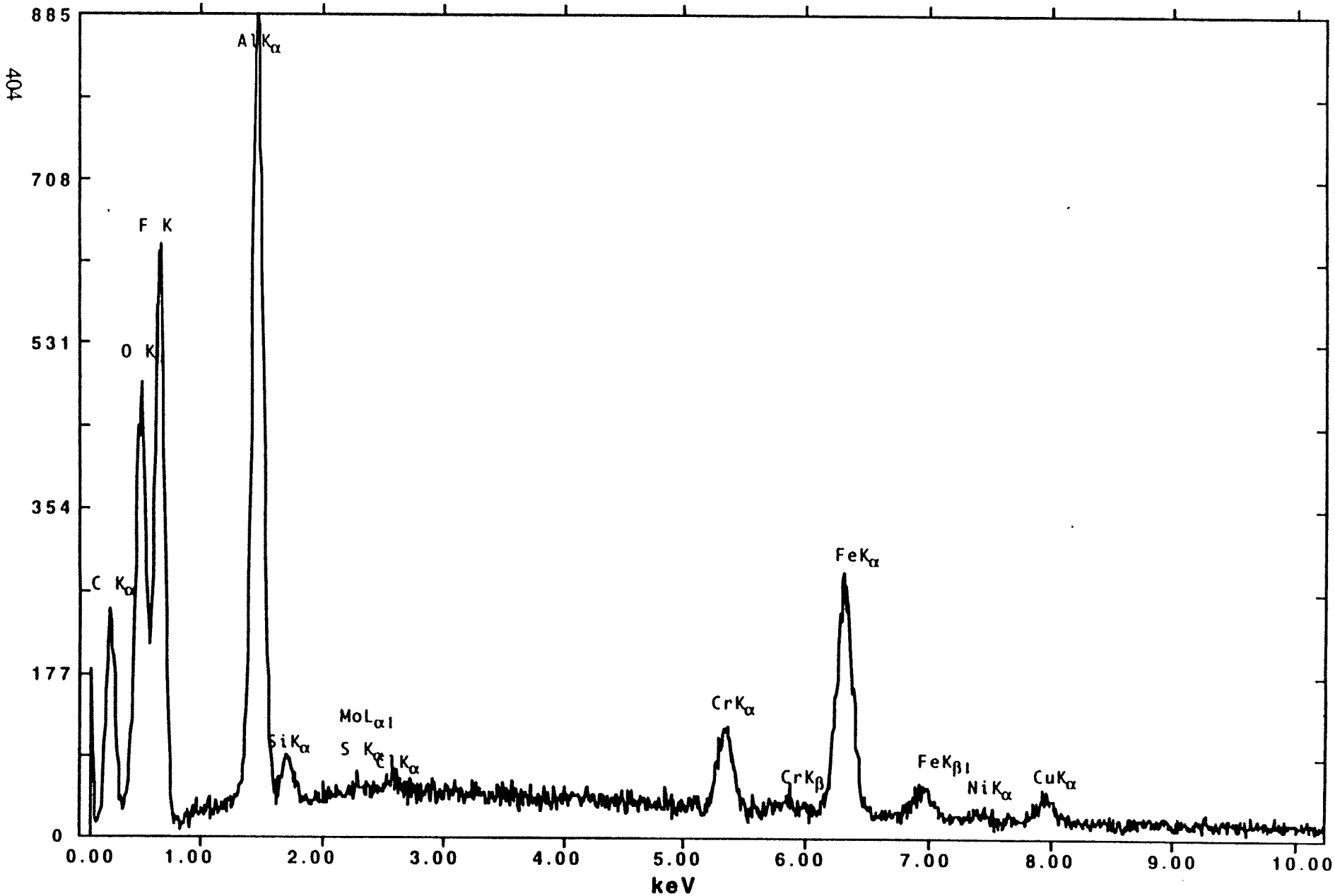

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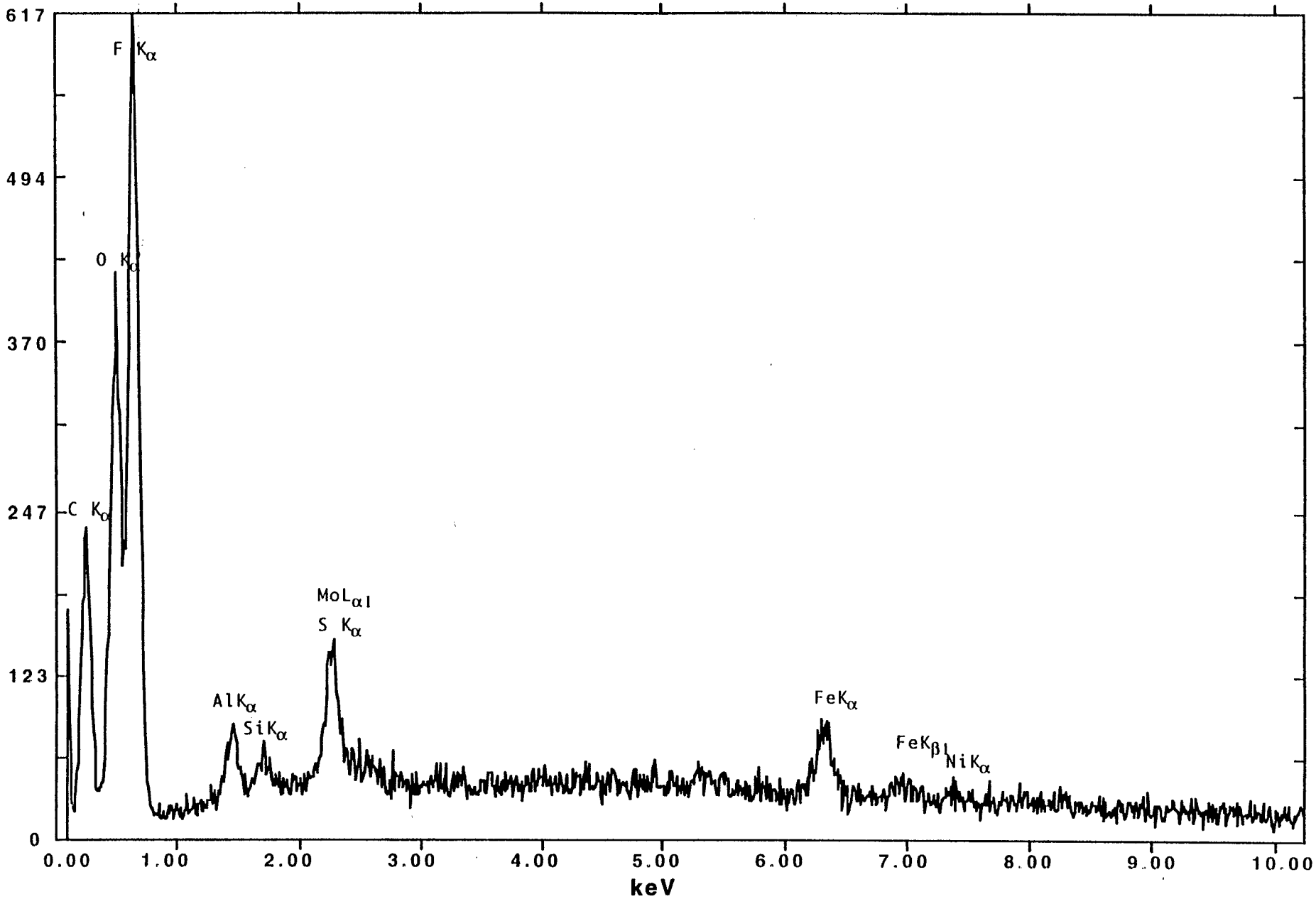

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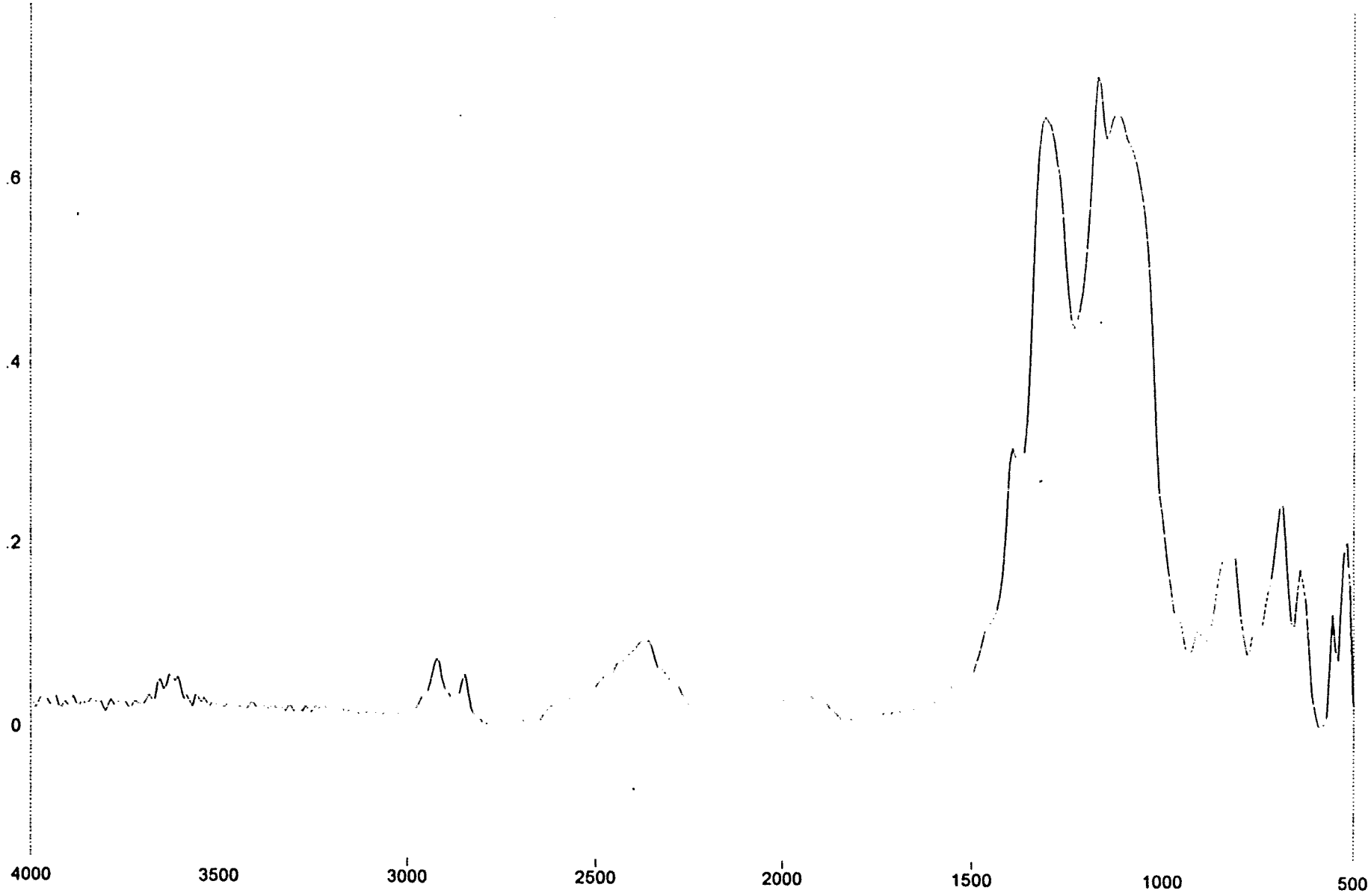

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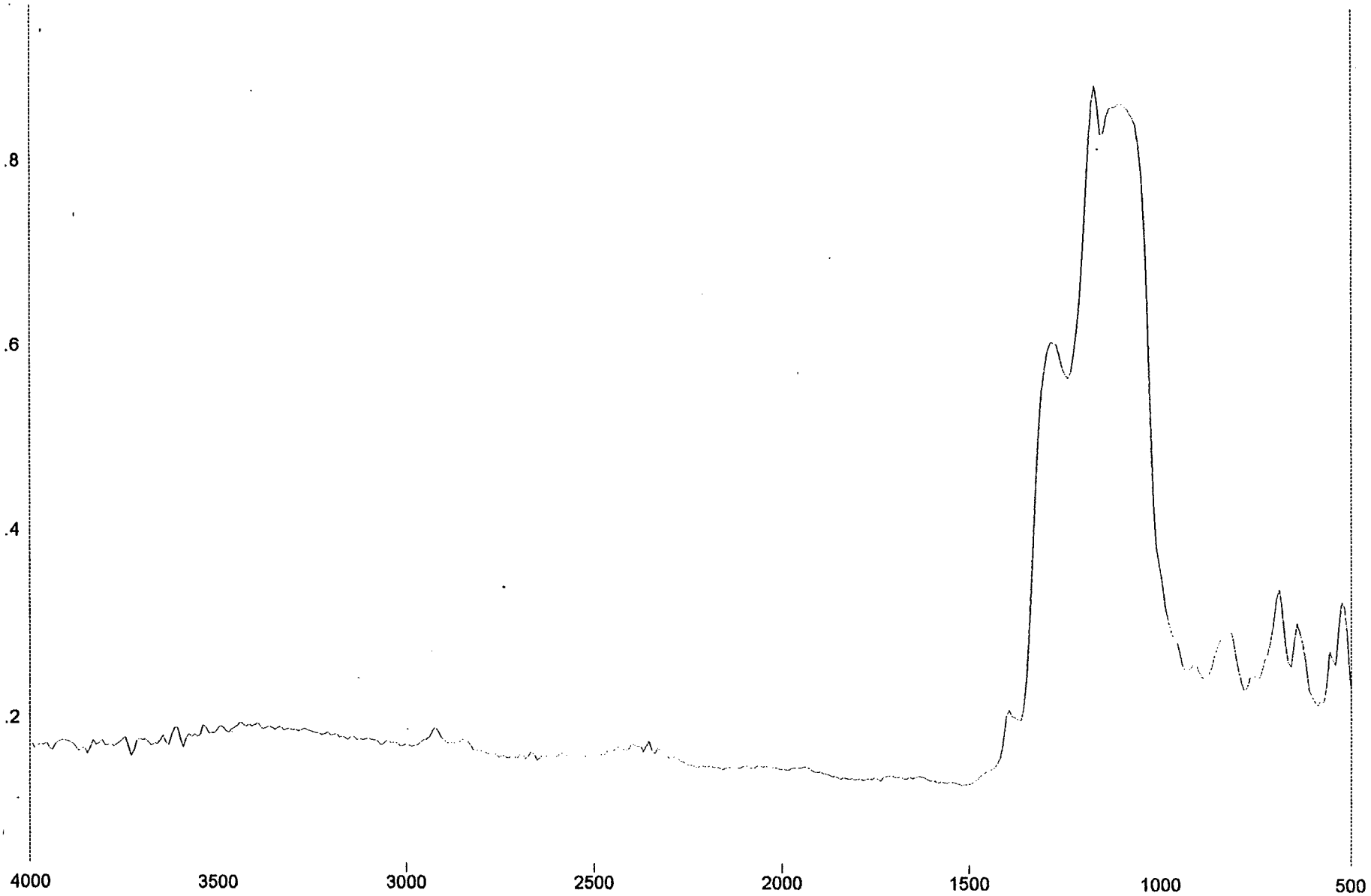

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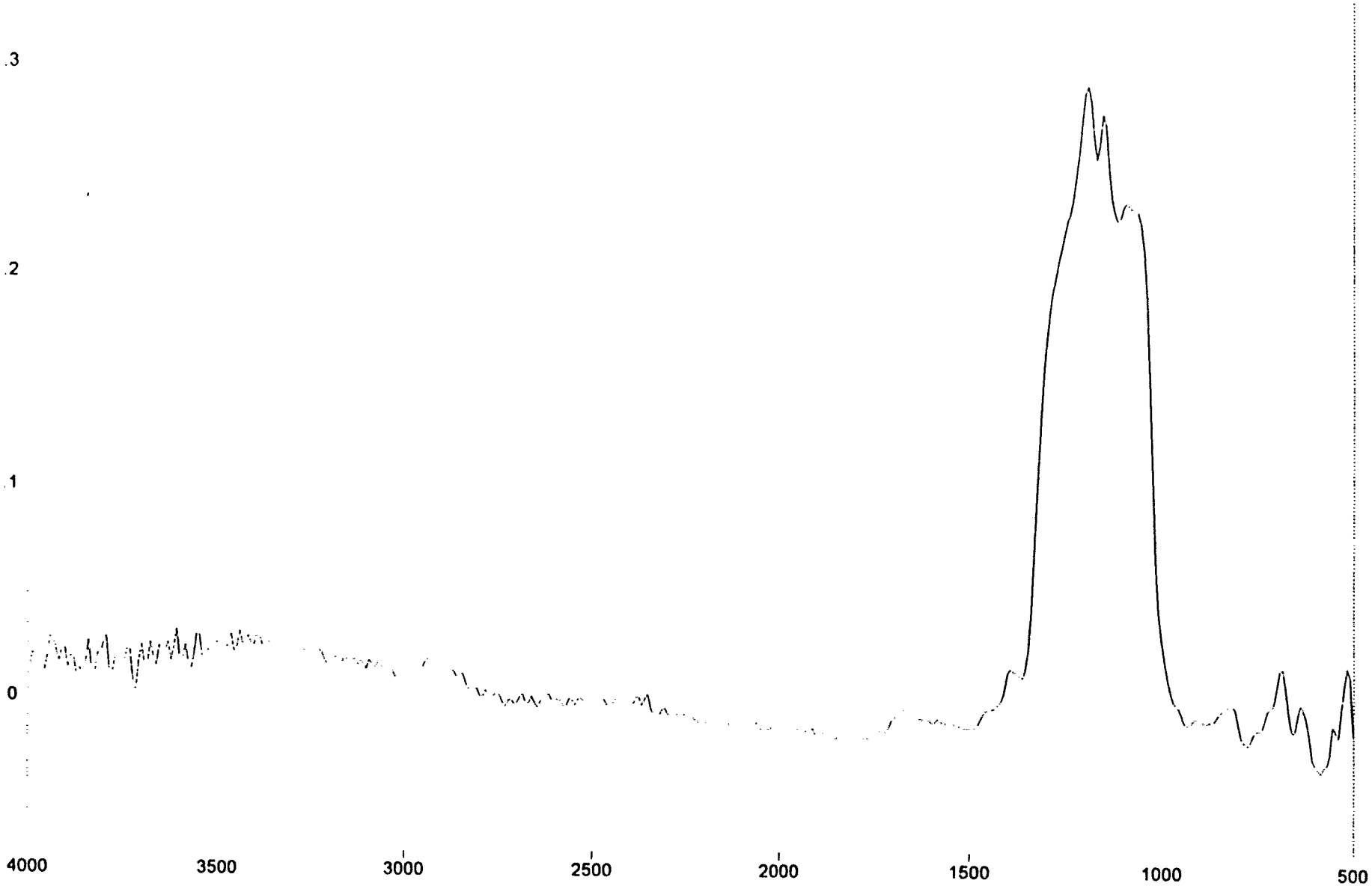

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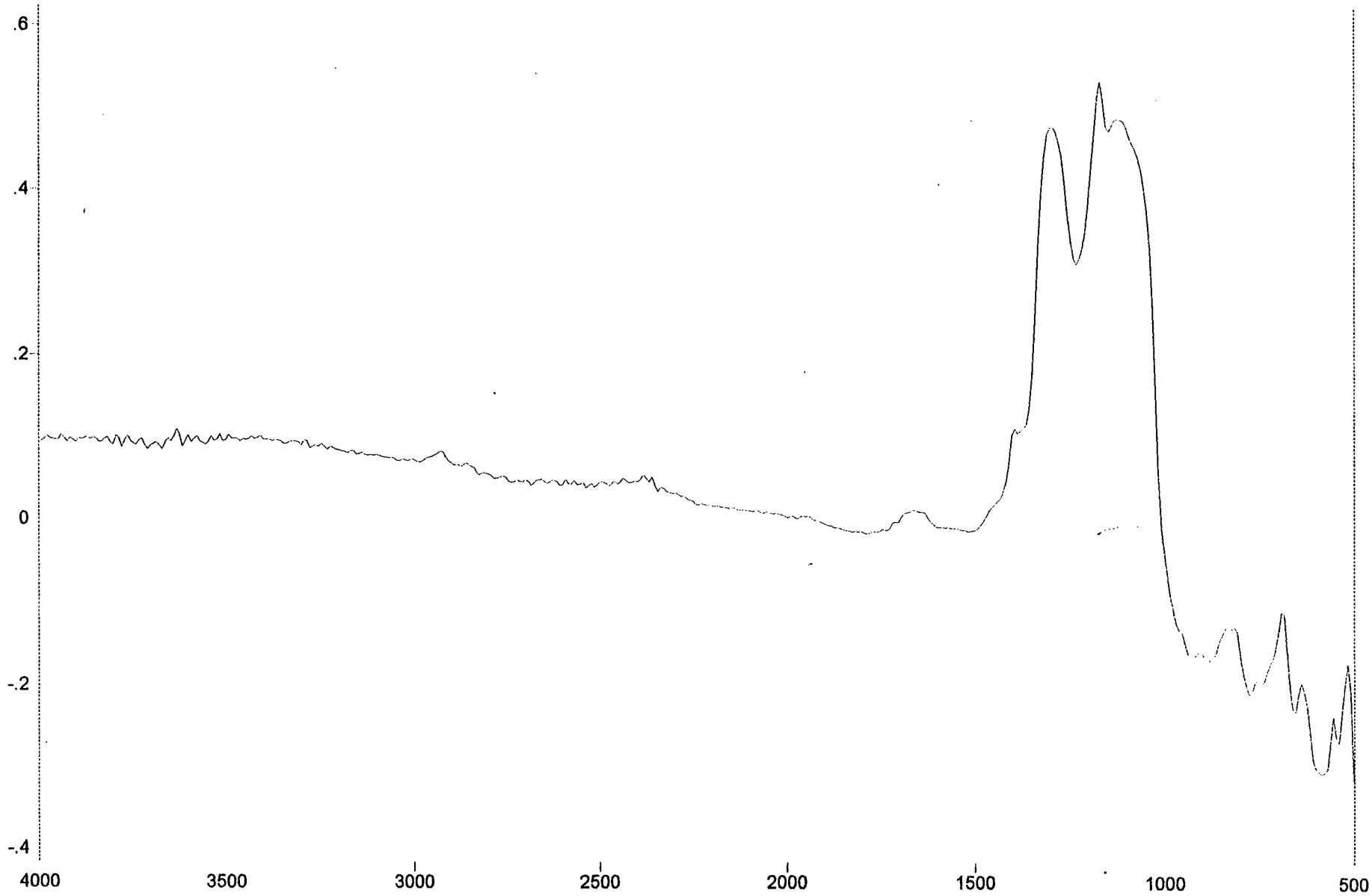

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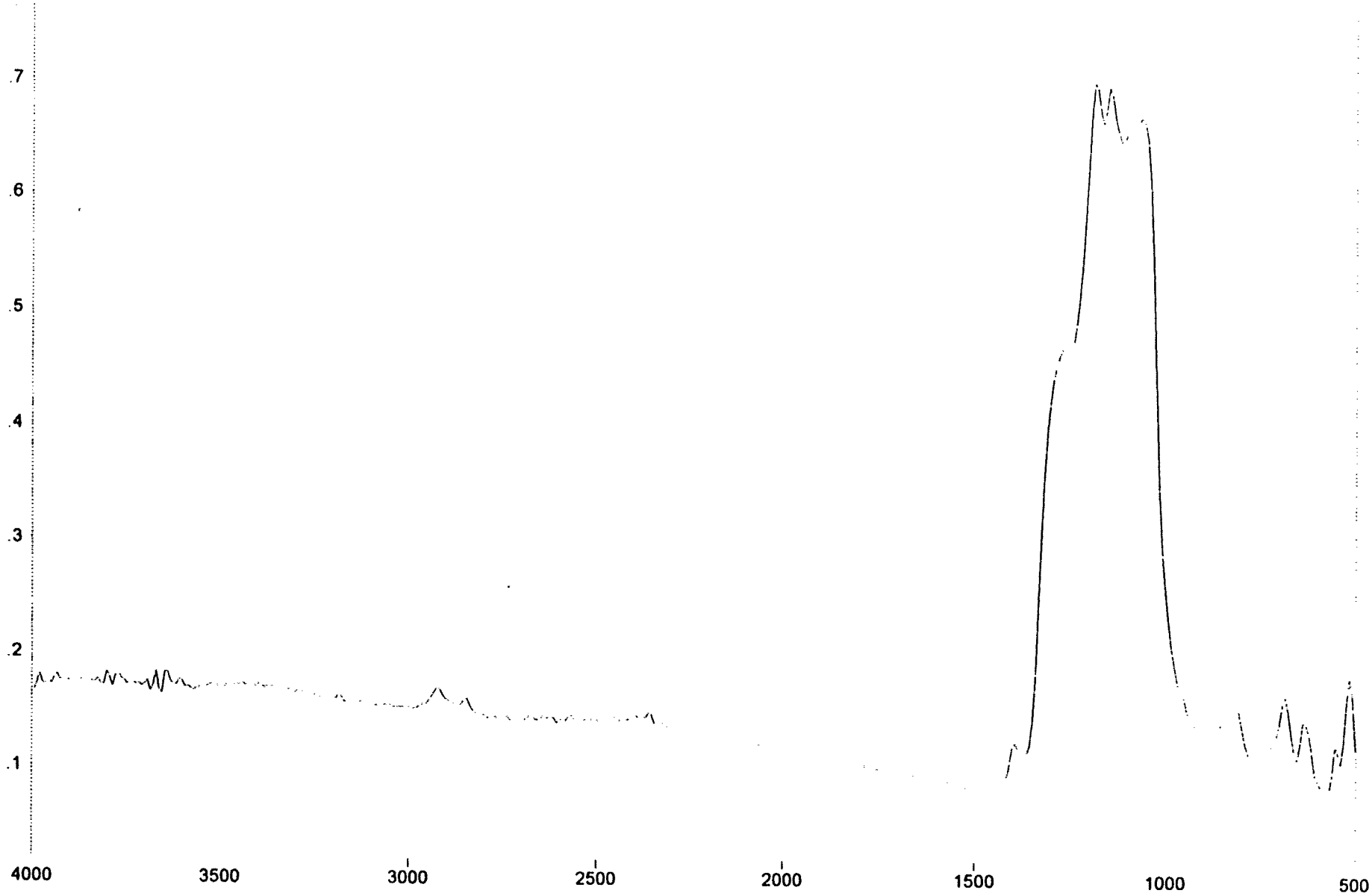

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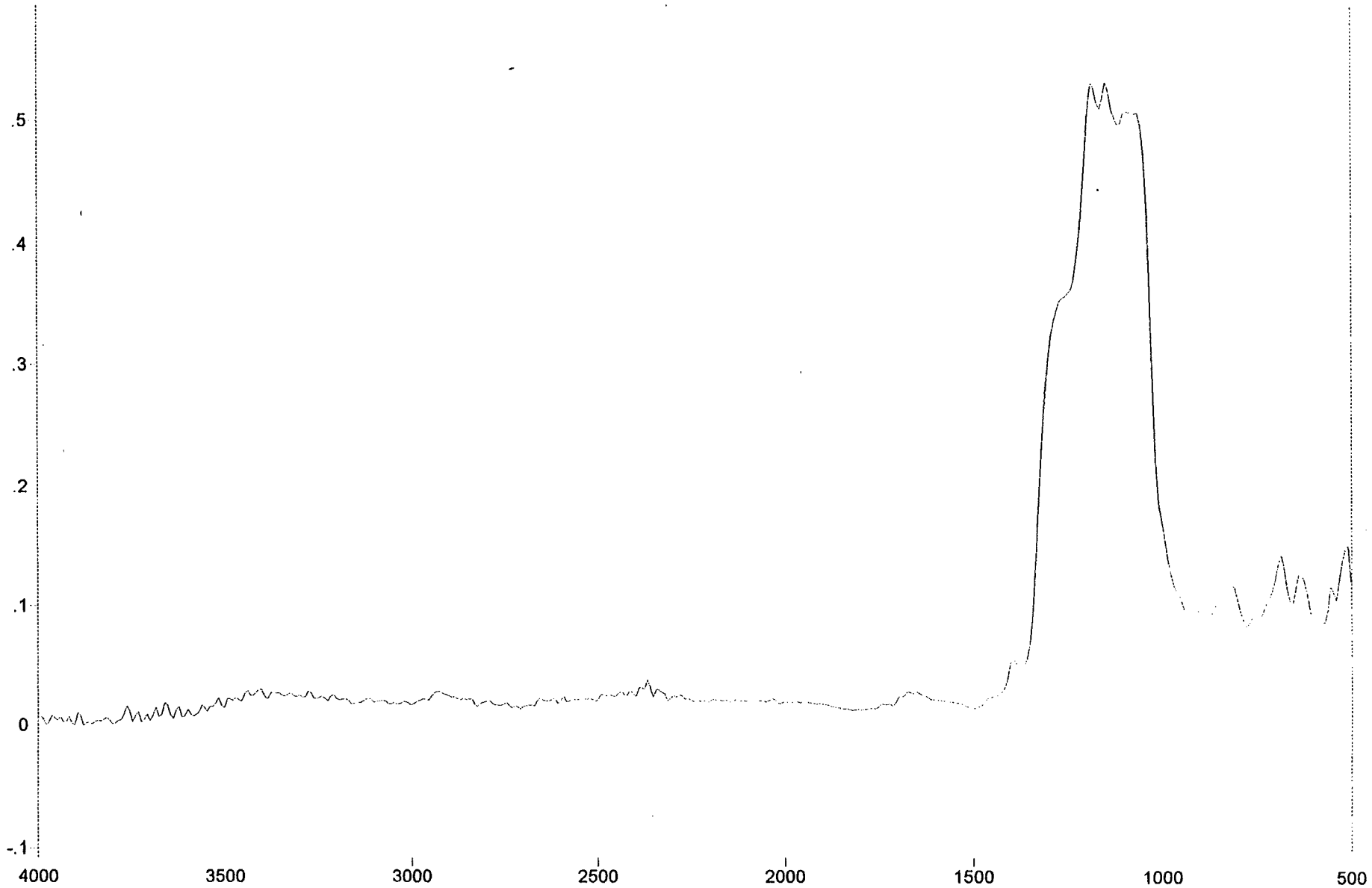

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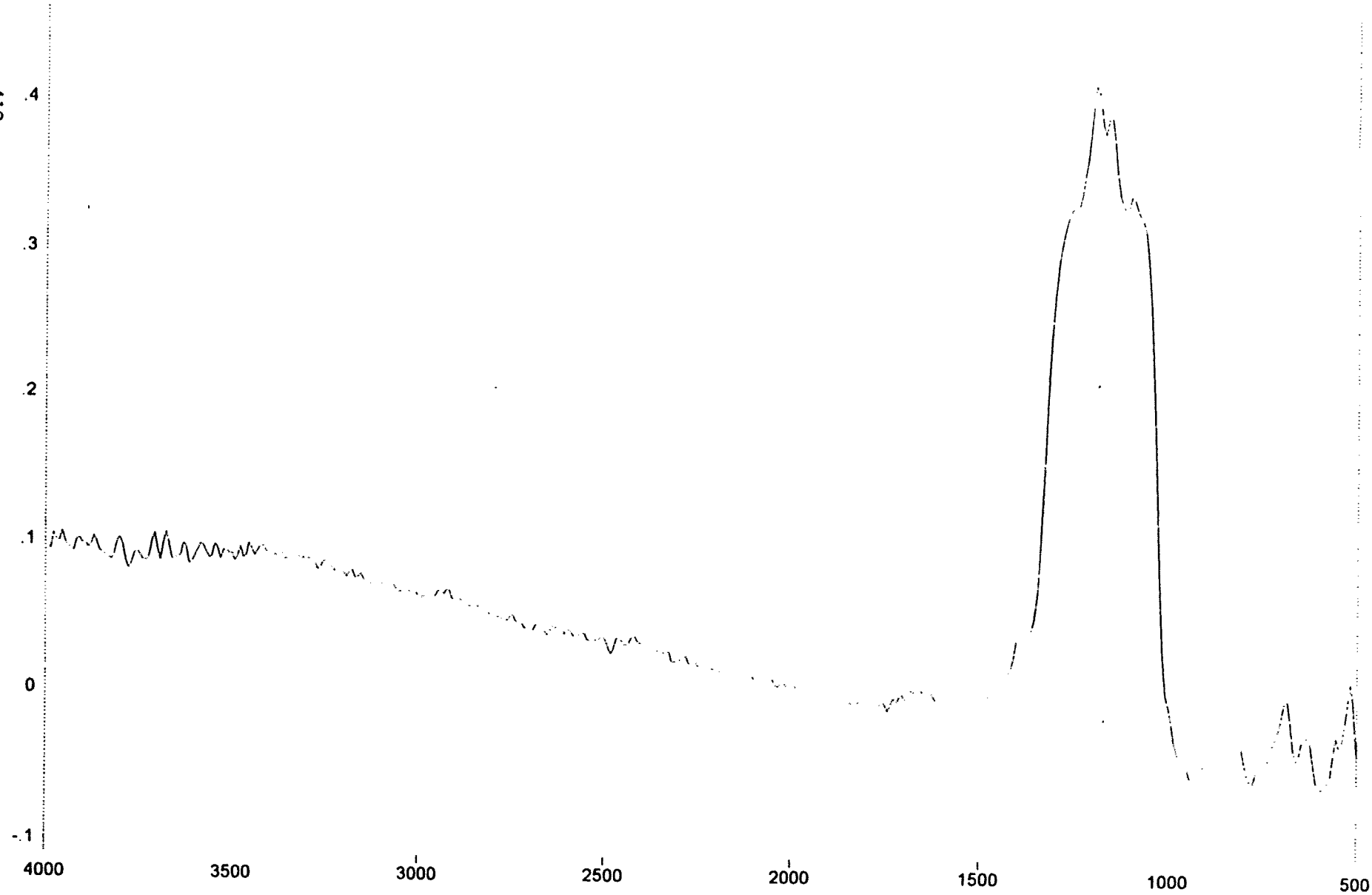

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DEVELOPMENT AND IMPLEMENTATION OF ENVIRONMENTALLY COMPATIBLE SOLID FILM LUBRICANTS

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ABSTRACT

Multi-body launch vehicles require the use of Solid Film Lubricants (SFLs) to allow for unrestricted relative motion between structural assemblies and components during lift-off and ascent into orbit. The Space Shuttle Solid Rocket Booster (SRB), uses a dual coat, ceramic-bonded high temperature SFL in several locations such as restraint hardware between the SRB aft skirt and the Mobile Launch Platform (MLP), the aft SRB/External Tank (ET) attach struts, and the forward skirt SRB/ET attach ball assembly. The proposed National Launch System (NLS) may require similar applications of SFLs for attachment and restraint hardware. A family of environmentally compatible non-lead/antimony bearing alternative SFLs have been developed including a compatible repair material. In addition, commercial applications for SFLs on transportation equipment, all types of lubricated fasteners, and energy related equipment allow for wide usage's of these new lubricants. The new SFLs named BOOSTERLUBE is a family of single layer thin film (0.001 inch maximum) coatings that are a unique mixture of non-hazardous pigments in a compatible resin system that allows for low temperature curing (450°F). Significant savings in energy and processing time as well as elimination of hazardous material usage and disposal would result from the non-toxic one-step SFL application. Compatible air-dry field repair lubricants will help eliminate disassembly of launch vehicle restraint hardware during critical time sensitive assembly operations.

INTRODUCTION

USBI Co. is responsible for the assembly and refurbishment of the non-motor components of the SRB as part of the Space Shuttle system shown in Figures 1 and 2, and which is developed and managed by Marshall Space Flight Center (MSFC) in Huntsville, Alabama. Programs are underway to develop and evaluate environmentally acceptable SFLs for use on aerospace flight hardware in order to eliminate lead, mitigate corrosion by substitution of graphite pigments, and ultimately extend the useful service life of these unique and expensive hardware items. Figure 3 shows the typical areas of lubricant application on SRB flight hardware. All SRB bearing material is made from Inconel 718 which interfaces with either Inconel 718 or 15-5 P.H. materials. The initial study focused on the replacement of a lead bearing dual coat SFL with that of a unique environmentally compatible single coat system. The existing dual coat SFL system required a complex masking and basecoat application and then curing at 1000°F, followed by additional masking and the application of a topcoat followed by a second curing operation at 500°F. The basecoat contains lead and other hazardous air pollutants as does the topcoat and extensive precautions are taken during the application and disposal of such materials. The new family of single coat SFLs named BOOSTERLUBE do not contain lead or hazardous air pollutants and can be easily applied in a single step with curing at 450°F. A compatible air dry SFL was also developed as a field repair material. Both the MSFC, and the Pratt & Whitney Government Engine - Space Propulsion (P&W, GESP) Tribology Laboratories assisted in the testing of the new lubricants. E/M Corporation located in West Lafayette, Indiana helped manufacture the unique SFL system. A significant joint effort was required between USBI Co. and E/M Corp. in order to establish a production test article in a relatively short time frame. Initial screening of all lubricants was performed at E/M Corp. The new SFL also had to be compatible with the existing production equipment at Kennedy Space Center in order to make the process economical. Subsequent application of SFLs to all qualification test articles were performed by production technicians at USBI Co. production facilities.

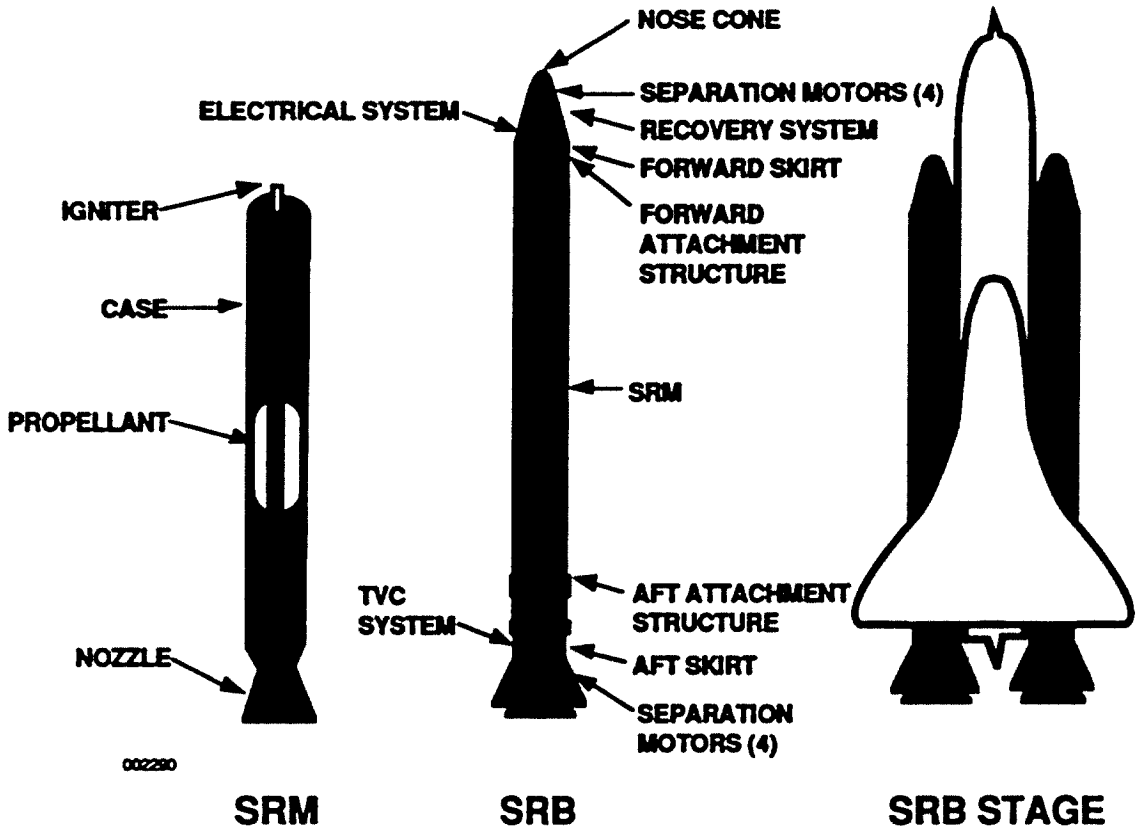

Figure 1. Space Shuttle's SRB

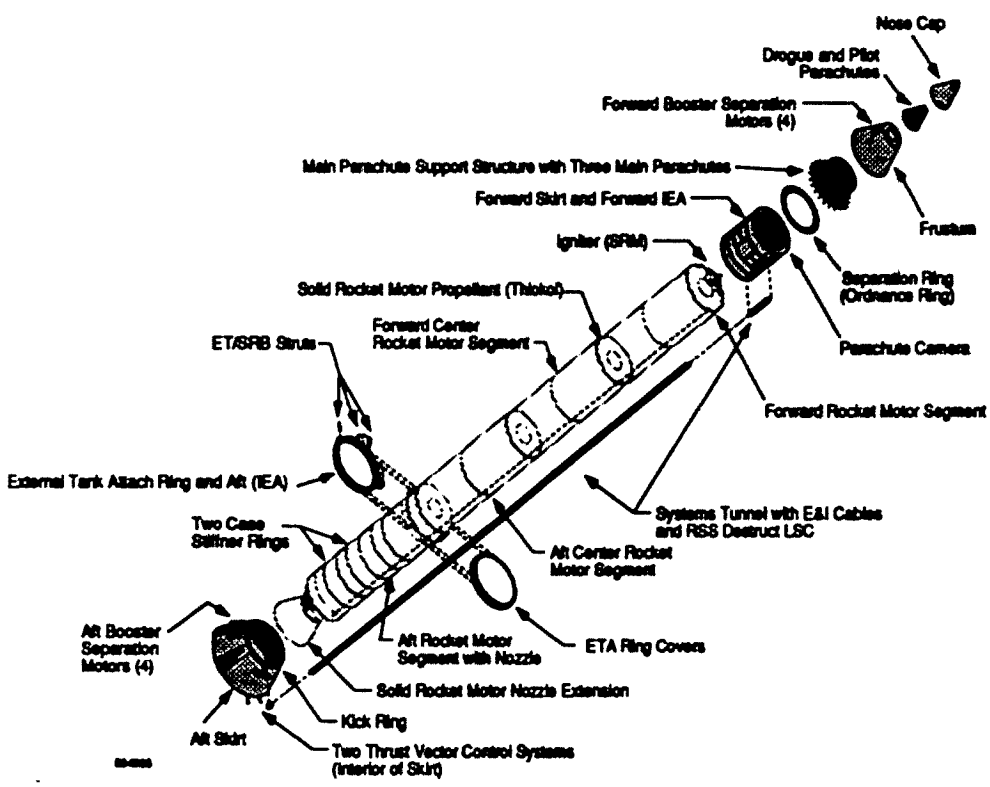

Figure 2. Solid Rocket Booster

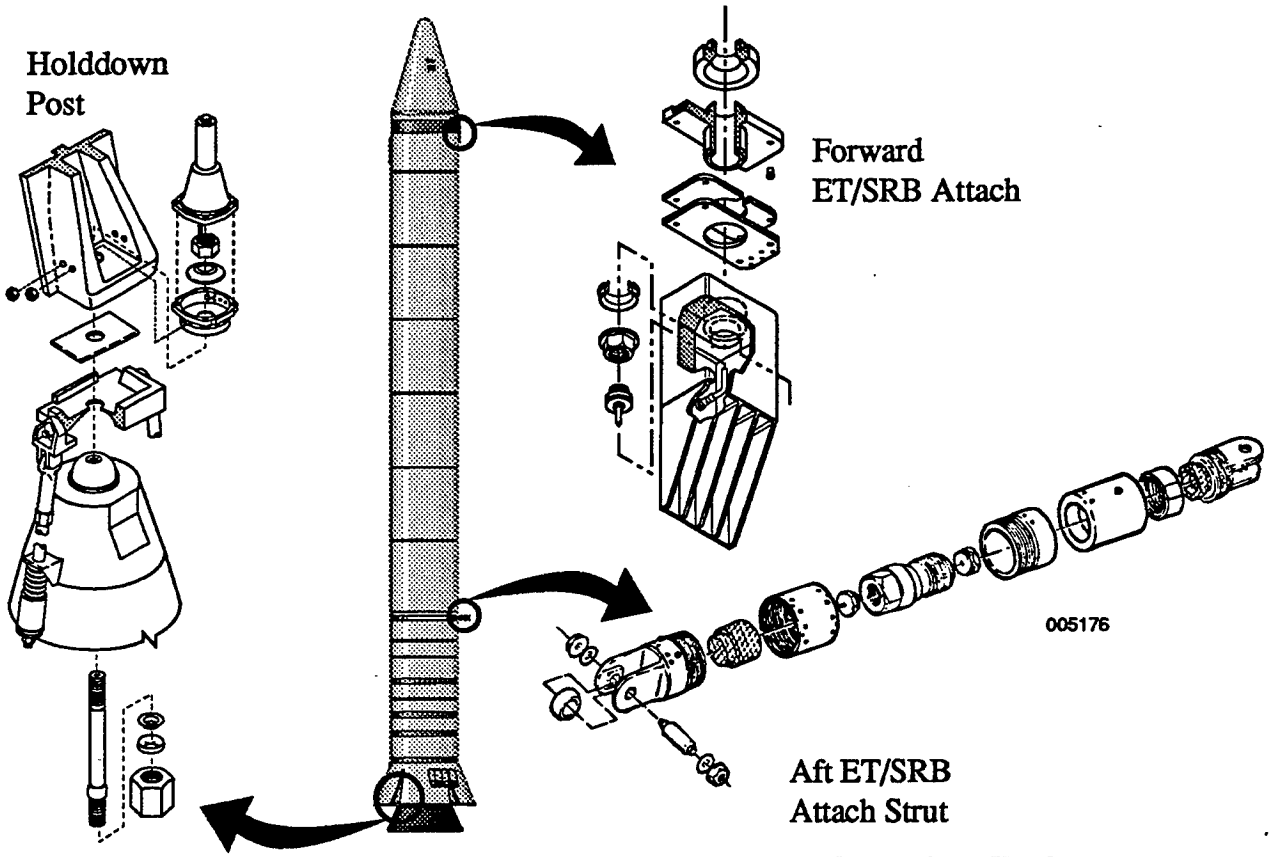

Figure 3. Typical Areas of Lubricant Application on SRB Flight Hardware

DISCUSSION

Pigment and Resin Evaluation and Selection

The first phase of this program involved the selection and screening of five resin systems consisting of epoxy, silicone, phenolic, polyimide and epoxy/silicone blends. Pigments consisting of molybdenum disulfide, graphite, antimony trioxide, lead oxide and boron oxide were all evaluated. The existing dual coat ceramic bonded lead oxide bearing system was used as a baseline for coefficient of friction, load bearing capacity, and endurance life. Testing of the various SFL systems were performed in accordance with ASTM D 2625 Parts A & B (1) (Falex Pin and V-Blocks, testing endurance life and load carrying capacity) as shown in Figure 4; ASTM D 2714 (1) (Falex Block-on-Ring, testing coefficient of friction and wear life) shown in Figure 5, and a mono-ball test developed by MSFC and an alternate device developed by USBI Co. and P&W, GESP shown in Figure 6. The MSFC mono-ball test simulates the very high load conditions at the holddown post and upper external tank attach point, and is the most critical of all tests for verifying SFL performance. Screening the above lubricant systems resulted in the selection of an epoxy/silicone resin blend with pigments consisting of molybdenum disulfide, graphite, and boron oxide. The substitution of graphite with boron oxide, where required, provided a means of eliminating galvanic corrosion when in contact with dissimilar metals in a sea water or salt fog environment. Development of a new device for extreme pressure testing of SFLs allowed USBI Co. and MSFC to run their test programs in parallel, thus saving many months of serial time. Another future part of this program involved the potential application of Ion Vapor Deposited (IVD) aluminum to CRES fasteners that experience dissimilar metal interfaces and potential galvanic corrosion. This is the case on the SRB between 2219 aluminum alloy structures and A286 fasteners. Future testing and evaluation is contemplated for BOOSTERLUBE in such environments.

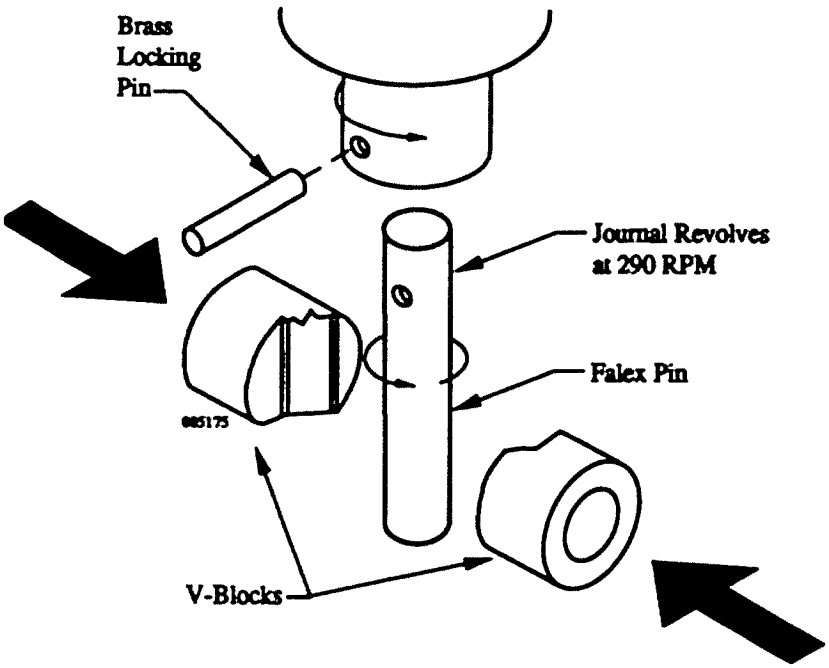

Figure 4. Standard Falex Pin and V-Blocks for Lubrication Tests

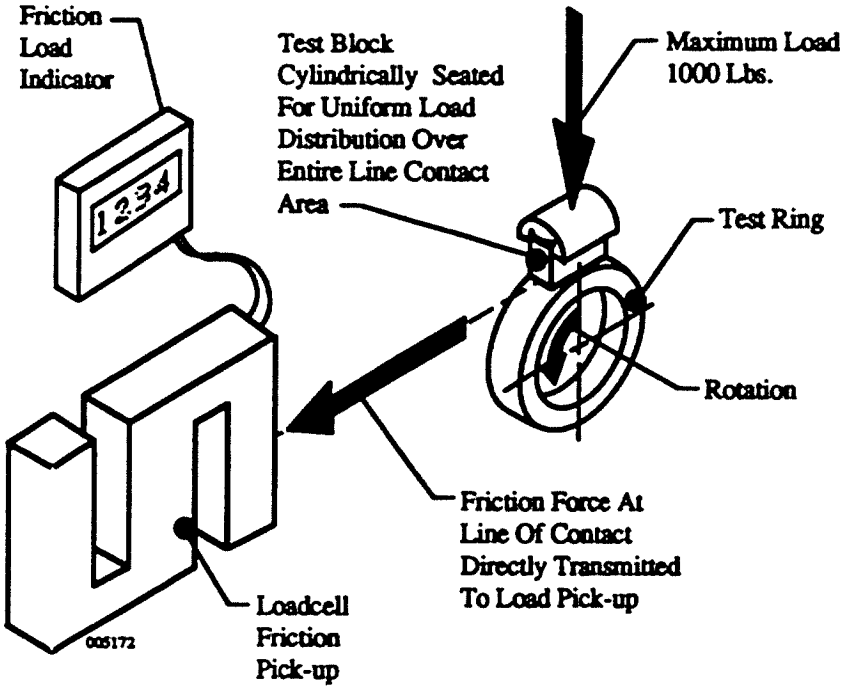

Figure 5. Function Diagram of the Falex Block-On-Ring Testing Machine

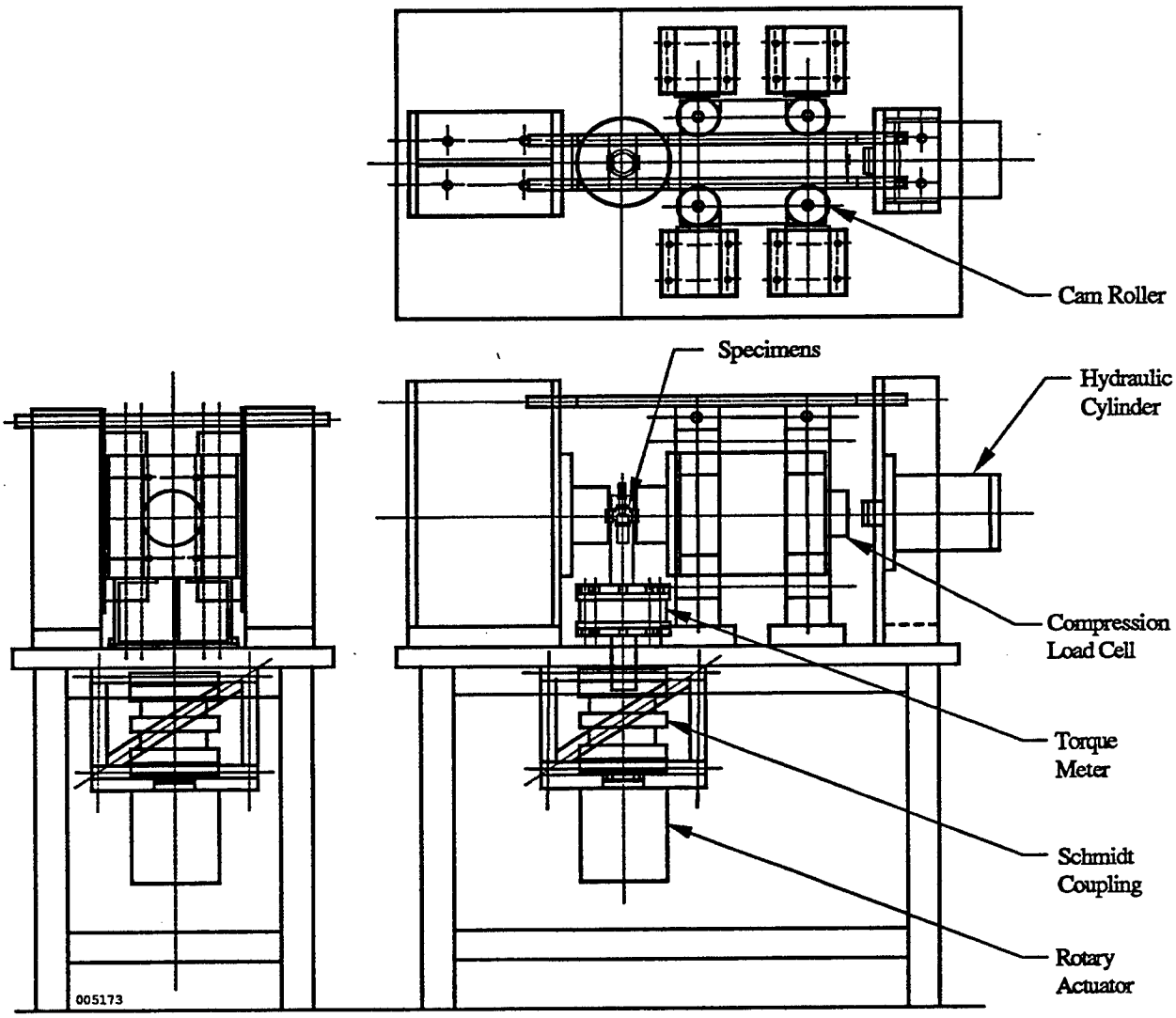

Figure 6. USBI Co./P&W Monoball Tester

Figure 6. USBI Co./P&W Mono-ball Tester

Test Results

Initial testing of BOOSTERLUBE properties at the manufacturer's site, using the Falex Pin and V-Block, ASTM D 2625 Parts A & B and the Falex Block-on-Ring, ASTM D 2714 confirmed the acceptable properties of the Silicone/Epoxy resin system. The Block-on-Ring test showed a significant improvement in wear life of the BOOSTERLUBE materials as compared to the Ceramic Bonded dual coat SFL. Coefficients of friction (μ) were 0.8 - 0.12 and durability of the new SFLs were excellent as confirmed by burnishing with a lint-free cloth. One of the problems associated with the original dual coat system was the relatively soft topcoat that was prone to damage. Significant inspection time was required to determine whether surface marks were caused by actual damage or by burnishing during normal handling. BOOSTERLUBE is a much tougher resin system and is less susceptible to marking and/or damage. A compatible air dry repair lubricant was also developed to allow for minor area repairs to lubricated parts that are inadvertently damaged in the field. Testing of its properties using ASTM procedures and the MSFC mono-ball tester are underway. Final tests of BOOSTERLUBE were performed on optimized pigment volume concentrations using MoS2/graphite and MoS2/boron oxide. This, in combination with optimum blends of silicone and epoxy resin systems, allowed for tailoring properties to their required applications. All test specimens were precision cleaned, grit blasted, lubricated, and oven cured by production technicians and on production line facilities at USBI Co. operations. Specimens were then sent to MSFC, Tribology Labs. for qualification testing. Results of testing can be seen in Figure 7. The most relevant of all tests, MSFC/EH14 High Load Test (mono-ball

test) showed superior properties of BOOSTERLUBE (WL-1158-20) over the existing ceramic bonded dual coat SFL (Ceramic B) and second only to Ceramic A, a material that also contains lead and hazardous air pollutants.

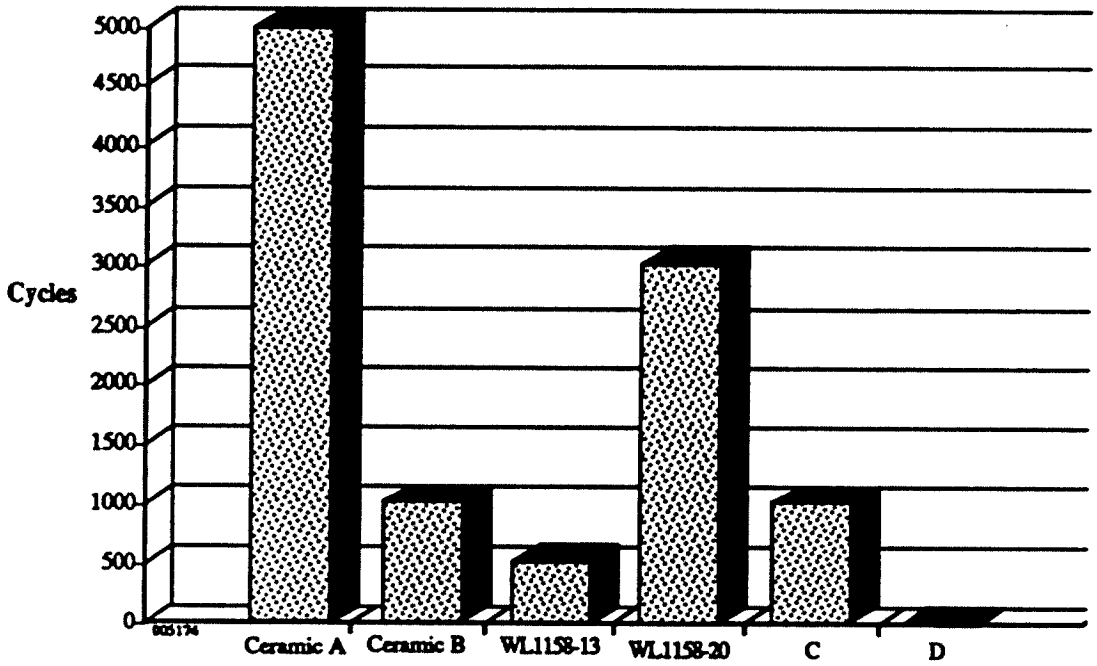

Figure 7. MSFC/EH14 High Load Test (110 KSI)

CONCLUSION

Development and testing of a new family of environmentally compatible SFLs allowed for the potential replacement of lead bearing, hazardous air polluting, energy inefficient, SFL materials. The single coat SFL named BOOSTERLUBE, showed excellent performance as compared to other lubricant systems and met with significant operator acceptance. Eliminating lead exposure to personnel during application and disposal of those materials was in itself a major accomplishment. The economics of a single coat system will cut application costs as well as energy related charges for SFL curing, by 50%. The costs of disposing of and utilizing hazardous materials continue to escalate and in time will be prohibitive. Applications for many other fields than aerospace exist. Energy and power generation, chemicals, transportation, machinery of all types, exo-atmosphere and low earth orbit vehicles can benefit from implementation.

ACKNOWLEDGMENTS

The authors would like to thank the various USBI departments both in Huntsville, Alabama and Kennedy Space Center, Florida for supporting and assisting in program management, production operations, logistics and testing. Many thanks to NASA Marshall Space Flight Center Materials and Processes Laboratory, Tribology Branch, and the SRB Program Office personnel who were supportive of this program and to Pratt & Whitney Government Engines Space Propulsion Tribology Branch for help in developing the new lubricant test machine. Additional thanks are given to E/M Co. management and laboratory personnel who helped make this program a success.

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HAZARDOUS MATERIALS TRACKING AND WASTE MINIMIZATION

Lockheed Martin Tactical Aircraft Systems Impliments Computerized System to Monitor Water Quality

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Abstract

The ever increasing environmental regulations/requirements facing industries and municipalities over the last several years has resulted in these organizations dedicating considerable resources to keep pace. Lockheed Martin Tactical Aircraft Systems (LMTAS) is committed to meet and exceed the regulatory requirements. A fundamental element of a successful environmental program is dependable, accurate and timely monitoring of the facility's outfalls. Lockheed Martin Tactical Aircraft Systems operates Air Force Plant No. 4, a government owned, contractor operated facility. The facility is a conglomeration of buildings spread over 650 acres, bounded by Lake Worth to the north and Naval Air Station Fort Worth, Joint Reserve Base to the east. The primary activity is the design, fabrication, assembly and testing of tactical fighter aircraft.

In support of the water discharge monitoring requirements, and in support of a proactive monitoring program, The Environmental Resources Management group(ERM) at LMTAS saw a need to develop an automated water quality monitoring system. The original design concept was to: monitor water quality parameters; notify LMTAS personnel in the event of an alarm condition; and perform various sampling requirements. Radio frequency communication is used to link the field sites to the office-based control center. A pilot test was initiated in March of 1993, with system installation completed in may of 1993. The system was designed to integrate basically "off-the-shelf" components. This allows proven, reliable components to be integrated at low cost and with minimal design and engineering effort.

Due to the numerous requirements, designing and developing a water quality monitoring system versatile enough to meet present and future needs challenging. An Integrated Remote Monitoring and Notification System (IRMNS) was designed. It is built around a Geomation, Inc. control system which provides the platform for various instrument interfaces. The Measurement and Control Units (MCU's) are located at the field sites accept and process numerous instruments outputs including 4-20 mA and RS 232. Once programmed, the MCU operates independently from the office based Monitoring Station (NMS) for extended periods of time. System programming is performed at the monitoring station and information is downloaded to the MCU's.

The NMS is PC based, utilizing manufacturers designed software. The network controller also activates a auto dialer unit, which can auto dial multiple lines and deliver multiple messages when triggered. Alarm conditions at a monitoring site will activate the notification option. LMTAS has modified the network control station tying in a second PC which is used for data management functions. The system is capable of hosting multiple PC's through phone modems. Monitoring is accomplished with the use of multi-sensor probes. Upon implementation of the final project phase, IRMNS will be monitoring between 65 and 75 inputs (channels) from the ten water discharge sites.

Introduction

A fundamental element of a successful environmental program is dependable, accurate and timely monitoring of a facility's outfalls and various discharge streams. It is the mission goal for the Environmental Resources Management (ERM) organization at Lockheed Martin Tactical Aircraft Systems (LMTAS) to comply with or meet regulatory and organizational environmental requirements and goals. Beyond just meeting or complying with various organizations, it is the groups practice to exceed in these areas. The technology and know-how exists to accomplish environmental excellence through the many advances and accomplishments of persons involved with protecting and preserving the environment. Such goals and accomplishments move LMTAS closer to zero discharge; and also help maintain a partnership with the regulatory community.

In support of the water discharge monitoring requirements at LMTAS, and in support of a proactive monitoring program, LMTAS conceptualized an Integrated Remote Monitoring and Notification System (IRMNS) in January of 1993. The system needed to accomplish three basic things: provide early warning of a spill or release; provide continuous real-time water quality monitoring; and save resources. To accomplish all of this, it was necessary to utilize automation. A team approach was used to pull together the expertise and products of EMSI, Inc.(prime contractor for first deployments), Geomation, Inc. Hydrolab, Inc. and ISCO, Inc. The objective was to develop a system able to perform water quality monitoring unattended, once programmed. Presently, four of the facility's NPDES permitted outfalls are monitored by IRMNS. Four more permitted outfall and the plants lake water pumping facility will be brought on line by fall of 1996.

Overview

Due to the large area of LMTAS Faciliy and the distribution of the facility's discharge sites, a multiple node network architecture was selected (Figure 1).

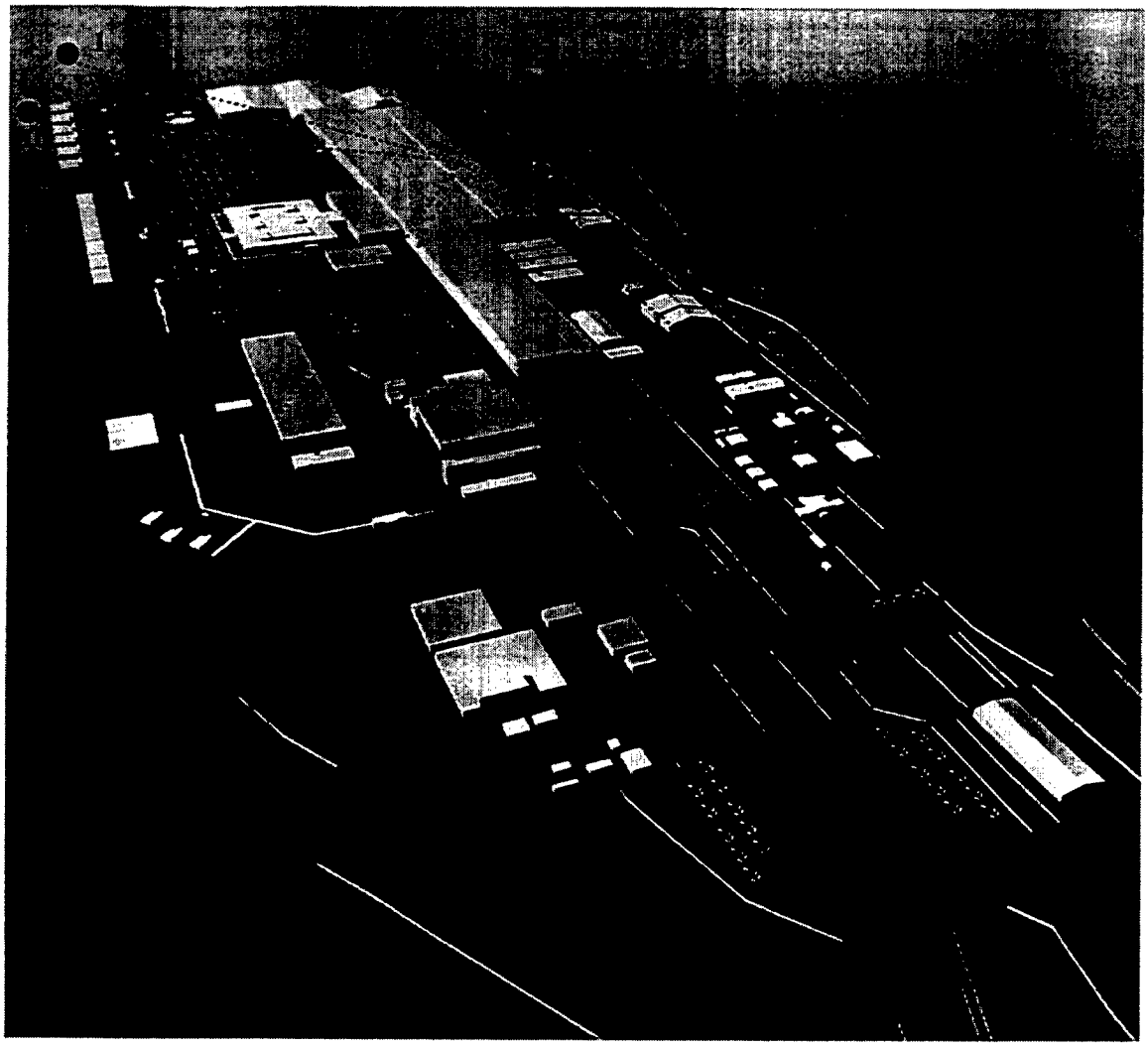

Figure 1. LMTAS Facility With Outfall Monitoring Sites Shown

Located at each outfall monitoring site is a Measurements Control Unit (MCU). Once programmed, the MCU's to communicate to a central Network Monitoring Station (NMS), which provides an operator interface for observing and controlling the MCU's. The various water quality monitoring sensors are connected to the MCU's at the monitoring site. The PC based NMS is connected to a repeater unit, which communicates to the MCU's via FM radio frequency. The combination of the MCU's and NMS make up what Geomation refers to as System 2300. It is defined as a distributed data acquisition and control system comprised of standard product building blocks and units.

System Development

Why did we need an automated water quality monitoring system? This was the question asked by management and other facility planners. The following points were given for justification:

- We were physically inspecting the outfalls for only a short period each day. An automated system would provide continuous real time monitoring.
- An automated system would reduce the time spent in the field and time spent logging in monitoring results.
- An automated system would be consistent with LMTAS's Risk Management Program and Storm Water Pollution Prevention Plan (considered a Best Management Practice (BMP)).
- Such a system could be considered proactive, sending the message to the community and regulatory agencies that LMTAS is willing to go beyond permit requirements designed to protect surrounding surface waters.

Once it was decided to pursue an automated system designed to monitor water quality and provide alarm notification, an initial project scope was developed. The purpose of initiating the project was two-fold: to replace aging existing outfall monitoring equipment used to support the facility's NPDES permit requirements and to create an outfall early warning notification system. As research and development proceeded, additional uses began to become apparent.

Type of System

Supporting the monitoring functions of the system, field sensors provide the input to the MCU's. The information gathered by the sensors is used by the MCU's to generate data log files and to be incorporated into various programming configuration . The LMTAS system utilized a separate MCU at each monitoring site. All the MCU's communicate directly to a Gateway Unit, which is hardwired to the NMS. In the event of poor radio communication between an MCU and the Gateway Unit, communications from one MCU can be directed to another MCU in the field which has clear communication with the Gateway. This would also be a possible method to communicate over long distances. In this case each MCU logs and communicates it's own data sets, but at the same time can act as a Network Repeater or gateway unit to get the information to the NMS. This is possible because each MCU has it's own distinct address, which is associated with each string of communication into and out of the MCU. Flexibility and simplicity in system architecture is a feature of the System 2300 that allows for such versatility in networking and communication protocol (Figure 2).

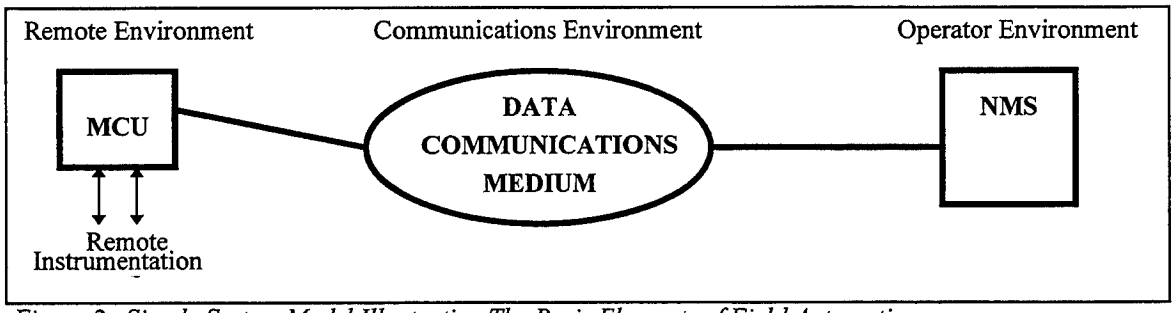

Figure 2. Simple System Model Illustrating The Basic Elements of Field Automation

The MCU's located at each monitoring station are intelligent, stand-alone unit capable of performing all data acquisition and control functions. Programming the MCU's is done at the NMS which in LMTAS case, is located in the main plant. The PC used at the NMS can be set up to be stand-alone or tied into the facility's computer network. A phone modem is used for remote users (guest) access into the NMS PC. Depending on the level of access granted, a remote user can either view or program/control the system. This feature is used by LMTAS as an alarm notification tool. In this application, when the monitoring system activates the alarm notification components of IRMNS, a phone call is made via a designated phone line to the appropriate personnel, whether it be at the facility, at their home, or by pager. In any case, the system will call until the alarm message is acknowledged by pushing the star button on the phone. From a home based computer, a user can call up the system and tie into the NMS, allowing access to data screens and control commands.

An example of a scenario that could take place with the LMTAS monitoring system is as follows: an alarm notification call is placed in the middle of the night and the auto dialer does not get a response at any of the facility extensions. The next call is made to the home of an on-call ERM individual, who then acknowledges the call and instructs the NMS (via home computer) to monitor the alarm condition at the outfall. At the same time the responder can call the facility's emergency response personnel and give specific response instructions to carry out and keep him posted. The auto dialer in the LMTAS system has multiple digitally recorded messages that are activated by the MCU.

Depending on the alarm which is tripped, a message provides the location and nature of the alarm, e.g., "Outfall #1, pH High" or "Treatment unit #2, effluent concentration high." The potential application for an automated monitoring and control system can be numerous if versatility is designed in up front. The automated monitoring system implemented at LMTAS was designed primarily for water quality monitoring at NPDES permitted outfalls. It was also designed to support other projects and applications at AFP#4 (Figure 3).

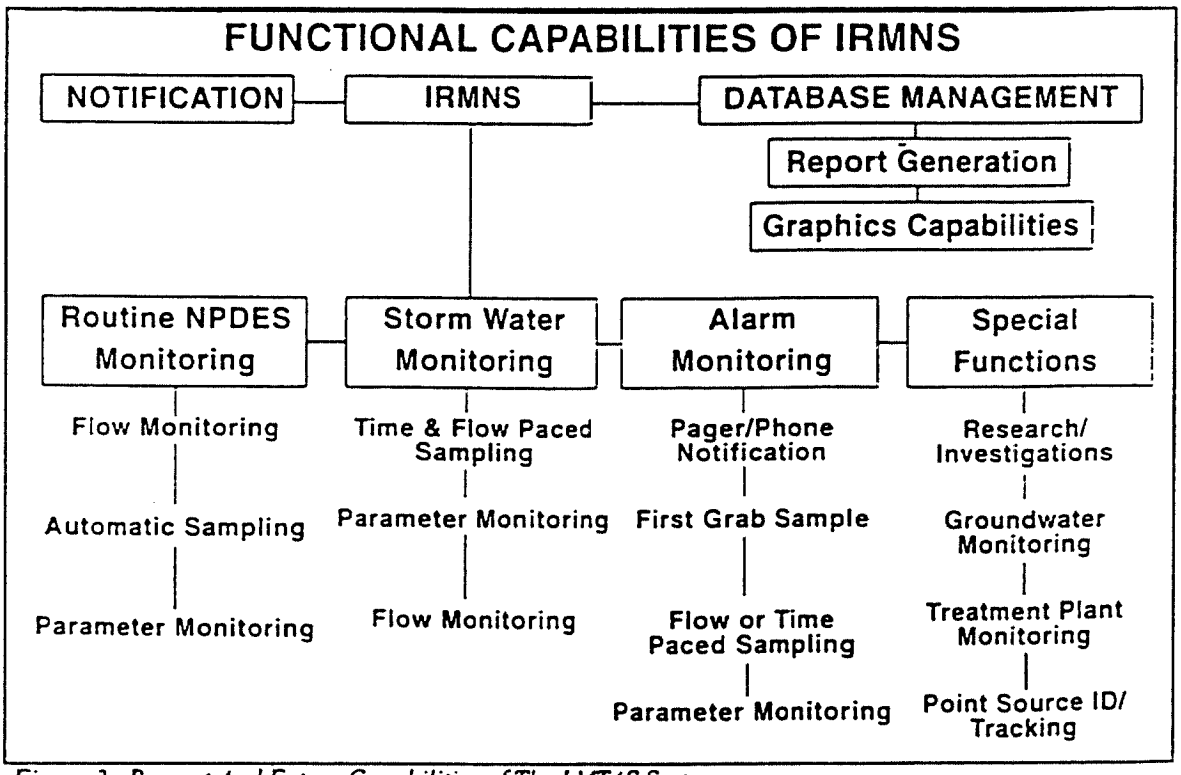

Figure 3. Present And Future Capabilities of The LMTAS System

Types of Sensors

Data acquisition and control components may be at the heart of a monitoring system, but data collection begins with field sensors. The parameters monitored will determine what type sensors will be required. Sensor technology has grown considerably since the 80's. Miniaturization of electronic components and the development of new types of detectors have allowed sensor manufacturers to provide field instruments capable of producing analytical results previously possible by elaborate instruments and apparatuses. It is important to keep in mind that some analyses performed in the laboratory will have greater accuracy than a field sensor monitoring the same parameter. A given sensor may be a very good qualitative instrument, but typically, a laboratory instrument measuring the same parameter or analyte should have a quantitative advantage. The desired detection limit for a given measurement should be considered when selecting field sensors.

In some cases, the regulatory community will not accept data for reporting purposes coming from some types field sensors. However, that particular sensor could be deployed for other purposes such as: early warning detection; providing the input signals for controlling a process; or research and investigations.

The sensors used for monitoring water quality at LMTAS are applied to both permit required monitoring and non-permit required monitoring. To acquire a more complete, real time picture of the water being monitored, a variety of sensors were selected. There is not always a field sensor available to directly monitor a particular parameter. In the area of real-time or near real-time field monitoring, the need is sometimes ahead of the technology. To overcome this, selecting a sensor that is able to indirectly detect a specific parameter is possible in some applications. An example of this is the continuous monitoring for metals in a water stream. A simple way to get an indication of metals in a waste water stream is by measuring for increases in Specific Conductivity. Metals generally increase the conductivity of water. A second example is the detection of chlorine or other oxidizers in a waste water stream. When present, these chemicals will cause the water to be in an oxidative state. This can be detected with a Reduction/Oxidation (Redox) probe. In both of these examples, the sensors utilize reliable well proven technologies.

At this time, all sensors used in the LMTAS automated monitoring system monitor the condition of the water and certain groups of compounds present in or on the water. The rate and volume of flow is also monitored. Compound-specific sensors for continuous field monitoring are not used due to their availability and practicality. It was decided to get as much information on water quality as practical and be able to detect as many potential pollutants as possible at the facility outfalls. It was especially important for the sensors, probes and meters used for permit monitoring to be very accurate and stable. The system required sensors and probes designed for continuous operation and exposure to the environment. The type of output signal of each instrument had to be capable of interfacing with the MCU's. This was greatly simplified since the MCU's were designed to accept a wide variety of inputs ranging from Analog to RS232. We needed sensors that were able to run off of 12 VDC and designed to interface and be controlled by a MCU. When possible, the sensors needed to be packaged together (multi-parameter probe) to simplify and stream-line the monitoring station installation.

Integration and Configuration

This system may be assembled "tinker toy" fashioned with off the shelf components. This concept insures that IRMNS: has easy serviceability; has interchangeable modular components; lower costs; a system that can be easily upgraded as need and technology changes. The last feature mentioned above is perhaps the most important. The monitoring system installed at AFP#4 in the 70's was very complex and expensive. It also required permanent installation and could not be easily expanded. If additional parameters needed to be monitored, extra equipment could not be integrated into the monitoring station. By selecting more intelligent, versatile components such as ones used in IRMNS, a system as a whole will have a much longer service life while at the same time allowing for expansion and modernization. A typical outfall water monitoring site at LMTAS includes four basic elements (Figure 4).

Figure 4. Solar Powered Remote Monitoring Site; LMTAS Outfall 3

1. Sensor package for water quality monitoring.
2. Flow monitoring equipment.
3. Data acquisition and control unit, which includes the communication elements.
4. A 12 VDC power supply, which can be adapted for solar operation.

When developing the scope of the project, other uses were considered. Applications do not have to be limited to outfall discharge monitoring and alarm notification. Sensors designed to monitor atmospheric conditions can be supported by the MCU's.

Based on a specific condition, IRMNS is capable of responding with unattended tasks such as controlling a valve, controlling a pump, and process control functions. The following is a summary of additional applications being considered at LMTAS facility:

1. Controlling a de-chlorinating metering pump used to deliver a chlorine-neutralizing chemical.
2. Monitoring for hydrocarbon breakthrough in a ground water treatment unit's carbon beds; when detected the treatment unit feed pump would be automatically shut off.
3. Monitoring for releases within secondary containment pits and sumps.
4. Closing the discharge valve at a storm water outfall's containment dam in the event a contaminant is released. This application requires a hydrocarbon sensor and a motorized gate valve. All of the above applications and future applications utilize Geomation equipment for system measurements controls, and communications.

Equipment Selections

Selecting the all around best components for an automated monitoring system involved searching the marked for off-the-shelf, well proven equipment. As much as any one factor, budget constraints has to be factored in. Fortunately, self-contained modular components are inherently less expensive. Wherever possible, re-engineering types of components to perform specific tasks was eliminated. The following summarizes the selection criteria used on the IRMNS project:

- Affordability
- Easy to operate and maintain
- Simplified Installation
- Good Precision and Accuracy
- Versatile and Expandable
- Easily integrated into the system
- Off-the-shelf type components
- Tried and true, proven components

Based on this selection criteria, a comparison of the available pieces of equipment in each of the following categories was completed. The selection are summarized in the following paragraphs.

Date Acquisition and Control System

The Geomation, Inc.'s System 2300 family of measurement and control products as mentioned earlier, was the selected data acquisition and control component for IRMNS. GEONET for Windows software is a standard package that provides a menu driven interface for programming the System 2300. Remote logging and telemetry equipment is also supplied by Geomation and is based on the node driven MCU technology. All data is transmitted to the Network Monitoring Station (NMS), which will use a 100 mHz Pentium PC running the GEONET program. Figure 5. shows integrating the NMS with field equipment.

To carry out the notification function once the system is in an alarm status, a RACO, Inc. Verbatim Auto Dialer was selected. The Auto dialer can automatically dial multiple numbers and deliver multiple messages once triggered by the NMS. Messages are pre-recorded using digital technology. The IRMNS presently has 16 different messages stored, with plans to expand to 32. The Auto dialer has full battery backup and is easily interfaced with the NMS computer and facility phone lines.

Sensors

Utilizing an instrument that has packaged together up to eight sensors into a single probe seemed a little risky to pursue in the early design phase. If the probe malfunctioned, then many parameters would not get logged. After thoroughly studying the available products, the Hydrolab, Inc. Data Sonde 3 and H20 Multiprobes were chosen to perform the real time, water quality monitoring functions for IRMNS. When properly maintained, the multiprobes meet and in some cases exceed published performance specifications. The Multiprobes can be deployed in totally submerge or partially submerged environments. Long term exposure or climatic extremes do not seem to interface with the probes performance. When using Multiprobes for continuous, year around deployment, it is important toperform routine maintenance.

This should include: cleaning the sensors; replacing reference solutions and membranes; calibrating against standard solutions. Between calibrations, the probes seldom need servicing. The Data Sonde 3 multiprobe is capable of independent operations with a logging capacity of 256k bytes of memory. Overall, the Multiprobes are turning out to be rugged, dependable instruments in their present applications.

At this time, the only type of hydrocarbon sensor used at IRMNS sites is a probe designed to detect floatable hydrocarbons such as fuels and oils floating on water. Determining the type of hydrocarbon was not a priority for the intended application. The sensor's intended application is spill detection. The Agar, Inc. Hydrocarbon Sensor was select to fulfill the hydrocarbon sensing for the IRMNS project.

Flow Meters And Samplers

Flows at the various outfalls differ a great deal in nature from one monitoring point to another. Because of this, no single type of flow meter can be used at all of the discharge monitoring sites. The range varies from dry most of the time to over two feet of continuous flow through a four foot pipe. Generally, where a flume or weir is available, an ISCO, Inc., an Bubbler Flow Meter is used. This type of flow meter has very good accuracy and resolution. These flow meters are very versatile and easily programmed to fit the specifications of the channel, weir, or flume being measured. They are capable of stand-alone logging and controlling or can be interfaced with the MCU's. An ISCO Doppler Velocity flow meter is used for measuring very high and fast moving flows within a four foot pipe. Both flow meters are designed to control an auto sampler.

Automatic samplers capable of complex sampling configurations and stand-alone operations were selected to fill the sampling requirements of IRMNS. LMTAS is presently using ISCO, Inc. Auto Samplers to perform all required sampling. The auto samplers are capable of performing time or flow paced sampling or a combination of the two. The ISCO Auto Samplers are not able to fully interface with the MCU's, but can be "woken up" by a simple impulse from the MCU. Once activated, the sampler can then carry out it's pre-programmed sampling configuration, being paced by the flow meter for flow proportional sampling if desired.

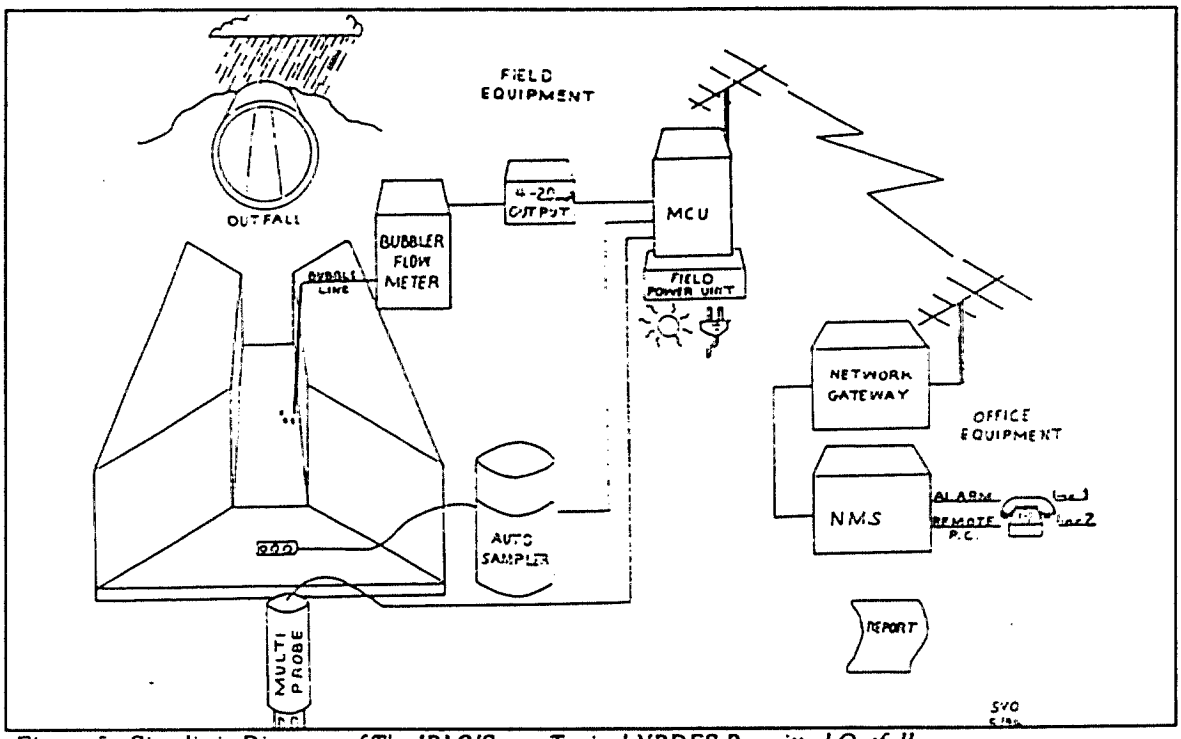

Figure 5. Simplistic Diagram of The IRMNS at a Typical NPDES Permitted Outfall

Implementation

Site selection for field automation was a two phase process. In phase one of the IRMNS project, four of the facility's National Pollution Discharge Elimination System (NPDES) permitted outfalls were selected. These sites are permitted to discharge non-storm water and storm water flows. Phase two of the project picked up one other non-storm water permitted outfall, three NPDES Storm Water Permitted outfalls and the plant's lake water pumping station. All automated sites presently use or will soon have a radio equipped MCU. Sites 2, 3, 6, 8 & 10 (see figure 1.) require solar power operation, with the remaining sites running off of AC power with DC converters. All sites, with the exception of Outfall 6 are using or will soon use multiprobe sensor. All sites are designed to support auto samplers. Each monitoring site has the capability to be configured for limited or more comprehensive monitoring requirements.

The individual field components are either directly hardwired into the MCU or indirectly, using an interface device such as a 4-20 mA converter. In most cases, the equipment can be directly connected to the MCU. Hydrolab Multiprobes use an integrated Serial Digital Interface (SDI) to directly communicate with the MCU. A common Input/Output (I/O) communication protocol used is 4-20 mA signal. Other inputs used to communicate with the MCU's includes: pulse inputs; voltage inputs; RS 232; and resistance.

Other site design features include: using protective enclosures for exposed locations; deep cycle marine storage batteries for the solar powered sites; and wetting devices to keep the sensors wet during dry weather. One of the solar powered monitoring site equipment packages was designed to be portable, allowing for rapid deployment throughout the LMTAS facility. A skid mount design was used, using size and weight restrictions to allow the unit to be lifted by two people into the back of a pick-up truck. The portable unit includes the following items: MCU, Antenna, Auto Sampler and flow meter, solar power unit, and a Multiprobe. Several physical problem have been encountered such as animal tampering with cables and buildings blocking signals. These problems and others have been corrected, only requiring minor system modifications.

Setting Up and Programming the NMS

As illustrated in Figure 1., the system architecture represents a distributed intelligence, node driven network. Each "node" represents a network site where an MCU is deployed. The specific topology of the LMTAS system is comparatively simple. Each MCU, or network node communicates to the Network Gateway. The Network Gateway is connected the NMS through an RS-232 communication channel. Network topology is programmed by the user at the NMS and is downloaded to the network nodes or MCU's. Each MCU is associated with a numerical address. Building a network topology is done by configuring the Network Routs screen within GEONET (GEONET is the user configurable work station software package). One node can be set up to communicate to another node or directly to the Network Gateway.

Once the MCU's and NMS can identify and communicate to one another, programming the field units by completing the appropriate Geonet configuration screens can be started. The approach is to first get communications established between the MCU and the piece of equipment attached to the MCU. Once this is accomplished, the next programming step is to tell the MCU what to do with the signal coming in. For example; a 4-20 mA signal is recognized by the MCU, the signal is then converted (by using a fill-in-the-blank Geonet configuration screen) into a corresponding useable value such as Gallons Per Second. Continuing in a logical manor, subsequent configuration are completed until the final desired configuration is reached. Most programming is easy once the user gets accustomed to working with the software. More complex programming requires a little more experience or even a little customer support. Programming the system to perform some type of task based on pre-determined values monitored by one or more sensors or meter would represent a more complex programming exercise.

The frequency that GEONET evaluates or "wakes up" the sensors is selected by the user. The frequency that the MCU transmits data to the NMS for logging is also determined by the user. Sensors may be evaluated every two minutes, but the minimum, maximum and average values from those sensors can be transmitted to the NMS for viewing or logging once per hour or even once daily. Logging priorities can also be programmed by the user while configuring the various GEONET setup screens. This feature allows unscheduled messages to be transmitted to the NMS. Once the data is stored in the NMS database, it can be exported into another PC database or into a network. At LMTAS, the data is imported into a Microsoft, Inc. ACCESS database, where it can be incorporated into various reports, graphs and spread sheets.

Conclusions

On a piece-by piece basis, monitoring instrumentation technology exists and is easily outfitted. Integrating the components into a complete water quality monitoring system is where skill and experience is essential. Developing a system that can be expanded and modified as monitoring requirements and monitoring technology changes should be a priority. During the early phases of the IRMNS project, integrating a system capable of NPDES monitoring, alarm notification and equipment controlling was not commercially available in it's entirety. Since then, numerous companies have created system developing and integration capabilities targeted at the environmental industry. The "tinker toy", off-the-shelf approach to building computerized remote monitoring systems will allow more facilities to implement their own monitoring system. Developments in the electronics industry have made it possible for manufacturers to design and build intelligent, modular and versatile components.

In developing and implementing the computerized water quality monitoring system at LMTAS, several lessons were learned. With the added monitoring capability IRMNS provides, some of the "snags" encountered did not have obvious fixes. The system simplifies performing multiple, continuos and unattended tasks, but in doing so introduces "behind the scene" complexities. Using IRMNS is easy for the system operator; it is the system administrator that needs to fully understand the system architecture in order to insure that all elements of the system continue to operate as intended. Another area of concern if implementing an automated monitoring is what and how often field data is logged. The language in many of the environmental regulations address continuous monitoring and logging as opposed to "grab" sampling. Whatever is logged into the database may be subject to regulatory reporting or review. This may not be a problem if what the sensors report is actual, but on occasion, a sensor such as a pH probe may drift or break, possibly causing the values to exceed permit limits. In the example, a manual reading to verify the true pH can be obtained and the database's erroneous value be properly documented as a false reading. In any case, it is a good idea to research and address regulatory issues arising out of continuos monitoring and logging system. Has the system meet all of the expected goals? Most, but not all goals have been met. Indications are that the Integrated Remote Monitoring And Notification System will soon be performing all anticipated functions.

Acknowledgments

The author wishes to thank several manufacturers for their technical catalogues and support data. This information was instrumental in communicating specific system components and their operations. Specifically, the catalogues and other information from Geomation, Inc.; Hydrolab, Inc.; ISCO, Inc.; Microsoft, Inc.; Agar, Inc.; EMSI, Inc. were utilized as reference materials and visual aids in this report.

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DEVELOPMENT OF AN ELECTROCHEMICAL WASTE TREATMENT FACILITY

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ABSTRACT

Electrochemical Oxidation can offer a viable alternative to incineration, landfill, and deep well injection for disposal of harmful chemicals. The U.S. Navy generates about one million pounds of Otto Fuel II waste per year. About two thirds of the waste is liquid and one third of it is solid waste contaminated with the fuel. Otto Fuel II is a three component liquid monopropellant used for torpedo propulsion. The Indian Head Division, Naval Surface Warfare Center has been tasked to conduct a feasibility study utilizing an indirect electrochemical oxidation process for the destruction of Otto Fuel II waste, and provide technical and engineering support for construction of a full scale disposal facility at the Naval Undersea Warfare Center, Keyport, WA. Indirect electrochemical oxidation of organic materials is facilitated by using metals ions in a mineral acid electrolyte as a regenerative catalyst or mediator. Silver, cobalt, nickel, cerium, magnesium, and iron have been used as regenerative oxidants[1].

Catalyzed Electrochemical Oxidation (CEO), a low temperature and low pressure electrochemical oxidation process developed by Battelle Pacific Northwest Laboratories (PNL) is being examined for use in the destruction of Otto Fuel II Waste[2,3]. The CEO process uses the regenerative oxidant cerium (Ce^{3+} / Ce^{4+}) for the treatment of organic waste. Laboratory and bench scale studies showed that Otto Fuel II is readily destroyed by the CEO process. Pilot scale CEO studies are planned to determine the operational requirements for a full scale CEO plant to treat Otto Fuel II waste. A summary of this work will be presented in this paper. The primary focus of the paper centers around the establishment of requirements for a full scale CEO facility.

INTRODUCTION

Otto Fuel II is a non-corrosive liquid monopropellant used in underwater torpedo propulsion systems. The fuel is composed of three ingredients: a) the nitrate ester, propylene glycol dinitrate (PGDN, 76 $\pm$ 0.2%); b) the diluent, di-n-butyl sebacate (DBS, 22.5 $\pm$ 0.3%; c) the stabilizer, 2-nitrodiphenylamine (2NDPA, 1.5 + 0.1 %). Traditionally, incineration, landfill, and deep well injection have been the methods of first resort for the disposal of hazardous and toxic waste[4].

About one million pounds of Otto Fuel II waste (2/3 liquid and 1/3 solid) is generated each year. The Otto Fuel II waste is generated in a variety of ways, torpedo maintenance is required after various Fleet and propulsion testing. Torpedoes which are "spent" or expired shelf - life torpedoes also require refurbishment. These activities generate a wide range of liquid and solid waste; denatured alcohol, engine oil, lubricant oil, isopropyl alcohol, rubber and plastic gloves, cotton wipes, preservation oil, etc.

The Catalyzed Electrochemical Oxidation (CEO) process has been evaluated as an alternative to deep well injection and landfill for the disposal of Otto Fuel II waste.

STATE-OF-THE-ART: CEO/MEO PROCESS

Electrochemical processes are being developed throughout the world for the near ambient temperature and pressure destruction of hazardous waste using indirect electrochemical oxidation in an aqueous solution containing HNO_3 or H_2SO_4. An oxidizing agent generated by anolyte oxidation, reacts with organics to produce CO_2 and water[1-3]. For organic materials containing heteroatoms such as Cl, N, P, S, and metal, hydrochloric, nitric, phosphoric, and sulfuric acids and cations respectively are produced[2,6-8,10] Cobalt, nickel, cerium, magnesium, and iron have been used as regenerative oxidants: Co (II)[11], Ni (III)[2], Ce (III)[2], Mn (II)[1], and Fe (II)[12]. Shown in Table 1 are metallic redox system parameters with performing organizations[13-14].

Table 1. Metallic Redox Systems, Oxidation-Reduction Potentials (E°) and Research Laboratories

Mediators	Volt E° Value In Acidic Media	Research Activity[(a)]				
Ag^{+}/Ag^{2+}	1.98	PNL	AEA	SRL	LLNL	–
Co^{2+}/Co^{3+}	1.82	PNL	–	SRL	LLNL	–
Ni^{2+}/Ni^{3+}	1.68	PNL	–	–	–	CCC
Ce^{3+}/Ce^{4+}	1.61	PNL	–	–	–	–
Mn^{2+}/Mn^{3+}	1.51	–	–	–	–	–
Fe^{2+}/Fe^{3+}	0.77	–	–	–	LLNL	CCC

[(a)] Battelle Pacific Northwest Laboratories (PNL), United Kingdom Atomic Energy Authority (AEA), Savannah River Laboratory, Lawrence Livermore National Laboratory (LLNL), Chevron Chemical Co. (CCC)

SILVER (II) - BASED PROCESS IN HNO_3

Silver is an exceptionally powerful oxidant, Ag I / Ag II with a potential of +1.92V in nitric acid. This patented process was developed by United Kingdom Atomic Energy Authority (AEA) and has been used for the treatment of mixed hazardous waste in a pilot plant unit. Their pilot-plant facility treated aromatic and aliphalic hydrocarbons, hydraulic fluid, lubricating oil, cellulose, rubber gloves, polyurethane, epoxy and ion-exchange resins. The AEA process was also used to destroy Otto Fuel II waste.

The obvious problem with the Ag I / Ag II process is precipitation of silver as a halide salt by anions liberated during the destruction of halogenated organics. Otto Fuel II contains 4 elements, carbon, hydrogen, oxygen, and nitrogen. Hence, the only possible source of halide ions would be from Otto Fuel II contaminated with seawater.

CERIUM AND COBALT MEDIATOR PROCESSES

The electrochemical oxidation processes which use cerium and cobalt as the catalyst are being commercialized by EO Systems of San Jose, CA under a license from PNL and Lawrence Livermore National Laboratory (LLNL) respectively. Cerium and cobalt has a series of unique advantages over other potential mediators. Cerium resembles aluminum in its pharmacological action as well as in its chemical properties. The insoluble salts of cerium, such as the oxalate, are stated to be non-toxic even in large doses. It is used to prevent vomiting in pregnancy. Both cerium and cobalt are halide-tolerant, these salts do not precipitate from nitric solutions. The cobalt mediated process has a number of unique advantages, it can be used with either nitric acid or sulfuric acid serving as the electrolyte. In addition to eliminating the problem of mediator precipitation, this process chemistry also eliminates the need for an electrode separator. Gaseous H_2 is evolved at the cathode, so there is no deposition of metallic cobalt. Furthermore, Co (III) reacts with dissolved organics in close proximity to the anode, so it never reaches the cathode. If it did, it would be reduced.

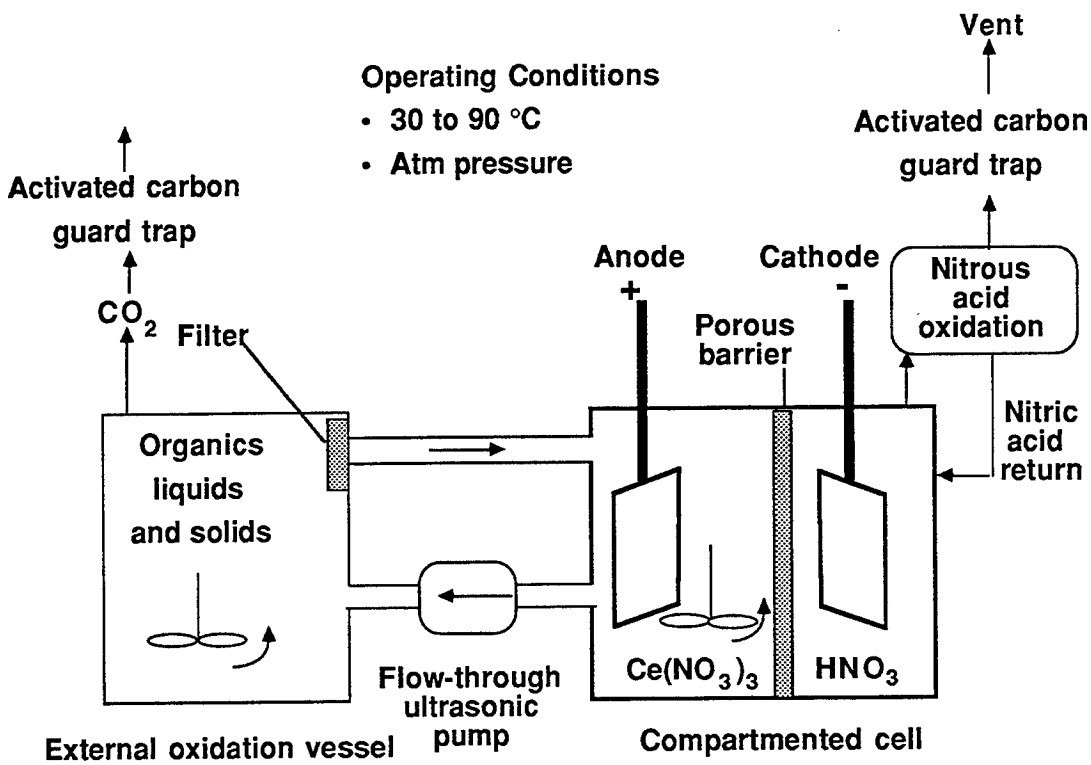
IRON-BASED AND OTHER PROCESSES

Fe (III) is an attractive mediator due to its non-toxicity. This process was developed by Chevron Chemical Co. (Richmond, CA). Because it requires a high operation temperature 150-180°C, a pressure cell is used[12]. The major advantage of the Fe (III) based process is that it can be used to destroy high thermally stable materials: chlorinated aromatic hydrocarbons, polychlorinated biphenyls waste, mineral, and silicone oils. However, this system probably would not be appropriate for Otto Fuel II because of the high temperature used. Nickel and magnesium also has a low toxicity, but very little research on these mediators have been done.

PROCESS CHEMISTRY

Two electrochemical processes have been used to destroy Otto Fuel II. Battelle Pacific Northwest Laboratory conducted Otto Fuel II catalyzed electrochemistry oxidation destruction test exclusively using cerium as the catalyst. A detailed report on PNL's Otto Fuel II waste treatment studies will be published in October 1996. A summary of the AEA's successful laboratory destruction of Otto Fuel II and 67 toxic organic compounds using Silver as the mediator was reported in the literature[14]. AEA plans to build a transportable pilot plant based on the Silver process. A simplified diagram of the cerium process is shown in Figure 1.

Figure 1. Simplified MEO Support



Cerium in the plus 4 state generated by the anodic oxidation of Ce^{3+} is reduced by reactions with water and Otto Fuel II. The reaction of Ce and PGDN is represented as follows.

$$CH_3 - \underset{|}{\overset{O_2NO}{CH}} - \underset{|}{\overset{ONO_2}{CH_2}} + 6\,H_2O \xrightarrow{Ce^{3+}/Ce^{4+}} 2\,HNO_3 + 3\,CO_2 + 16\,H^+ + 16\,e^-$$

PGDN oxidation products are nitric acid, carbon dioxide, and water. Hydrogen ions migrate through the electrode separator membrane to produce water at the cathode. The solubility's at 25°C of Otto Fuel II, PGDN, DBS, and diphenylamine (DPA) in water are 3,100, ~ 3,000, 400 and 300 ppm respectively. DPA is reported because there is no data on 2-nitrodiphenylamine (2NDPA) solubility in water reported in the literature. Shown in Table 1 are products of oxidation for materials containing various elements.

Table 1. Anode Electrochemical Oxidation Reactions

Components	Products	Process
Hydrocarbons	$CO_2 + H_2O$	Vented/distilled
Chlorine	HCl	Acid recycle
Sulfur	Sulfuric Acid	Acid Recycle
Nitrogen	Nitric Acid	Reused In System
Phosphorus	Phosphoric Acid	Acid Recycle
Metals	Metallic Cations and Oxides	Recovered
Spent Ce Catalyst	Non RCRA	Cerium Reprocessed

CATHODIC PROCESSES

The use of electrochemical reduction processes in the environmental arena is almost exclusively limited to the recovery of metals. The electrochemical reduction of organic materials is limited by the fact that the process does not completely destroy organics. The reduction of nitric acid esters yield nitrous acid and the parent alcohols, propylene glycol as illustrated by PGDN below:

$$CH_3 - \overset{ONO_2}{\underset{|}{CH}} - \overset{ONO_2}{\underset{|}{CH_2}} \xrightarrow[(2)\,4H^+]{(1)\,4e^-} CH_3 - \overset{OH}{\underset{|}{CH}} - \overset{OH}{\underset{|}{CH_2}} + 2\,HNO_2$$

The MEO cell catholyte is 8M HNO_3 and the anolyte is 4M HNO_3, resulting in a concentration gradient. The principal cathode reaction is the reduction of nitric acid to nitrous acid as shown below.

$$HNO_3 + 2\,H^+ + 2e^- \longrightarrow HNO_2 + H_2O$$

The nitrous acid at the cathode can be regenerated simply by contacting it with air in a scrubber, so that there are no cathodic off-gas products. The overall reaction is noted below.

$$2\,HNO_2 + O_2 \longrightarrow 2\,HNO_3$$

The treatment of organics using the MEO process does not lead to oxides of nitrogen (NO_x) emissions into the environment.

EXPERIMENTAL SECTION (MATERIAL AND METHODS)

The chemicals used were reagent grade. The Otto Fuel II used was Mil. Spec. grade obtained from the Naval Undersea Warfare Center, Keyport, WA.

The experiments were conducted using ICI Chemicals and Polymers Ltd FM-01 flow through electrochemical cell. Platinum-coated titanium was the material of construction for both the anode and the cathode in the cell. The surface area of the cell was 64 cm^2. The electrolyte, nitric acid was 4M at the anode and 8M (175 mL) at the cathode. Test solutions were pumped through the cell at a rate of 250-275 mL / min. A DuPont Nafion 124 fluoropolymer membrane was used as the cell separator.

To 175 mL (262.2 g) of solution 1.5M in Ce $(NO_2)_3$ and 4M HNO_3 was added 11.2 mL (13.8 g) of Otto Fuel II. The mixture, with 5 % by weight Otto Fuel II was heated to 75 °C in a vessel equipped with a pump. The electric potential necessary (4.5 to 5.0 volts) to generate sufficient current in the cell, 22.4 amps, which is equivalent to 3500 amps / m^2. The 5 wt % Otto Fuel II test solution was pumped through the electrochemical cell for 3 hours with power at 4V and 22.5 amps. A 1 mL anolyte sample was taken every 15 minutes during the test. On analysis of the samples by HPLC, no organics were found after 15 minutes of testing.

Otto Fuel II destruction test was conducted using anolyte solutions of 1 wt %, 5 wt %, 10 wt %, and 20 wt %. Only the 20 wt % sample showed evidence of immiscibility in the 70°C anolyte solution. For 20 wt % Otto Fuel II, only 3.5 amps at 12.5V was obtained versus 22.5 at 4V for the 5 wt % solution. PGDN in all samples was destroyed in two hours with the exception of the one 20 wt % Otto Fuel II.

For the aforementioned test with 20 wt % Otto Fuel II, the solution was processed through the cell for two hours, during which an average current and voltage of about 3.5 amps and 12.5 colts was used. Although CO_2 was evolving from the anolyte chamber, the rate of Otto Fuel II destruction was too low at this concentration, and testing was suspended.

DISCUSSION AND RECOMMENDATIONS

Naval Undersea Warfare Center (NUWC), Keyport, WA is responsible for Otto Fuel II disposal world wide. Otto Fuel II is shipped from various Navy installations to NUWC for disposal. Wastes, including liquids from cleaning or spills or liquids otherwise contaminated with Otto Fuel II. Additionally, 30-40 torpedoes per month require disassembly, cleaning, reassembly and reproofing. Shown in Figure 2 is a diagram of the Otto Fuel II recycle and reclamation systems.

The wastewater separated from reclamation of Otto Fuel II contains about 2,000 ppm of PGDN contaminate. The wastewater is treated with activated carbon to reduce the PGDN levels. The PGDN contamination ranges between 1,800 to 2,200 ppm; the treatment process reduces the level to below 0.75 ppm. The spent carbon waste is disposed of as spent carbon from the treatment of wastewater containing explosives, EPA Hazardous Waste Number K045. Figure 3 is a diagram of the activated carbon treatment process for Otto Fuel II wastewater.

Figure 2. Otto Fuel II Life Cycle Reclamation and Waste Management Systems

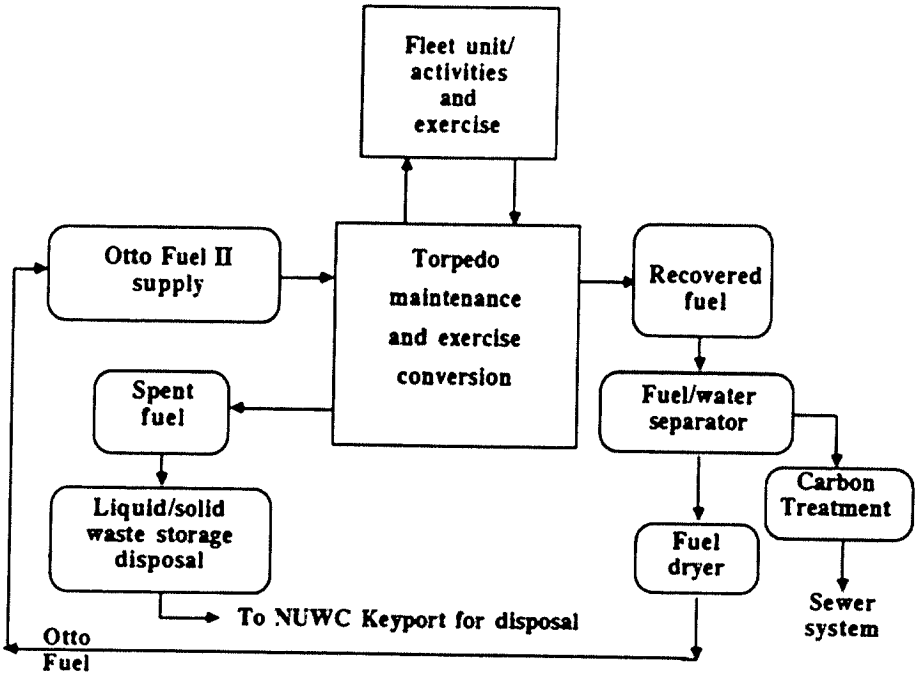
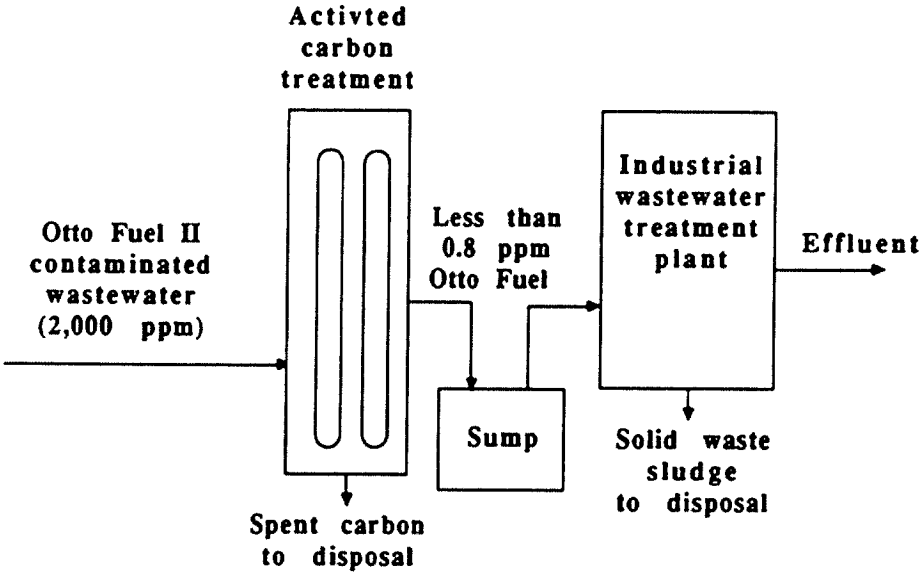


Figure 3. Keyport's Otto Fuel II Waste Water Process



Otto Fuel II has been used for more than 30 years for the propulsion system of torpedoes. Although the environmental requirements and regulations are different today than they were 30 years ago, a continuous effort has been made by NUWC to improve their Otto Fuel II utilization, recycling, and disposal practices. Specific recommendations based on this study are:

- Continue to pursue alternative destruction methods for hazardous wastes: mediated electrochemical oxidation is recommended for treatment of Otto Fuel II wastes.

- Mediated electrochemical oxidation treatment of Otto Fuel II should be a supplement to NUWC's present Otto Fuel reclamation and recycle process.

- Otto Fuel II contaminated seawater should continue to be treated with activated carbon.

- It is recommended that the MEO process be used to regenerate the spent activated carbon laden with PGDN used for wastewater treatment.

- An advanced aqueous cleaning procedures could be used to remove Otto Fuel II from all the contaminated solid waste. The solids can then be disposed of as trash, and the aqueous solutions contaminated with Otto Fuel II can be run through activated carbon.

CONCLUSION

It has been demonstrated that Otto Fuel II liquid waste and solid waste contaminated with Otto Fuel II can be destroyed using electrochemical oxidation. Virtually all types of organic waste has been successfully destroyed on the laboratory and pilot plant level. The waste includes: diesel fuel, motor and lubricant oils, aromatic and aliphatic hydrocarbons, various types rubber, plastics, resins, cheese cloth, and Kim Wipes.

CEO or MEO treatment of waste is a potentially valuable process and should be developed further.

ACKNOWLEDGMENTS

The financial support and the technical advice provided by John Dow of the Naval Surface Warfare Center, Indian Head, Maryland is gratefully acknowledged. We thank Gautam Pillay and his colleagues at Pacific Northwest Laboratory Richland, Washington for conducting most of the electrochemistry experiments on OTTO Fuel II destruction (mineralization).

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MINIMIZATION OF CYANIDE WASTE: REJUVENATION of SILVER CYANIDE PLATING BATH

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Summary

The LMMS Sunnyvale Facility has been generating about 1000 lb. of cyanide laden waste solution each year. The waste is a result of having to dispose of silver cyanide plating bath due to carbonate build up. In this presentation we will report on a method that we evaluated and used to rejuvenate a Silver Cyanide Plating bath. The method we used is too added Barium Hydroxide to the plating bath which selectively removes the carbonate as Barium Carbonate. The implementation of this rejuvenation has enabled us to:

Minimize the cyanide waste
Improve the process control
Save a significant amount of silver

All these have resulted in a considerable cost savings to the company.

INTRODUCTION

Beginning 1989, due to the California Hazardous Waste Source Reduction and Management Review, commonly known as Senate Bill (SB 14) , all California businesses that generate waste are required to conduct a waste source analysis. The waste streams were analyzed at two levels:

Hazardous Waste (HW)
Extremely Hazardous Waste (EH)

If a business generates more that 24,400 lb (12,000 kg) of HW or 26.4 lb (12 kg) of EH, the company is required to evaluate and implement cost effective ways to reduce the waste stream at the source. The review and planning process repeats ever four years.

In 1995, Lockheed Martin Missiles and Space (LMMS) has identified that the Sunnyvale facility, generated about 1,000 lb of cyanide waste, which is classified as EH, thus requiring the actions described above.

This presentation will discuss our effort in eliminating this waste stream.

BACKGROUND

Waste Stream Analysis. The LMMS production facility has been using two silver cyanide baths for the production of molybdenum solar cell interconnects. Table 1 shows the controlling parameters for the cyanide plating baths.

Table 1 Control Parameters for the Silver Cyanide Plating Baths

Parameters	**Concentration g/L**
Silver	30 - 45
Free KCN	120 - 135
K2CO3	22.5 - 75

The control of this bath is relatively straight forward, with the exception of potassium carbonate. Figure 1 shows a trend chart on the build-up of K_2CO_3 in the process solution. Addition of potassium carbonate to the silver cyanide plating solution during the initial make-up is a standard practice. The purpose is to enhance conductance of the plating solution in order to produce good silver deposits. If the concentration of potassium carbonate gets too high (>120 g/L), the deposits can become dull or rough[1]. For this reason, the bath has to be replaced as carbonate build up over time.

There are two sources that cause the build-up of carbonate in the solution (see Figure 2):

- Absorption of carbon dioxide from the air

- Oxidation of Cyanide during electroplating[2]

To minimize the cyanide laden hazardous waste, it was decided that a rejuvenation method is needed.

There are three methods suggested by the literature to remove the carbonate from the plating solution to extend the bath life:

Freezing
Barium cyanide treatment
Barium hydroxide treatment

The first method is to freeze-out the carbonate salt by chilling the solution to 0°C. This method will not work for LMMS's silver cyanide baths that use potassium salts, because K_2CO_3 is extremely soluble in water. Its solubility in water is about 1050 g/L at 0°C[3], far exceeded the 75 g/L maximum concentration limit that LMMS used to control the bath.

The second method is to add barium cyanide[4] to a carbonated silver plating solution to precipitate the carbonate as barium carbonate:

$$Ba(CN)_2 + CO_3^{=} = BaCO_3 + CN^-$$

This could be an ideal method for two reasons:

It removes the carbonate ion as solid barium carbonate.
It replenishes the cyanide lost during the plating operation.

The problem with this method is that by using Energy Dispersion Spectroscopy (see Figure 3) and a titrimetric method a high level of chloride (30%) was found in the commercial grade barium cyanide. A high chloride concentration in solution will produce a deposit having an undesirable iridescent appearance[5]. Thus far we were unable to find a supplier to provide us a chloride free BaCN salt.

The third method is to add barium hydroxide[3] to a carbonated silver plating solution to precipitate the carbonate as barium carbonate:

$$Ba(OH)_2 + CO_3^{=} = BaCO_3 + OH^-$$

Although this method will remove carbonate as barium carbonate, there were several concerns that needed to be addressed:

I: After each treatment, an increase of hydroxide concentration in solution is anticipated. The question is what impact will the increase in hydroxide ion have to the quality of plated silver?
II: How effective is barium hydroxide in removing carbonate?
III: Will there be barium ions left in the solution after treatment, and will the residual barium be included into the plated silver?

MATERIALS, EQUIPMENT AND PROCEDURES

Anode

Pure Silver bars wrapped with anode bags were used as the anodes for plating the test articles

Cathode

Two types of cathodes were used for the silver plating

- Stainless steel (S/S) panels (4 in x 4 in) were used for extended plating to test the stability of the bath
- Gold plated molybdenum foils were also used. These foils were prepared by using a 1 mil thick molybdenum (moly) foil plated two times with gold and fused in a hydrogen furnace between the successive platings, than followed by a final gold plate. A 1 inch plating tape was used to mask off the edges of the 4 in x 4 in moly. panel. This leaves a 2 in x 2 in area in the middle of the panel for plating. All the moly. panels were hand wiped with acetone to remove contaminants before plating

Plating Cell

Figure 4 shows the 2 liter plating cell that was used for this study. The cell has two side slots that hold the silver anodes, and one middle slot for the cathode. Nitrogen gas was bubbled through the solution to keep the carbon dioxide out during plating. This will minimize the build-up of carbonate in the solution. A rectifier made by Kookier Co., model 15A was used as the power source for plating.

Solution

A 20 gallon silver cyanide solution was obtained from the Moly. Interconnect Facility. De-ionized water was added to adjust the concentration K_2CO_3 to about 70 g/L. KCN was than added to the solution so that the mole ratio of free CN^- to Ag is 6.4. Concentrations of Ag, K_2CO_3 and KCN were determined by titrimetric methods[6]

Known weights of solid KOH were to added to the silver cyanide solution and the concentrations of KOH were verified by titrimetric method.

Plating Procedure

1. Filter about 2.2 L of silver cyanide solution with Whitman #42 filter paper
2. Deliver 2 L of filtered silver cyanide solution to the plating cell
3. Retain 100 ml sample for chemical analysis
4. Wrap the silver anode with anode bags and place them into the two side slots of the plating cell
5. Place the 4 in x4 in stainless steel panel into the middle slot
6. Bubble a small stream of nitrogen gas continuously through the solution
7. Apply a current of 2 amp. (9.1 amp/ft^2) to plate the silver onto the S/S panel for 4 hours
8. Replace the S/S panel with masked molybdenum panel
9. Apply a current of 0.5 amp (9 amp/ft^2) to plate the silver onto the moly. panel for 30 minutes
10. The plated panel was than rinsed several times with de-ionized water and dried with nitrogen gas
11. Wrap the plated panel with silver saving paper and submit them for certification tests
12. Retained a 100 ml sample of the post silver cyanide solution for chemical analysis.

Removal of carbonate by $Ba(OH)_2 \cdot 8H_2O$

Method 1

1. Suspend 2 g of $Ba(OH)_2 \cdot 8H_2O$ into 2 ml of de-ionized water at room temperature
2. Add 20 ml of silver cyanide solution to the suspension
3. Let the solution sit at room temperature for 1 hour
4. Filter out the white precipitate with a Whatman #42 filter paper
5. Analyze the clear solution for Ag, KCN, and K_2CO_3 concentrations

Method 2

1. Suspend 2 g of $Ba(OH)_2 \cdot 8H_2O$ into 2ml of de-ionized water
2. Heat the solution to near boiling temperature (95°C)
3. Add 20 ml of silver cyanide solution to the heated solution
4. Cool the solution to room temperature
5. Filter out the white precipitate with a Whatman #42 filter paper
6. Analyze the clear solution for Ag, KCN, and K_2CO_3 concentrations

Method 3

1. Heat 1 L of silver cyanide solution to 90°C
2. Add about 150 g of $Ba(OH)_2 \cdot 8H_2O$ to the heated solution
3. Let the solution stand at 95°C with stirring for 1 hour
4. Cool the solution to room temperature
5. Filter out the white precipitate with a Whatman #42 filter paper
6. Analyze the filtered solution for Ag, KCN, and K_2CO_3 concentrations

Determination of barium in silver cyanide plate

A small piece molybdenum interconnect was treated with 1:1 H2O:HNO3 to strip off the Silver. The solution was than analyzed by Inductive Coupled Plasma (ICP) Spectrophotometer.

RESULTS AND DISCUSSION

Stability of the silver cyanide solution. Table 1 shows the process control limits of the silver cyanide bath.

In the study the free cyanide to Ag ratio was maintained at 6.5 (see table 2). Also, a stream of nitrogen gas was bubbled through the solution during plating to inhibit the absorption of carbon dioxide from the air. When the plating was done under these conditions for 4 hours, the potassium carbonate and potassium cyanide concentrations remained constant. So by maintaining the Free cyanide to silver ratio at about 6.5 it was possible to retard the decomposition of cyanide[7].

Plating at Variable OH^-. Samples of silver plated panels were prepared by plating the moly. panels at a different concentration of OH^-. The panels were put to the following tests:

- Thickness
- Plating adhesion
- Ductility
- Solderability
- Scanning Electron Microscope (SEM) analysis (Plate I, II, and III)

All the above tests performed on the test panels passed the test criteria (see Table 2). SEM data shows that there is no change in the surface morphology. When the OH^-

Table 2 Silver Cyanide solutions used for Silver Plating

	Ag(g/L)		K2CO3(g/L)		KCN(g/L)		KOH(g/L)		Thickness(in)	Ductility	Adhesion	Solder-ability
SAMPLE #	Pre-plate	Post-plate	Pre-plate	Post-plate	Pre-plate	Post-plate	Pre-plate	Post-plate				
11/30/95	33.1	33.7	70.2	71.4	129	129	0.84	3.19	0.0004	P	P	P
10/31/95	33.5	34.2	72.7	74.2	131	132	28.3	28.3	0.0003	P	P	P
11/1/95	32.8	32.6	71	71.7	128	130	40.9	40.7	0.0003	P	P	P
11/2/95	31	30.9	66.7	68.6	120	120	62.3	62.3	0.0004	P	P	P
11/8/95	31.9	32.3	70.8	72.4	129	126	95.1	95.5	0.0004	P	P	P
11/9/95	31.6	32.2	69.8	70.6	122	125	113.5	113.1	0.0004	P	P	P
11/20/95*	32.4		40		119				0.0004	P	P	P

* [Ba2+]= 240 ppm

concentration reaches at about 113 g/L, it began to 'eat' away the plating bag. For this reason, 95g/L of KOH can be considered as the upper control limit for KOH.

Barium Hydroxide treatment. The carbonate in the silver cyanide solution can be selectively removed by precipitation and filtration after adding $Ba(OH)_2$:

$$Ba(OH)_2 + CO_3^{=} = BaCO_3 + 2OH^-$$

Three methods (1, 2 and 3) of mixing Ba(OH)2 and silver cyanide solution were tried. The findings were:

- Methods 2 and 3 gave better than 90% efficiency in removing carbonate from the solution(see Table 3). The reason is that the solubility of $Ba(OH)_2$ in water is greatly enhanced at elevated temperature (3.9 g/100 ml @ 20°C , 101 g/100 ml @ 80°C) [1]
- pH of the silver solution tends to increase after the Ba(OH)2 treatment, and is due to the release of hydroxide ion from the $Ba(OH)_2$.
- The concentration of Ba^{2+} in silver solution after Ba(OH)2 treatment is 240 ppm (see sample 11/20/95, Table 2)
- There is no elemental barium in the silver metal plated from the $Ba(OH)_2$ treated solution

Table3 Efficiency of carbonate removal

Method	Parameters	Before	Expected	Actual	% Efficiency
I					
	Ag	40.5	36.8	36.4	
	KCN	130.0	118.0	115.0	
	K2CO3	81.2	31.5	58.6	
	Wt.of K2CO3 removed		49.7	22.6	45
	pH	12.3		13.6	
II					
	Ag	40.5	36.8	36.2	
	KCN	130.0	118.0	116.0	
	K2CO3	81.2	30.2	29.0	
	Wt.of K2CO3 removed		51.0	52.2	102
	pH	12.3		14.0	
III					
	Ag	33.0	33.0	31.7	
	KCN	128.0	128.0	109.0	
	K2CO3	69.7	4.7	10.3	
	Wt.of K2CO3 removed		65.0	59.4	91
Note : All units are in g/L					

Cost Analysis

Table 4 shows a simple cost calculation comparing the conventional use & dispose method against the rejuvenation method:

Table 4 A Simple Cost Analysis on the Rejuvenation of Silver Cyanide Bath

	Use & Dispose	**Rejuv.**
Disposal (8 gallons)	$70	
KAgCN($201/lb)	$522	
KCN ($9/lb)	$59	
Ba(OH)2* 8H2O($12/lb)		$125
Labor (push)		
Estimated material	$651 -	$125= $526

Note: We have two 16 gallons silver cyanide baths. When the carbonate concentration reaches the upper control limit, we replace half the bath (8 gallons) with fresh solutions.

From this calculation we estimated that the rejuvenation method saves about $6,000 per year mostly from the materials costs.

CONCLUSION

In this study we concluded the following:

- Silver cyanide solution can be rejuvenated by using $Ba(OH)_2*8H_20$
- When the ratio Free-CN to Ag (M/M) is kept at 6.5 or higher, we can retard the decomposition of the CN^- during plating
- Hydroxide ion concentration up to 95g/L should have no impact on the quality the silver plated

This treatment procedure are now being implemented in LMMS's plating facility, and has eliminated the cyanide laden waste stream.

[1] Metal Finishing Guidebook & Directory , L. Greenspan, p 288, 1975

[2] 71st AES Annual Technical Conference Proceedings, NY, NY, H. F. Edward, p1984

[3] Lang's Handbook of Chemistry. John A. Dean, K2CO3 p5.17, Ba(OH)2 p5.11, 1992

[4] Metal Finishing, 'Silver Plating Baths, Mohler, J.B. p35, 1986

[5] Metal Finishing, Guidebook & Directory Issue '87. Silver Plating, Carriero, W.G. p304, 1987

[6] Titrimetrice methods

Determination of carbonate concentration in silver cyanide solution, Electroplating Engineering Handbook, 4th Edition, p302, method 11.

Determination of cyanide concentration in silver cyanide solution, skkog and Wset, Analytical Chemistry, 1976.

Determination of hydroxide concentration in silver cyanide solution, Electroplating Engineering Handbook, Reinhold Pub., Co.

Determination of silver in silver cyanide solution, Hillebrand, Lundell, Bright, and Hoffman, Applied Inorganic Analysis, 2nd Edition , John Wiley & Son Inc., N.Y. 1953

[7] Dingley W., Bednar, J., and Rogers, R.R. , " Improved Silver Cyanide Plating Baths: Laboratory Development', Plating, p1129, 1969

Figure 1 Trend Chart on the build-up of K2CO3 (g/L)

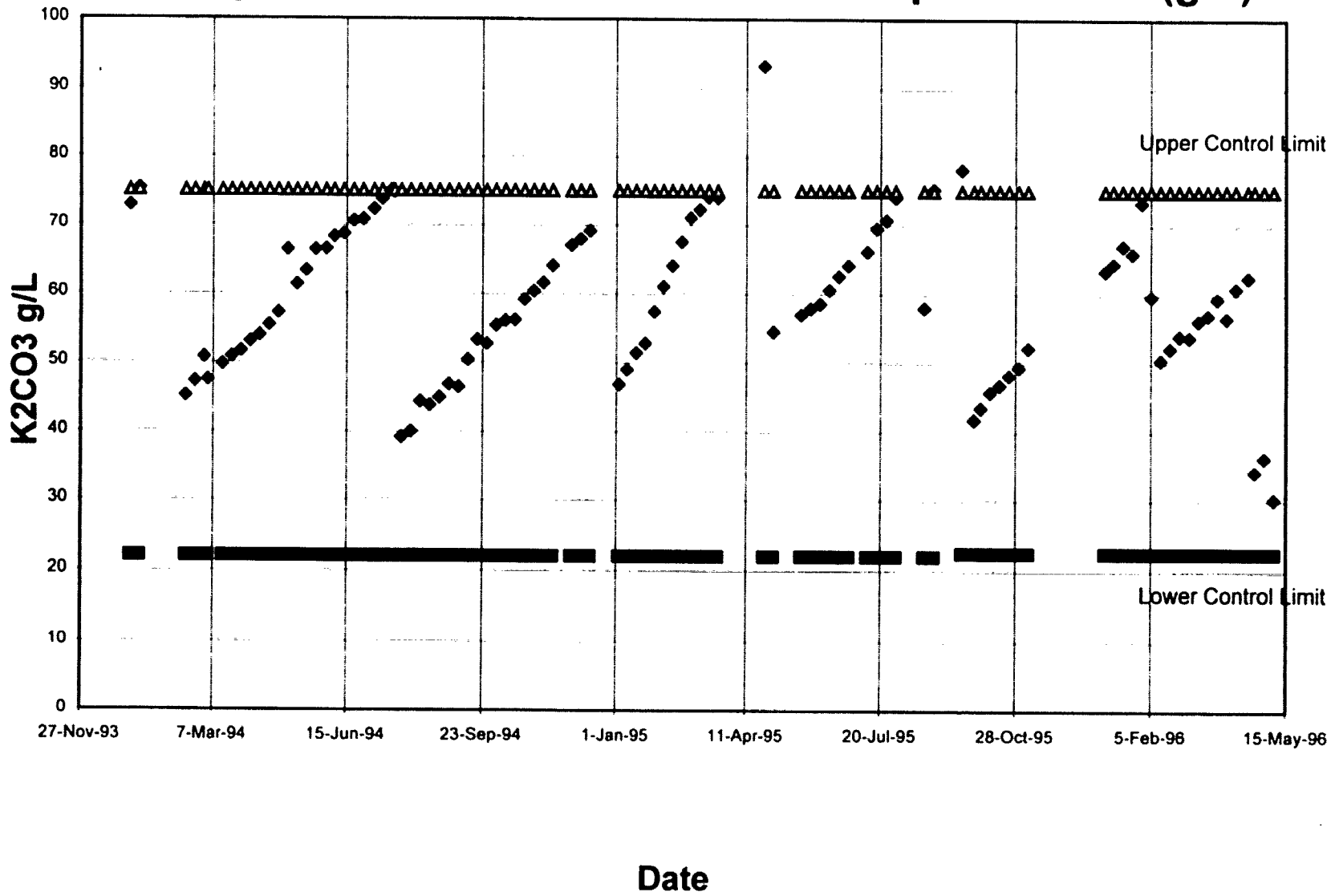


Figure 2 Waste Stream Analysis

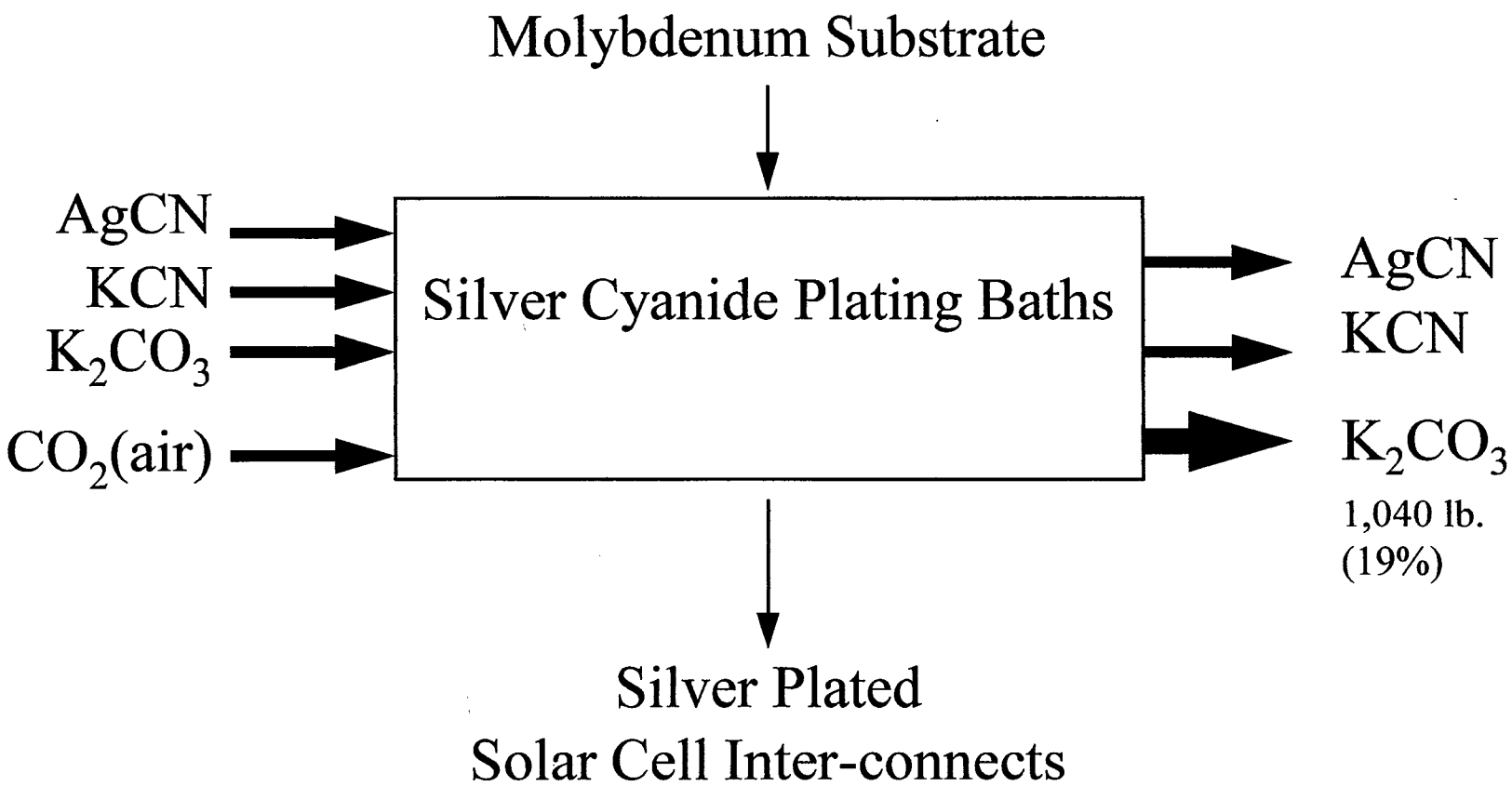


Figure 3 Energy Dispersion Spectrophotometric of BaCN Contaminated by Chloride ion

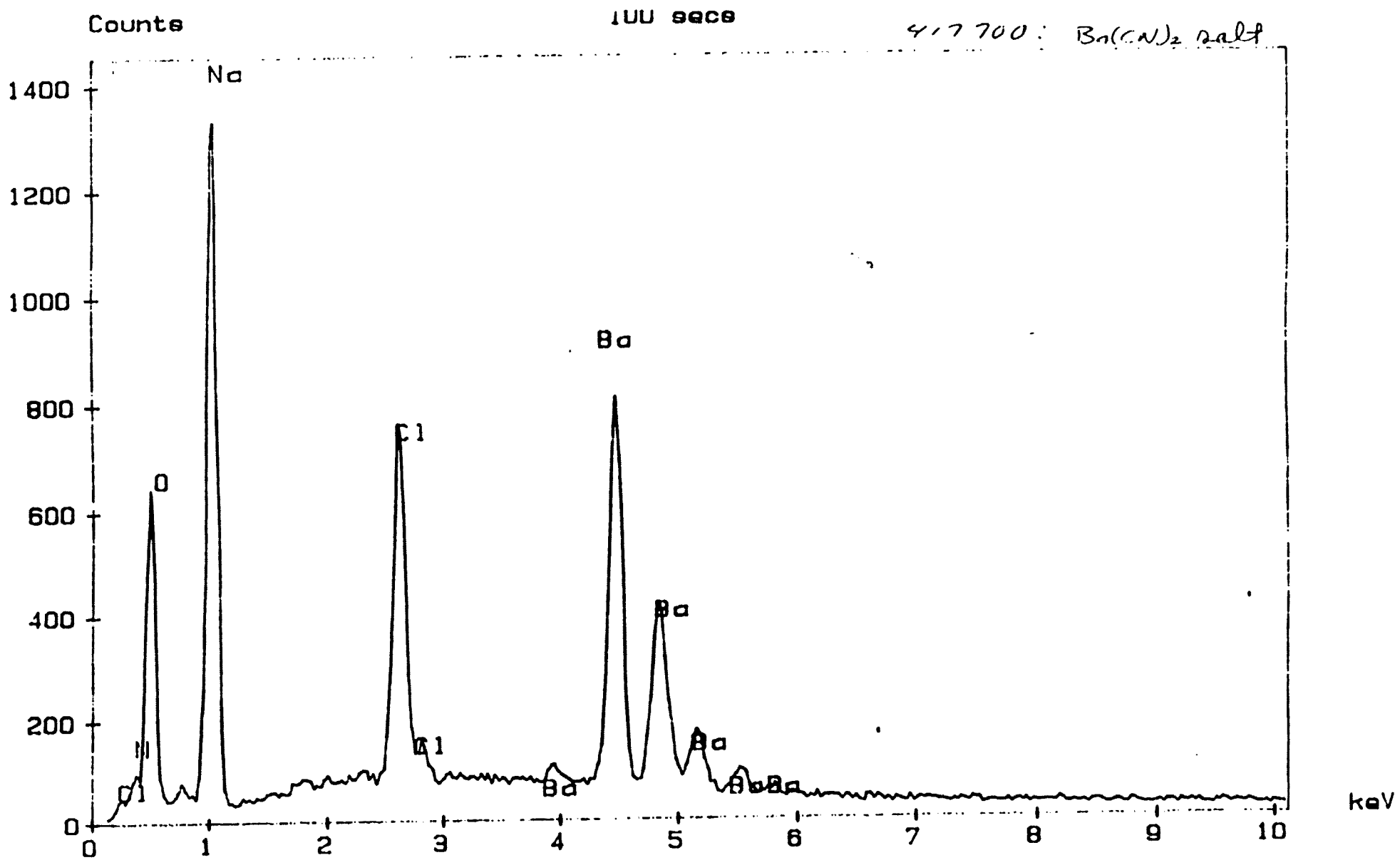
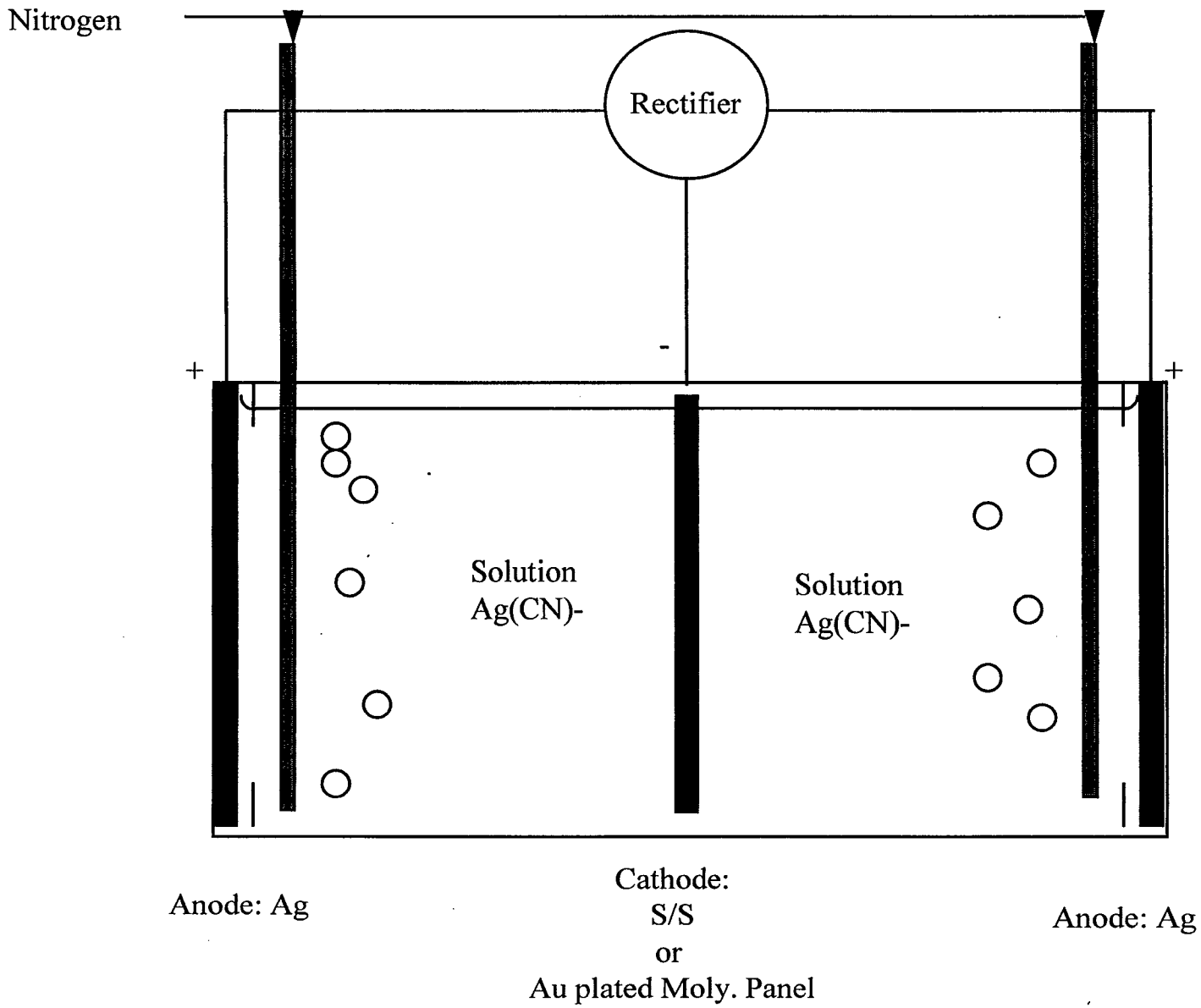


Figure 4 Test Cell for the Electrolysis of Silver Cyanide Plating



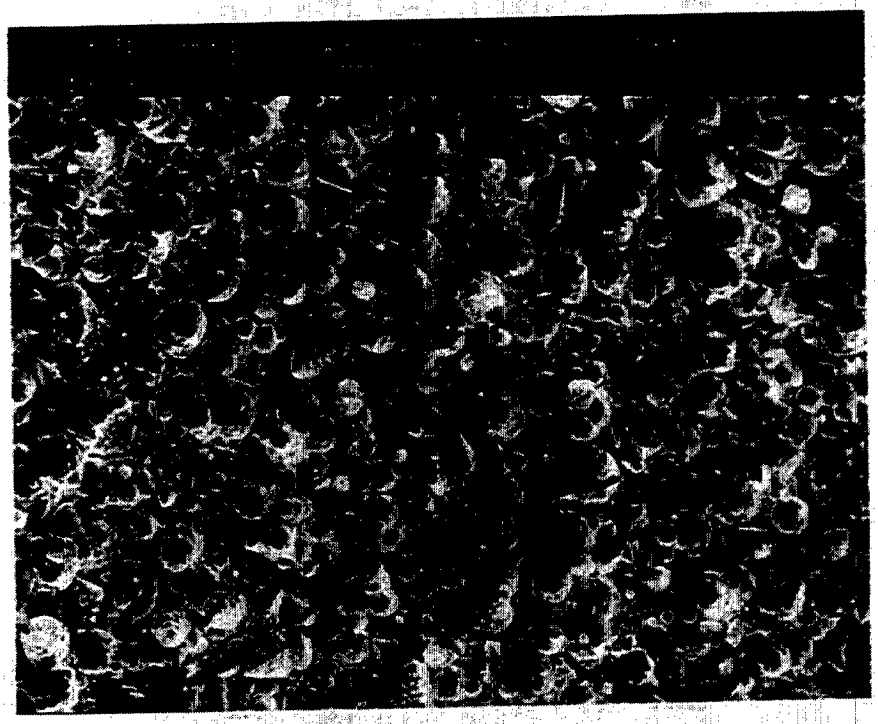


Plate I SEM of Plated Silver (Sample # 10-30-95)

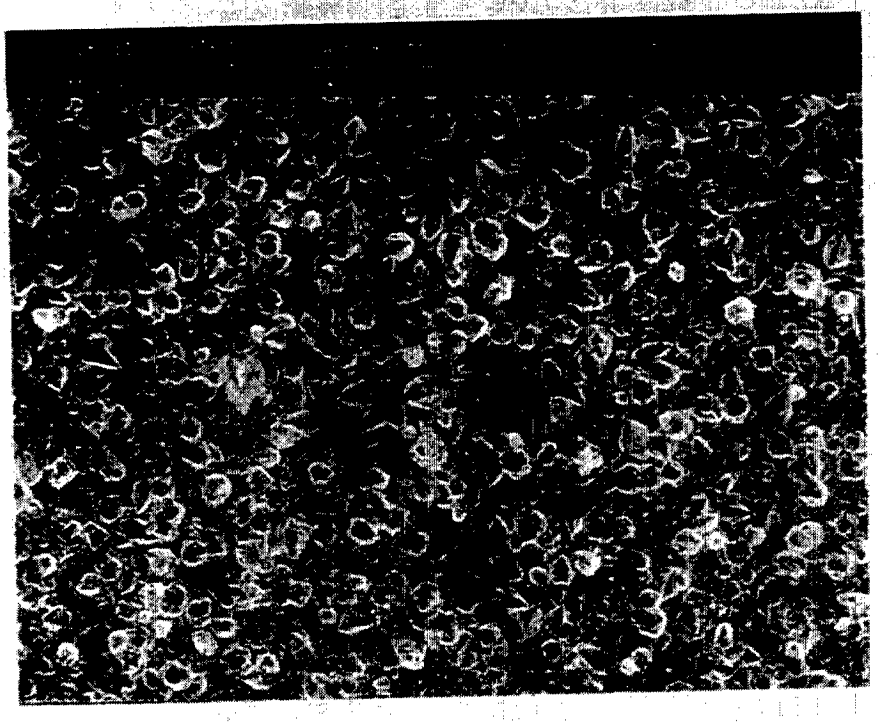


Plate II SEM of Plated Silver (Sample # 11-2-95)

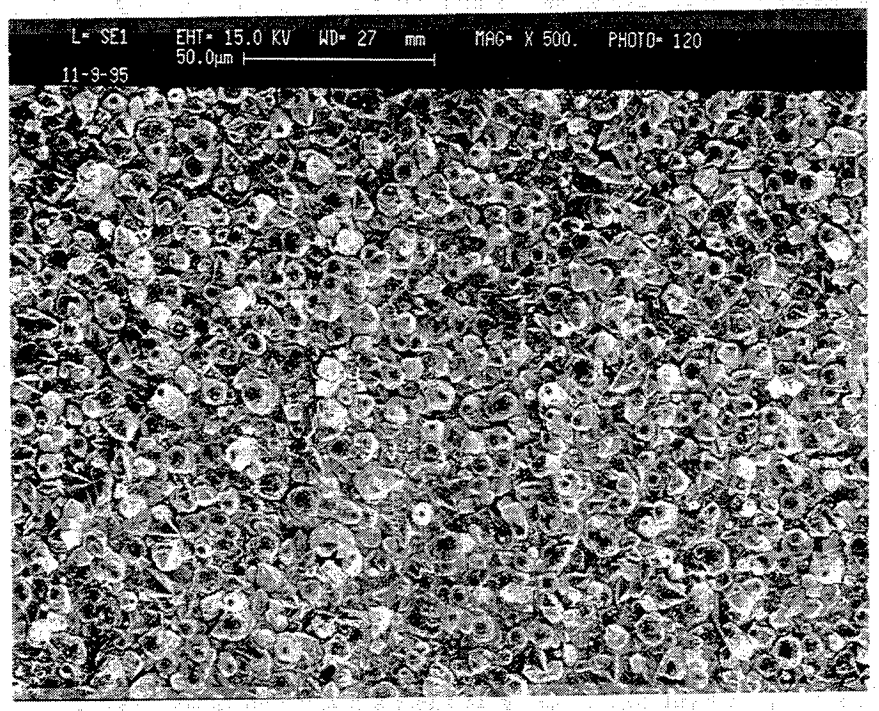


Plate III SEM of Plated Silver (Sample # 11-9-95)

AN AIR FORCE POLLUTION PREVENTION INITIATIVE "DEMONSTRATION OF A NON-CHROMATE CONVERSION COATING FOR ION VAPOR DEPOSITION (IVD) ALUMINUM"

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ABSTRACT

The goal of this project is to demonstrate a non-chromate alternative to chromate conversion coatings currently used for IVD aluminum-coated parts. When successful, this effort will improve the work environment at Air Force Air Logistics Centers (ALCs), reduce hazardous waste production from the IVD aluminum/conversion coating process, and virtually eliminate the need for expensive pollution control equipment. This alternative technology will replace the chromate conversion coating, comply with MIL-C-83488, and reduces hazardous waste generation and disposal.

Stringent environmental and occupational health regulations for Air Force electroplating facilities are restricting pollutant discharges from the ALCs and have escalated the cost of waste disposal. Chromate conversion coatings contain hexavalent chrome, a known human carcinogen. Demonstration and validation of alternative conversion coatings for IVD aluminum are needed to ensure that coatings for Air Force aircraft parts will meet performance criteria in military specifications in an environmentally friendly manner.

The Air Force ALCs are eliminating the use of cadmium processing for aircraft maintenance and overhaul in order to eliminate hazardous cadmium wastestreams. With the exception of a sacrificial, corrosion-resistant barrier, the replacement process, ion vapor deposition (IVD) of aluminum, eliminates many of the environmental problems associated with cadmium processing. The traditional corrosion barrier used with the IVD process uses a chromate conversion coating to provide additional corrosion protection and an improved base for paint or primer adhesion. The Air Force (Armstrong Laboratory, Environics Directorate) entered a contract with McDonnell Douglas Aerospace-East (MDA-E) in 1993 to identify a non-chromate coating alternative to traditional chromate conversion coating for IVD aluminum. A number of conversion coating candidates were tested for adhesion and corrosion protection. In addition, the candidate coatings were subjected to a number of performance tests which included electrical resistance, adhesion, corrosion, humidity resistance, and fluid resistance. Results were then compared with a baseline chromate conversion coated panel. Following the full test cycle, the best candidate non-chromate conversion coatings were selected for the Armstrong Laboratory's demonstration and validation project which began in May, 1996. Acurex Environmental Corp. is the contractor performing the demonstration and WR-ALC, Robins Air Force Base, Georgia is the demonstration facility.

INTRODUCTION

In 1993, McDonnell Douglas Aerospace East (MDA-E), St Louis MO was contracted by the U.S. Air Force Armstrong Laboratory, Environics Directorate (AL/EQ) to identify a non-chromate alternative to the conventional chromate conversion coating for ion vapor deposition (IVD) aluminum. A Final Report was issued by MDA-E detailing the testing and recommending of a non-chromate conversion coating for further testing (Fournier). MDA-E tested coupons coated with IVD aluminum per MIL-C-83488 with candidate conversion coatings for corrosion resistance, primer paint adhesion, and contact electrical resistance. This May, Acurex Environmental Corporation, Research Triangle Park NC, teamed with Battelle, Columbus OH, was contracted by AL/EQ and tasked to demonstrate the recommended non-chromate conversion coating for IVD aluminum at Warner Robins Air Logistic Center (WR-ALC). The Program Manager for this project is 1Lt Ray Anthony Smith (AL/EQR).

BACKGROUND

MDA-E surveyed the industry/DoD and identified twelve candidate non-chromate conversion coating processes for potential use with IVD aluminum. Based on internal MDA-E data, six processes were identified and screened using Class 2 (0.5 mil minimum thickness) IVD aluminum coated AISI 4130 steel panels. The panels were exposed to neutral salt fog, primer adhesion, and contact electrical resistance tests. The process based on Sanchem's Sealing Step II, a potassium permanganate ($KMnO_4$) solution immersion at 140 °F for 1 minute, performed well in these tests with no failure at 3,000-h salt fog exposure, minor failure of scribed, wet, paint adhesion, and acceptable contact electrical resistance. Supplementary tests were run with Class 2 coated panels using variations on Sealing Step II.

Based on the results of the screening tests, four non-chromate conversion coatings were selected for expanded corrosion resistance testing by MDA-E including two variations on Sealing Step II. Class 1 (1.0 mil minimum thickness) IVD aluminum coated AISI 4130 steel panels were treated and subjected to neutral salt fog testing, sulfur dioxide (SO_2) salt fog testing, and extended outdoor exposure. Aluminum alloy panels, steel fasteners, and titanium fasteners were also coated with IVD aluminum and tested with the four candidate non-chromate conversions coatings. The parts were evaluated for corrosion resistance to neutral salt fog and SO_2 salt fog. These results led to selection of a Sealing Step II process and a process consisting of Sealing Step II followed by Sealing Step III (potassium silicate solution immersion) for optimization on a bench-scale pilot production line.

MDA-E set up a 20-gal pilot production line to further optimize the process. The variables investigated included immersion time, solution temperature, and solution concentration. Neutral salt fog testing indicated pitting on most of the panels, but there was no evidence of red rust at 672-h of exposure for any of the panels tested. Only panels treated with variations of Sealing Step II followed by Sealing Step III consistently passed the dry tape-adhesion test, and the scribed, wet, tape-adhesion test. The contact electrical resistance testing showed some inconsistencies, however, all panels treated with Sealing Step II followed by Sealing Step III exhibited relatively low contact electrical resistance after salt spray exposure.

MDA-E recommended a non-chromate conversion process including operating parameters for each of the sealing step tanks and the rinse tanks. These operating parameters met all the performance requirements of MIL-C-83488 during optimization testing with the exception that Sealing Step II was tested at a slightly higher pH on the pilot production line. The recommendations include:

- Sealing Step II: 140 to 150 °F
  6.0 to 7.0 pH
  1 part conc: 9 parts DI water
  2.8 to 4.8 ml titer
  3 min

- Rinse: Ambient DI water
  3 min

- Sealing Step III: 200 to 212 °F
  11.5 to 12.0 pH
  0.88 parts conc: 10 parts DI water
  1 min

- Rinse: Ambient DI water
  3 min

MDA-E recommended investigation, based on their optimization work, of doubling the concentration of Sealing Step II and of increasing the temperature of Sealing Step II to 170 °F. In addition, MDA-E recommended that a more thorough investigation be conducted if inconsistencies in the contact electrical resistance testing was encountered.

Battelle developed a conceptual coating model of the MDA-E recommended process based on discussions with Sanchem and MDA-E. A schematic representation of this model is shown in Figure 1. Permanganate will oxidize aluminum to form a manganese oxide - alumina coating. This is similar to the process taking place in the conventional chromate coating; however, the process occurs at milder pH conditions. Added protection is provided by a subsequent immersion in an alkaline potassium silicate solution. Dissolved alumina is precipitated as fine grained potassium alumina silicates that fills the pores in the manganese coating and seals the entire surface.

TEST PLAN

Under this current Air Force work effort, the MDA-E recommended non-chromate conversion process for IVD aluminum will be demonstrated in the plating shop at WR-ALC. The equipment required for retrofit will be identified and installed in four contiguous idle tanks. (The tanks intended for this demonstration are 30-in wide by 36-in long by 42-in deep.) The recommended process and process parameters will be validated with 4 by 6-in AISI 4130 steel panels coated with Class 1 IVD aluminum. Panels will be tested for neutral salt fog corrosion resistance, primer adhesion for three water-borne epoxy primers, and for contact electrical resistance. In addition, a set of panels will be tested by electrical impedence spectroscopy (EIS) to give a comparison with bench-scale optimization testing.

Optimization testing will be performed on the bench-scale using two accelerated test methods, EIS and SO_2 salt fog, to obtain results in time for implementation on the demonstration coating line. All optimization testing will be performed on 4 by 6-in AISI 4130 steel panels coated with Class 1 IVD aluminum at WR-ALC. Testing will be blocked and randomized to minimize the influence of nuisance variables such as IVD aluminum coating thickness and time elapsed since peening. The first stage of optimization testing will validate the ability of EIS and SO_2 salt fog testing to discriminate between Type 1 and Type 2 IVD aluminum coated panels. Panels to be coated with the non-chromate conversion coating will be treated per MDA-E recommendations corresponding to the center point process values in Table 1.

Eight process parameters will be screened in an eighth fraction factorial: Sealing Step II Safegard 3000 concentration, Sealing Step II temperature, Sealing Step II pH, Sealing Step II immersion time, Sealing Step III Safegard 4000 concentration, Sealing Step III temperature, Sealing Step III immersion time, and byproduct contamination. The screening is intended to reduce the number of factors under investigation in subsequent replicates to allow segregation of two factor interaction effects in a process model. (The values of each parameter to be investigated are shown in Table 1.) This fractional factorial clears each main effect from all two-factor interaction effects. This design reduces to a full factorial in five factors, complete replicate factorials in four or fewer factors, or a half fraction in six factors. Analysis of six factors is the

largest fraction that clears two factor interactions from each other. A center point will be run with each block to provide an estimate of error and curvature. By-product contamination will be evaluated by addition of reagent grade $KAl(OH)_4$ and KNO_3 to Sealing Step II and $KAl(OH)_4$ and K_2CO_3 to Sealing Step III.

Table 1. Process Parameters to be Tested

	Parameter	Factor Points		
		-1	Center	+1
Sealing Step II (Safegard™ 3000)				
	Concentration (vol %)	5	10	15
	Temperature (F)	125	145	165
	Immersion Time (min)	1.5	3.0	4.5
	pH	5.5	6.5	7.5
	$KAl(OH)_4$ Buildup	0	1/2 sat.	saturated
	KNO_3 Buildup (ppm)	0	500	1,000
Sealing Step III (Safegard™ 4000)				
	Concentration (vol %)	7.0	8.1	9.2
	Temperature (F)	190	200	210
	Immersion Time (min)	0.5	1.0	1.5
	$KAl(OH)_4$ Buildup	0	1/2 sat.	saturated
	K_2CO_3 Buildup (ppm)	0	500	1,000

Parameters judged to have significant main effects will be tested further in an additional factorial at the same factor levels. The remaining parameters will be run at their respective center point values. This effort will be limited to 36 replicated runs. These results will be added to the screening results to obtain a linear process model for each response variable: EIS and SO_2 salt fog corrosion resistance.

Optimum conditions will be determined from the process model with the highest correlation coefficient. Four runs will be performed at the optimum conditions to verify improvement over the center point condition.

In addition to the factorial process optimization, several factors relating to operability will be investigated. The elapsed time from IVD aluminum peening, 24 to 48-h, and the effectiveness of an acid preconditioning dip will be evaluated in a replicated 2^2 factorial. The effect of silicate contamination in the $KMnO_4$ bath will also be evaluated against the center point condition. Finally, the effect of impingement of large $KAlSi_3O_8$ crystals on the surface of panels, which could build up in the silicate bath with extended use in the silicate bath, will be evaluated during the testing phases. These tests should help to encompass "real-world" operating characteristics unlikely to be encounter during this test program.

Optimum conditions identified from the bench-scale test program will be validated on the demonstration line during the "test and operate" portion of the test program. The new parameters will be evaluated using 4 by 6-in AISI panels coated with Class 1 IVD aluminum. Panels will be tested for neutral salt fog corrosion resistance, primer adhesion for three water-borne epoxy primers, and for contact electrical resistance. In addition, a set of panels will be tested by EIS to give a comparison with bench-scale optimization testing.

Additional Class 1 coated steel panels will be treated under MDA-E recommended conditions on the demonstration line for use in evaluating coating repair and coating removal feasibility. Up to three non-chromate alternatives for coating repair will be evaluated, along with a no-wipe chromate repair coating. Coating removal will be evaluated using grit blasting and caustic immersion methods currently employed by the ALC.

In the latter stages of the project, condemned parts will be cycled through the demonstration process at the MDA-E recommended process conditions. Selected parts will be evaluated for neutral salt fog corrosion resistance. Non-chromate coated parts will be made available to the Air Force for independent evaluation. Control parts will be coated using the chromate conversion coating process and tested with the non-chromate conversion coated parts.

SCHEDULE

A draft Test Plan for all testing was submitted to AL/EQR in July, 1996. To establish optimization conditions for the pilot demonstration, bench-scale optimization was scheduled to begin last week of July 1996. Set up and shake down of the demonstration line is scheduled for September, 1996. Current plans are for operation of the demonstration coating line at MDA-E recommended conditions for two weeks. This will be followed by a three week test and operate period in October. At the end of this testing, the line will be operated as required by WR-ALC personnel.

Bench-scale optimization testing of panels are scheduled to be completed in September, 1996. Paint adhesion and contact electrical resistance of test panels coated on the demonstration line are scheduled for completion in December 1996. The panels coated on the demonstration line will be exposed to salt fog for 8,000 hours. This long exposure time results in testing completion no sooner than September, 1997. Early failure of pieces subjected to salt fog exposure will result in repeating the test condition and may extend the duration of testing.

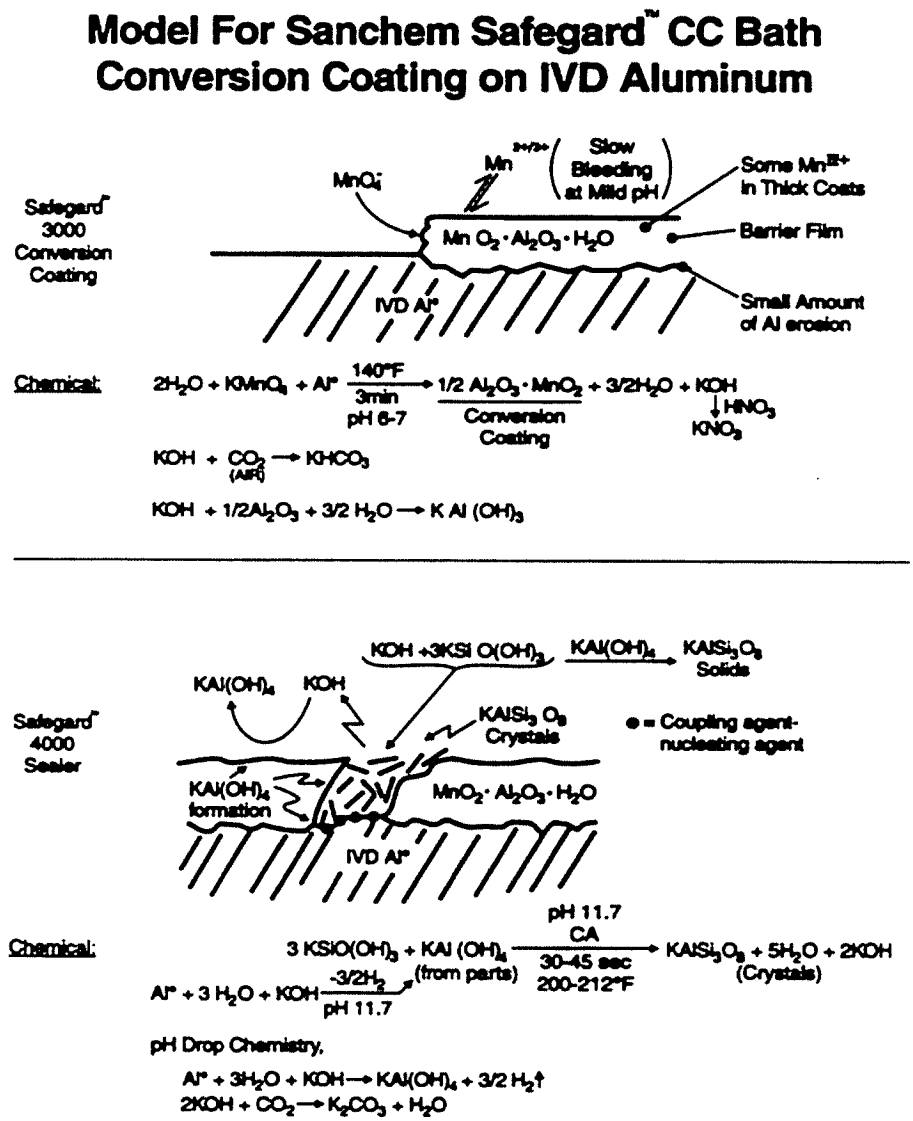
SUMMARY

Significant pollution prevention potential exists for the Air Force in eliminating chromate conversion coatings from the IVD aluminum coating process. MDA-E has identified a non-chromate conversion coating with the potential to replace the traditional chromate conversion coating and satisfy L-C-83488 performance requirements. Acurex Environmental and Battelle will demonstrate and validate this process on a pilot coating line at WR-ALC and will make a recommendation for ALC plating shops to transition to non-chromate conversion coating.

REFERENCES

1) Fournier, J.A. and J.J. Reilly, A Determination of the Effectiveness of Non-chromate Conversion Coatings for Use with IVD Aluminum Coatings, ≡ October 1995.

Figure 1. Model for Sanchem Safegard® CC Bath Conversion Coating on IVD Aluminum.



Low-Cost, Heavy-Metal-Bearing Wastewater Pollution Prevention Treatment: Demonstration of a Sodium Sulfide/Ferrous Sulfate-Based Batch Treatment System for the USAF

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As a part of its ongoing preventive and restorative maintenance program, the U.S. Air Force operates worldwide Corrosion Control Facilities to control the effects of environmental corrosion on its fleet of air and ground vehicles. The corrosion control implementation program employs industrial processes of abrasive and chemical paint removal; mechanical and chemical surface preparation; corrosion removal and metal treatment; protective coating application; and light metal plating. These operations typically generate considerable quantities of largely aqueous, yet hazardous, heavymetal-bearing wastes that must be controlled and prevented from entering the environment. Heavy-metal constituents of this waste stream typically include cadmium, chromium (hexavalent and trivalent), lead, and zinc that are routinely used to prevent exposed metal corrosion and structural integrity degradation.

In a project sponsored by the USAF Armstrong Laboratory, a consortia of academic and industry representatives refined and demonstrated a low-cost sodium sulfide/ferrous sulfate-based chemical batch-treatment process. In this chemical process, undesired heavy-metal ions are precipitated from the aqueous stream as insoluble sulfide salts or hydroxides. An experimental batch-processing station employing this process was successfully demonstrated to treat metals bearing wastewater generated by the Corrosion Control Facility at Columbus AFB, Mississippi. Using readily available, low-cost commercial components and simple procedures, this process has been shown to effectively and rapidly reduce the heavy-metal contents of the waste stream below acceptable EPA safe release levels. Within 24 hours, wastewater can be safely discharged into sanitary sewer facilities, and the resultant concentrated metals-bearing sludge (approximately 5 gallons per 1,000 gallons of treated water) can be subsequently packaged for disposal or reclamation. This process and prototype system have the potential for wide application in low-volume heavy-metals wastewater treatment (on the order of 10,000 gallons per month) that may be encountered at various aerospace propulsion production and corrosion control facilities.

This paper, covering the topic areas of technologies for waste management and mitigation, pollution prevention, and paint stripping, describes the chemical process, provides the results of the experimental testing, and details a prototype design for a full-scale localized treatment facility.

Introduction

This paper describes the results of a field Demonstration/Validation testing effort and system concept definition for a metal treatment system at air bases generating relatively small quantities of heavy-metal contaminated wastewater per month. The paper first discusses the chemical processes and the field testing (validation) of the processes. It then proceeds to a short discussion of the various applications (operational) concepts that were evaluated for implementation and indicates the applications concept that was selected (with justification). Finally, the paper provides a summary description of the system recommended to implement the concept, to include general functional System Specifications and System Concept Drawings.

Treatment Process Description and Verification

The waste streams to be treated by this metal treatment process are effluents that may be generated from electroplating, degreasing, alkaline cleaning, electrocleaning, acidizing, and electromechanical deposition of protective metals. All of these general processes can generate effluents that contain common heavy metals such as hexavalent chromium, nickel, copper, cadmium, lead, and/or zinc.

The USAF concern centers around the fact that their base Corrosion Control Facilities (CCF) generate such waste streams as a part of normal operations. The basis of the process is to add selected chemicals to the waste streams to precipitate the metals into metals-bearing sludges considerably smaller (by two to three orders of magnitude) in volume than the original volume of contaminated wastewater.

The smaller volumes of sludges may then be disposed of more economically than the original waste stream volumes. For this system, the chemistry process is to precipitate the undesired heavy metal ions from the aqueous wastewater stream as insoluble sulfide salts or hydroxides. The concentration of metal ions remaining in solution after this process is a function of the solubility product constant (K_{sp}) for the corresponding metal sulfide or hydroxide. The appropriate solubility product constant equations for the above metals (which will precipitate in either the trivalent or divalent forms) are shown as follows:

$$S^{2-}(aq) + M^{2+}(aq) \rightarrow MS(s)$$
$$3S^{2-}(aq) + 2\,M^{3+}(aq) \rightarrow M_2S_3(s) \quad \text{or}$$

$$OH^-(aq) + M^{2+}(aq) \rightarrow M(OH)_2(s)$$
$$3OH^-(aq) + M^{3+}(aq) \rightarrow M(OH)_3(s) \quad \text{and}$$

$$K_{sp}\,\{MS(s)\} = [M^{2+}(aq)]\,[S^{2-}(aq)]$$
$$K_{sp}\,\{M_2S_3(s)\} = [M^{3+}(aq)]^2\,[S^{2-}(aq)]^3$$
$$K_{sp}\,\{M(OH)_2(s)\} = [M^{2+}(aq)]\,[OH^-(aq)]^2$$
$$K_{sp}\,\{M(OH)_3(s)\} = [M^{3+}(aq)]\,[OH^-(aq)]^3$$

where [ ] = the concentration of a particular species; M = a heavy metal; (aq) = an aqueous ion; and (s) = a solid precipitate.

Upon addition of the precipitating reagents, precipitation of the metal ions will begin. [Note: When a sulfide salt is used as the precipitating agent, the process must be executed in a solution that has a neutral or slightly basic pH; otherwise, hydrogen sulfide gas (a poison) will be generated and released during the reaction]. The metal ion concentration will decrease as the precipitating reagent concentration is increased; assurance of adequate precipitating reagent to ensure removal of all of the undesired metal ions can be controlled by adding excess precipitating reagent to the process. K_{sp} values for metal sulfides of interest, as mentioned above, include the following:

Metal Ion	Metal Sulfide	K_{sp}
Cd^{2+}	CdS	1.40×10^{-29}
Fe^{2+}	FeS	1.59×10^{-19}
Pb^{2+}	PbS	9.04×10^{-29}
Ni^{2+}	NiS	1.07×10^{-21}
Zn^{2+}	ZnS	2.93×10^{-25}

The sulfide ion necessary to precipitate the heavy metal contaminants is generated in this wastewater treatment process by dissolving sodium sulfide (Na_2S) in water (in a neutral or slightly basic solution, as indicated above). However, because the sulfide ion is extremely basic [its base dissociation constant (K_b) is approximately 1 in neutral water], most of the S^{2-} ion will be converted into the HS^- ion according to the following reactions:

$$Na_2S(s) \rightarrow 2\,Na^+(aq) + S^{2-}(aq)$$
$$S^{2-} + H_20 \rightarrow HS^- + OH^-$$

Further, chromium cannot be precipitated as its sulfide ion from chromate (hexavalent chromium) solutions (and most of the wastewater streams will contain hexavalent chromium). Therefore, it is necessary to reduce the hexavalent chromium to trivalent chromium as a part of the overall process to induce precipitation as a hydroxide. This is accomplished by exploiting the above condition (where most of the sulfide exists in the HS^- form), and by adding ferrous sulfate ($FeSO_4$) to the wastewater stream after the sodium sulfide is added. The following reaction equation illustrates the hexavlent chromium reduction process:

$$3\,HS^- + 6\,FeSO_4 + 4\,CrO_4^{2-} + 13\,H_20 + OH^- \rightarrow$$
$$3\,S^0(s) + 6\,Fe(OH)_3(s) + 4\,Cr(OH)_3(s) + 6\,S0_4^{\,2-}$$

This overall equation is the end product of three electron transfer processes and represents two oxidation reactions followed by a reduction reaction to convert the hexavalent chromium to trivalent chromium. The reactions are illustrated as follows:

$$6\ FeSO_4 + 18\ OH^- \rightarrow 6\ Fe(OH)_{3(s)} + 6\ SO_4^{2-} + 6\ e^-$$
$$3\ HS + 3OH^- \rightarrow 3\ S^0 + 3\ H_20 + 6e^-$$
$$4\ CrO_4^{2-} + 16\ H_20 + 12\ e^- \rightarrow 4\ Cr(OH)_3(s) + 20\ OH^-$$

The end result is the formation of both $Fe(OH)_3$ and $Cr(OH)_3$. The K_{sp} of $Fe(OH)_3$ is 2.64×10^{-39}, indicating that the iron will precipitate from solution at low concentrations. Likewise, while the solubility properties of $Cr(OH)_3$ are quite complicated and are not readily expressed by a K_{sp}, $Cr(OH)_3$ is only sparingly soluble and will precipitate in a slightly basic solution. Other metal ions (e.g., cadmium, lead, nickel, zinc, etc.) will precipitate as their sulfides.

Procedurally, a dilute sodium hydroxide (NaOH) solution is initially added to the wastewater batch to be treated until the solution reaches a pH of approximately 7.2 or slightly higher (as indicated by a pH meter). Next, the ferrous sulfate and sodium sulfide are added and the pH is raised to approximately 9.0. Basicity is maintained throughout the reaction by constantly monitoring the pH meter and manually adding either more NaOH or a dilute solution of sulfuric acid (H_2SO_4) as necessary to maintain the pH in the above indicated range.

The precipitate formed by the described process is light and does not settle rapidly. Thus, the resultant mixture is allowed to settle for approximately 24 hours, forming a sludge on the bottom of the reaction vessel. After this time, the settled sludge may be removed from the bottom of the tank, leaving the clean water above.

Temperature has some (but relatively little) effect on the rate of reaction and on solubility in the temperature ranges from +40°F to +110°F. Reactions should be executed within these temperature ranges. The mass and volume relationships to ensure the reduction of the Cr^{6+} to Cr^{3+}, and for the precipitation of metal ions as their hydroxide or sulfide salts, are shown in Table 1.

Note that Fe^{3+} and Cr^{3+} precipitate as their hydroxides, not sulfides. However, since the reaction is carried out in a slightly basic solution, excess hydroxide ion will always be present to ensure the precipitation of the trivalent iron and chromium ions. Therefore, it is not necessary to explicitly calculate the hydroxide stoichiometry as long as a basic reaction medium is maintained.

Thus, the final output of the system is remediated wastewater (an effluent meeting requirements related to heavy metal ion discharge) and metal-bearing sludge. The clean effluent, after positive verification of decontamination by laboratory sample analysis, may be disposed of through the base sewage system (provided the pH is between 6.0 and 9.0). The sludge, whose volume is 2-3 orders of magnitude less than the original contaminated effluent, is containerized and disposed of through the existing base hazardous waste removal arrangements.

If remediated wastewater is to be discharged through a base sewage system, it must at least meet the current Environmental Protection Agency standards for a metal-finishing industry discharging to a domestic sewage treatment system. These minimum discharge standards, for the heavy metals expected to be present in the waste stream of most USAF CCFs, are shown in Table 2.

A total of 15 experimental runs (performed at Columbus AFB, Mississippi, on the prototype batch processing system) were conducted between April and September 1995. For every one of these runs, the final results indicated that 100 percent of the Cr^{6+} was reduced to Cr^{3+}, and the final concentration of Cr^{6+} in the wastewater was non-detectable (below 0.1 part per million). For these same 15 runs, the final concentration of Cr^{3+} in the wastewater was nondetectable for 11 of the runs and was at 0.02 parts per million or below for the remainder. Other experimental data indicated that cadmium and zinc were remediated at or above the 97 percent level and that copper and nickel were remediated at approximately the 80 percent level. (It is believed that the copper/nickel levels were driven by the extremely low initial concentration of these metals in the waste stream itself). These results were sufficient to obtain approval to discharge the treated wastewater into the Columbus AFB sewage system.

TABLE 1. MASS/VOLUME RELATIONSHIPS

Cr^{6+} Reduction:

1 volume of 1 ppm Cr^{6+} (1mg/L, 19.2 μM) requires 3.46×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

1 volume of 1 ppm Cr^{6+} (1mg/L, 19.2 μM) requires 8.0×10^{-3} volume of 1 g/L $FeSO_4 \cdot 7H_2O$ (3.60 mM)

Metal Ion Precipitation as Sulfide

1 volume of 1 ppm Cd^{2+} (1mg/L, 8.90 μM) requires 2.14×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

1 volume of 1 ppm Cu^{2+} (1mg/L, 15.7 μM) requires 3.77×10^{-3} volume of 1 g/L Na_2S-$9H_2O$ (4.16 mM)

1 volume of 1 ppm Fe^{3+} (1mg/L, 17.9 μM) requires 4.30×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

1 volume of 1 ppm Pb^{2+} (1mg/L, 4.88 μM) requires 1.16×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

1 volume of 1 ppm Ni^{2+} (1mg/L, 17.0 μM) requires 4.09×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

1 volume of 1 ppm Zn^{2+} (1mg/L, 15.8 μM) requires 3.68×10^{-3} volume of 1 g/L $Na_2S \cdot 9H_2O$ (4.16 mM)

ppm = parts per million
mg = milligram
g/L = grams per Liter
Cu = Copper
Ni = Nickel
Pb = Lead
μM = micromole
mM = millimole
Cr^{6+} = Hexavalent Chromium
Cd = Cadmium
Fe = Iron
Zn = Zinc
$^{2+}$ = ionic charge

TABLE 2. CURRENT MINIMUM ACCEPTABLE DISCHARGE LEVELS

Pollutant/Property	Maximum/Day (mg/L)	Monthly Average (mg/L)
Cadmium (T)	0.69	0.26
Chromium (T)	2.77	1.77
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
pH	6.0 to 9.0	6.0 to 9.0

Temperature was found to have little effect on the removal of metals from the waste stream. Further, an excess of reagents (sodium sulfide and ferrous sulfate) did not interfere with the metal removals process. Experimental data regarding sludge settling indicated that, in a 200-gallon batch, there was an 8-inch layer of sludge at the bottom of the tank after 24 hours, that the level of Cr^{6+} in the clear water above the sludge was non-detectable, and that the total level of Cr (as Cr^{3+}) was 0.16 parts per million.

Based on these experimental data summary results, it appears that a batch processing system, using the chemical process described previously, shows significant promise for removing heavy metals from contaminant waste streams, not only at USAF CCFs but at any other facility that generates heavy-metal wastes.

Applications/Operational Concepts Considered

Three different operational concepts were evaluated for application of the batch treatment process at USAF CCF facilities. These concepts included (1) a small, mobile, trailer-mounted regional treatment system; (2) a small, modular, fixed-site treatment system for each airbase requiring a system; and (3) a large, centralized regional site treatment system, with the wastes being carried from remote sites to the regional site for treatment. Various suboptions were also examined as appropriate for each option, including system ownership (Government vs. contractor), chemical analysis options (Government vs. civilian laboratory), and maintenance options (Government vs. contractor). The need for dedicated operators/maintainers, with the attendant impact on force structure, was a driving consideration in evaluating each concept.

The results of the comparative evaluations indicated that a small, modular, fixed-site facility for each base was the preferable option from an economic standpoint. Based on the operational concepts evaluation, this option was also preferable from an operational standpoint, in that it avoids issues associated with transportation of a waste remediation system across multiple federal and state environmental jurisdictions.

The key economic driver for a small, fixed site at each base was that no full-time operators or maintainers would be required (based on the sensitivity of the design, which is covered in the next section of the paper), whereas dedicated operators and/or truckers would be required for either a mobile concept or a large, fixed regional facility. Other economic drivers were that routine maintenance would be cheaper for a small, fixed site than for a mobile concept; that initial construction costs for a small, fixed site would be cheaper than for a large, regional site; and that periodic replacement of the rolling stock for the mobile concept would be expensive.

System Concept Definition

The recommended Sodium Sulfide/Ferrous Sulfate Metals Treatment System option was a small, modular, self-contained chemical process treatment system designed to remove dissolved and particulate heavy metal wastes from the wastewater generated by Air Force CCFs. The system is designed to treat metals-bearing wastewater in 1,000 gallon batches using a combination of sodium sulfide and ferrous sulfate in a slightly basic solution. The results of the treatment are a low-volume metals-containing precipitate sludge and cleaned wastewater. Total system cycling requires a period of approximately 48 hours. It can process up to 10,000 gallons of contaminated wastewater per month using the batch-mode approach. It is recommended that one such system be installed at each base CCF facility that generates waste at or below these levels.

The system itself consists of one 1,000-gallon initial wastewater holding and (contaminant-level) sampling tank, four 250-gallon treatment and settling tanks, two 500-gallon final holding and sampling (decontamination verification) tanks, and one 50-gallon sludge concentration tank (See Figure 1). Ancillary equipment includes pumps and stirrers, pH meters, lockable containers for storing the various chemical reagents necessary for the reaction process, a portable hydrogen sulfide monitor, and small (approximately 5-gallon) sludge transfer containers. (Note: This system is designed to support a 1,000-gallon process. However, the system is completely modular; it can be scaled up or down simply by installing larger/smaller tanks and/or more/fewer tanks. The chemical process and the operational process are both essentially independent of batch size. The test data indicated that, due to reaction kinetics and sludge settling considerations, the treatment and settling tanks should not be larger than 250 gallons. Therefore, these tanks should not be made larger if the system is up-scaled; instead, more 250-gallon tanks should be added).

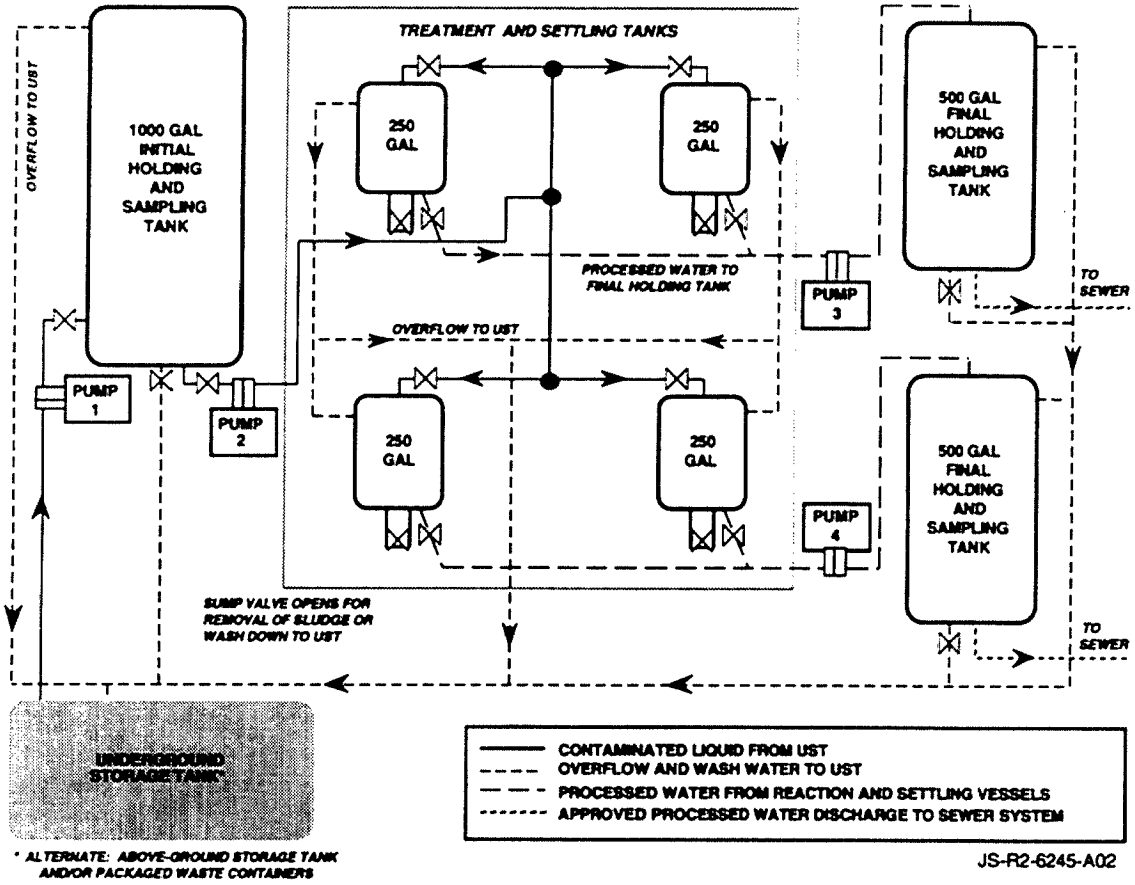

Figure 1. Treatment System Diagram

The operation of the system is supported by a portable (laptop/notebook) computer running analytical software. This software not only calculates the amount of chemical reagents necessary for treatment of each batch, but also provides all of the operational, safety, and maintenance procedures, in the correct sequence, to guide the actions of the operators. The portable computer also generates the appropriate environmental processing records required by statute and regulation, as well as appropriate system maintenance records. The software system also supports on-the-job operator and maintenance training through the use of a distributed, multimedia training concept.

The hardware components of the system are all available as Commercial-off-the-Shelf (COTS) materials, with qualification for hazardous materials handling already established by the manufacturers, U.S. Department of Transportation, and the U.S. Environmental Protection Agency. The analytical and records storage software for the portable computer requires a customized approach; however, it will be built using commercially available software tools.

The output of the system is remediated wastewater and metal-bearing sludge. The wastewater, after verification of decontamination, is transferred from the final holding and sampling tank to the base sewage and ground wastewater system. The sludge is containerized and disposed of off-site at a qualified hazardous waste acceptance site in accordance with the existing base procedures for disposal of hazardous wastes.

The system is designed to be installed on a drained concrete slab in a covered, open shed of approximate dimensions of 30 feet x 40 feet. (Alternately, the system can be installed on a similar slab inside a closed, walled building, depending on average base weather conditions; however, the building's ventilation rate must allow for fresh air turnover of at least 5 volumes per hour). The facility has 220V/110V; 200 amp, three-phase electrical service (Figure 2), conventional freshwater service, and a sump/dual underground pipe interconnect system that returns only to the wastewater storage tank. The slab is surrounded by a 6-inch berm to avert toxic runoff in the event of an accident and to support cleansing of the treatment system, with all system/slab drains designed to return *all* wastes into the

storage tank. Since operating temperatures for the chemistry and/or equipment require ambient temperatures between approximately 40° and 110° F, inside- or outside-siting will be base-dependent.

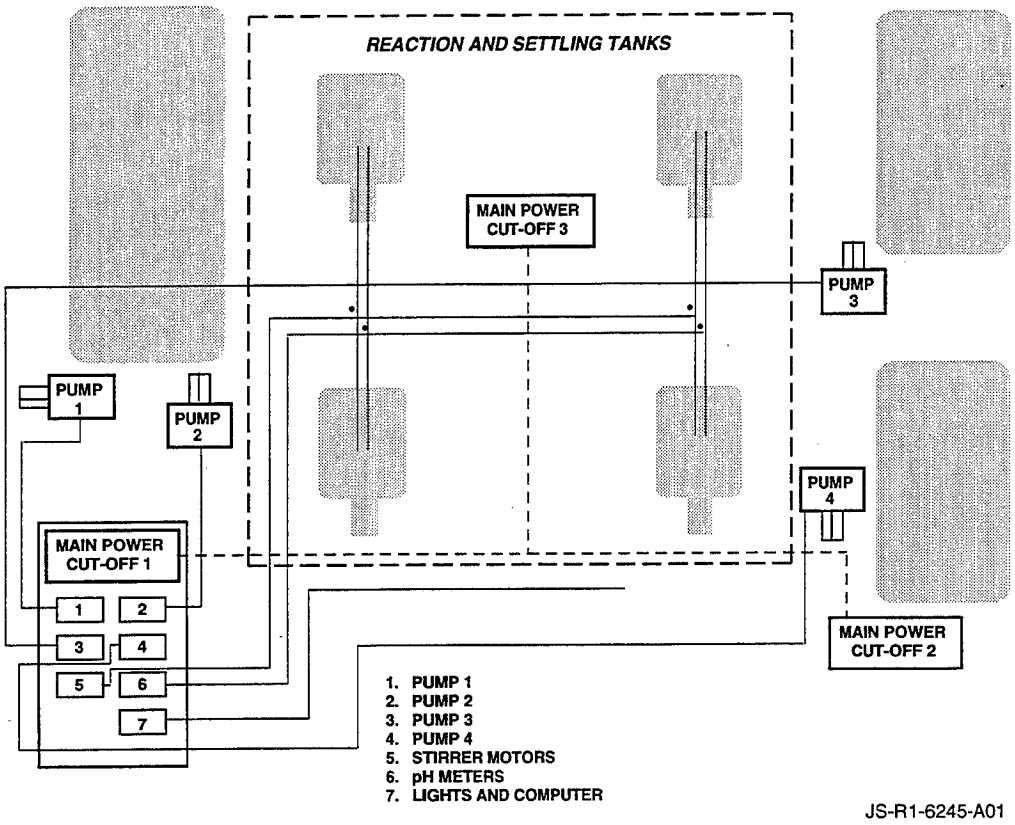

Figure 2. Electrical Power Supply Design

The modular system is specifically designed to be installed and maintained locally. It is designed for operation by a nondedicated, minimally skilled operator with general civil engineering and/or environmental training and minimal computer literacy. A complete single treatment cycle required approximately 96 hours; operators need only be on-site for approximately 6 to 8 hours during this period. Therefore, with appropriate on-the-job training, two nondedicated operators can easily run the system during each batch process. Chemical analysis of both the initial wastewater stream and the final treated wastewater will be performed by contracted laboratory services. All parts are certified commercial-off-the-shelf (COTS) and are readily available. Parts will conform with SAE (English) industry standard sizes, and the entire system will require approximately six nonspecialized tools for maintenance.

Conclusions

The testing program and the test data analyses showed that a batch mode operation, using a metals-precipitation approach, has excellent potential for remediating metals-contaminated waste streams at air bases and other facilities generating low volumes per month. The operational and economic analysis indicated that a simple, modular batch-processing system is the preferred option for each base that requires wastewater remediation. The results showed that for any base generating more than 2,050 gallons of waste per year, more money would be spent on packaging the wastes for landfill disposal than for building and operating such a facility at the base (assuming a 20-year life cycle for the system).

The testing program also showed that a continuous-flow process was too complex to be executed other than by highly trained and dedicated operators. Training full-time operators to operate complex systems also has implications on costly schooling requirements, equipment maintenance and calibration requirements, and other cost drivers. This implies that a simplified batch process approach is necessary to

avoid such implications. However, a mobile treatment approach, even if batch-processed, still requires dedicated operators and thus has additional cost implications.

Therefore, the proposed system was specifically designed and specified to permit installation, operation, and maintenance by nondedicated personnel, to essentially eliminate calibration requirements, and to permit on-the-job training of operators and maintainers (eliminating any requirements for formal schooling). This approach is possible because (1) all major equipment is off-the-shelf, SAE-standard, modular, and simple (there are only nine moving parts – four sealed pumps and five stirrers); (2) all plumbing and electrical parts are SAE-standard; (3) the water transfer, reagent addition, and system cleansing processes are all manually executed by the operators; (4) all of the "chemistry" and chemical procedures are solved by the computer "assistant" in real time; (5) all of the required chemical analyses (both the determination of the chemical composition of the wastewater and the verification of cleanliness of the treated water) are performed by a commercial chemical laboratory, eliminating operator training on complex analytical equipment and eliminating USAF requirements for purchase, maintenance, and calibration of such equipment; (6) all operational, safety, and maintenance operations are generated by the computer "assistant" in real time, in the appropriate sequence; (7) all necessary forms and records are generated by the computer "assistant" in real time, in the appropriate sequence; and (8) operator and maintainer on-the-job training (and testing/certification) is software-supported through state-of-the-art multimedia training approaches.

Acknowledgements

This project was executed in support of the United States Air Force, Armstrong Laboratory/Environics Directorate, Tyndall AFB, Florida, under contract number F08635-93-C-0020, Supplementary Support Group Subtask 9.02. The final products of this effort included detailed system-level "A" specifications, component "B" specifications, software support specifications, and recommended operator/maintenance/ safety procedures. The products were prepared for entry into the Defense Technical Information Center (DTIC) data base.

CLEANING: VERIFICATION AND INSTRUMENTATION—II

An OSEE Based Portable Surface Contamination Monitor

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Abstract

Many industrial and aerospace processes involving the joining of materials, require sufficient surface cleanliness to insure proper bonding. Processes as diverse as painting, welding, or the soldering of electronic circuits will be compromised if prior inspection and removal of surface contaminants is inadequate. As process requirements become more stringent and the number of different materials and identified contaminants increases, various instruments and techniques have been developed for improved inspection. One such technique based on the principle of Optically Stimulated Electron Emission (OSEE) has been explored for a number of years as a tool for surface contamination monitoring. Some of the benefits of OSEE are: it's non-contacting; requires little operator training; and has very high contamination sensitivity.

This paper describes the development of a portable OSEE based surface contamination monitor. The instrument is suitable for both hand-held and robotic inspections with either manual or automated control of instrument operation. In addition, instrument output data is visually displayed to the operator and may be output to an external computer for archiving or analysis.

Introduction

In early 1990 an investigation began at the NASA Langley Research Center (LaRC) into the mechanisms involved in using OSEE technology for the measurement of Conoco HD-2 grease contaminant on D6AC steel substrate although other contaminants and substrates are applicable to OSEE inspection. The resulting science studies enumerated several recommended improvements to the existing commercial instrumentation [1, 2, 3, 4, 5]. These recommendations, combined with system requirements from the NASA Marshall Space Flight Center (MSFC) and Thiokol Corporation OSEE user community were used by LaRC in the design of a prototype six channel OSEE instrument for use with robotic scanning equipment[6]. The design of the portable instrument described below was an extension of this prior work in the development of the six channel robotic version.

Some of the major recommendations for improvements cited in the science studies were a) the incorporation of a parallel electric field (PEF) configuration for the collector electrode b) a higher collector voltage c) a stable UV source and d) a dry argon atmosphere in the lamp and measurement region. The first improvement would ensure a more even distribution of the electric field thus minimizing the variation in sensitivity over the measurement region. A higher collector voltage would increase the collector current thereby improving the signal to noise ratio (SNR). Since the photo currents are linearly dependent upon the intensity of the UV source, a stable source will result in more repeatable measurements. Finally, the dry argon atmosphere is relatively non-ionizing and transparent to the UV region of interest. This will decrease the UV fluctuation due to possible absorption by oxygen and moisture in ambient air and will also decrease the photo chemistry (and hence photo fatigue) on the surface of the specimen under examination. Additional significant system requirements for the portable unit included a) a one inch diameter measurement area b) provisions for both robotic and manual inspections c) 30Hz signal bandwidth d) contamination data displayed at the instrument as well as data output capabilities e) operation in an electrically noisy environment with a minimum of 15 feet of cable between the sensor head and the control unit.

Theory of Operation

In general terms, OSEE operates by illuminating the measurement region with a source of ultraviolet (UV) radiation in the presence of a direct current (DC) electric field as shown in figure 1 [7]. The UV radiation frees electrons from the surface under inspection by the photoelectric effect. The electrons are collected on the positively charged anode, and the magnitude of the resulting current indicates the level of contamination on the surface. For the case of HD-2 grease on D6AC steel, contaminant in the measurement region absorbs the UV radiation thus reducing the number of electrons emitted from the substrate. The measured current, therefore is directly proportional to the level of contaminant. The greater the current, the cleaner the sample.

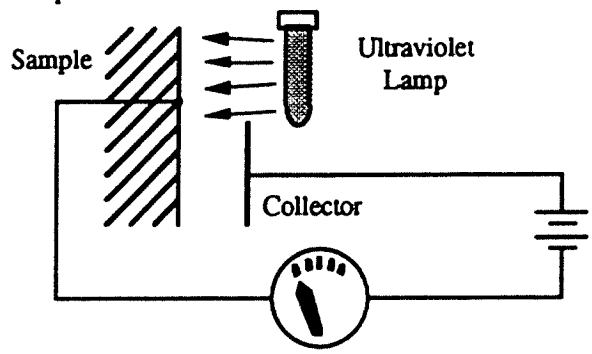

Figure 1. Basic principle of OSEE

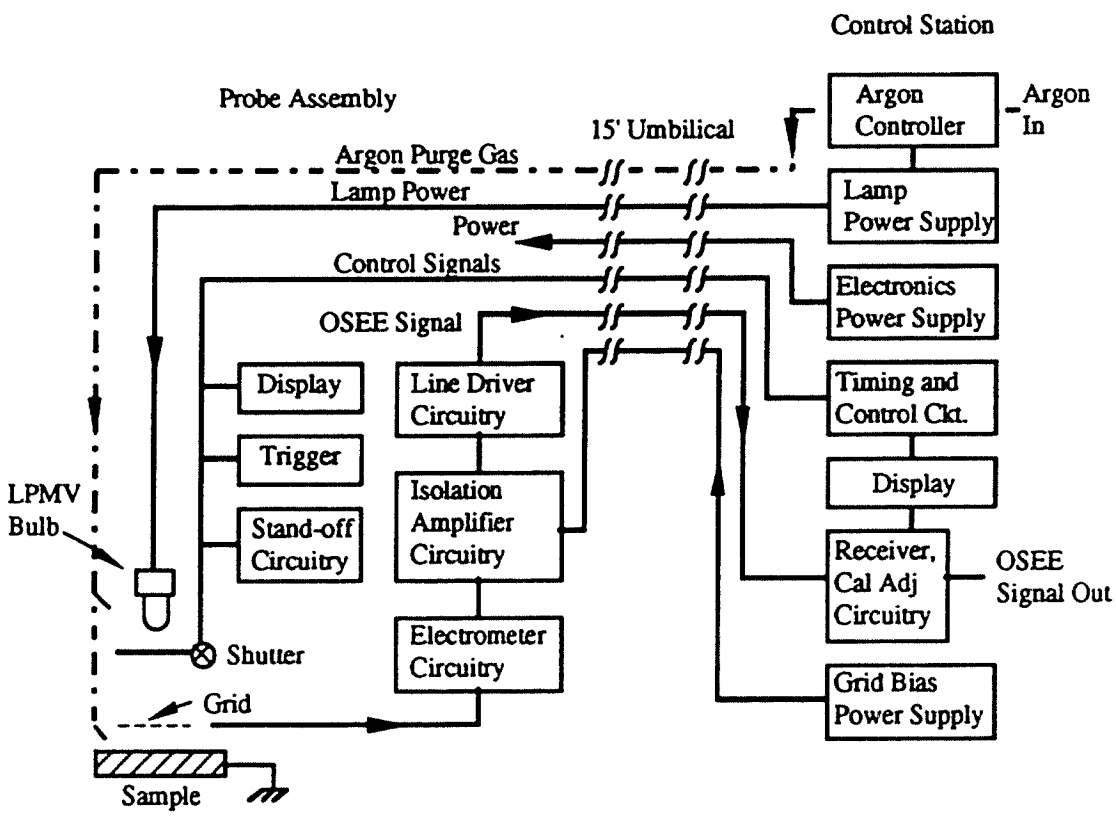

Figure 2. Block Diagram of Portable OSEE System

Instrument Overview

The instrument consists of a probe head and control station connected by a 15 foot umbilical. Figure 2 illustrates a block diagram of the instrument. The control station contains the power supplies for the lamp, grid, and associated electronics; the circuitry for system control, signal conditioning, and calibration; as well as the argon purge gas regulating system. The control station also includes the switches, indicator lamps, and meters necessary to operate and monitor the system and display the measurement results. The probe contains the UV source, electron collector grid, electrometer, isolation amplifier, and driver electronics to transmit the OSEE signal back to the control station. In addition, the probe also includes a manual trigger, a shutter mechanism to block the UV when not performing contamination measurements, and the necessary plumbing for the argon purge gas.

The Probe Assembly

Figure 3 shows a cross-sectional view of the OSEE probe head.

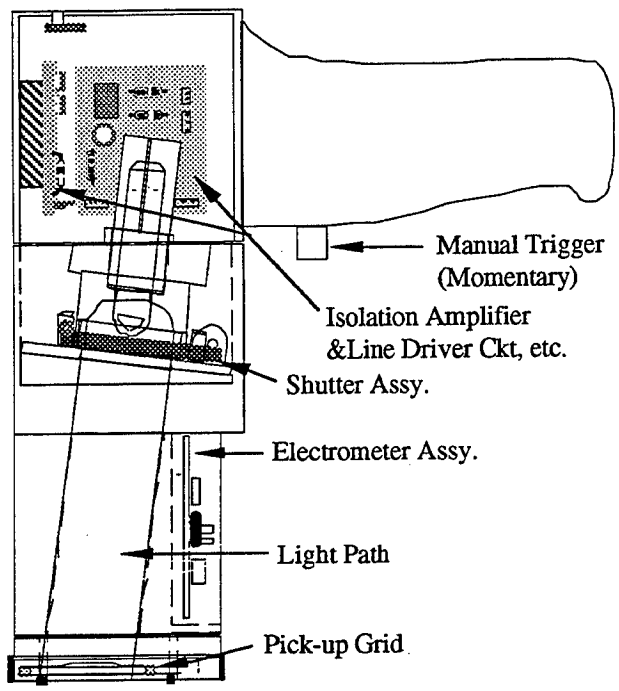

Figure 3. Cross Section of Probe Assembly

Lamp chamber and Collector

A commercially available, double bore, low pressure mercury vapor (LPMV) lamp with a lighted length of approximately 0.050 inches was chosen as the UV source. The LPMV lamp produces high efficiency UV light in distinct spectral lines. One of these, the 185 nm line, produces 95% of the OSEE response from the substrate and is also in the absorption spectrum of HD-2 grease. The lamp is powered from a high frequency power supply of approximately 40Khz to minimize interference with the low level OSEE current. One attribute of the LPMV lamp is that electromagnetic interference (EMI) emanating from the bulb is minimized by the double bore design which has a very small current loop. Additional noise reduction is achieved by surrounding the lamp chamber with an electrically grounded envelope thus

shielding the sensitive probe electronics from EMI radiation. The LPMV lamp is located at the focal point of a parabolic reflecting cavity. A threaded shaft forms the lamp base which is inserted into corresponding hole in the reflector. To align the assembly, the bulb is powered and inserted into the reflector until the source is at the focal point. The reflector is fabricated from an aluminum alloy billet machined by a numerically controlled (NC) mill for a one inch maximum diameter cavity with a focal point 0.2" from the base. A flash coating of elemental aluminum is then deposited on the reflector surface and coated with a magnesium fluoride coating. Directly below the lamp/reflector assembly is an optical shutter which is opened only when a measurement is made. Undesirable reflections below the reflector are minimized by using UV absorbing materials in the lamp chamber. The lamp is recessed in the probe assembly approximately four inches from the grid. This helps produce a uniform light source and minimizes "hot-spots" on the measurement surface. In the bottom of the lamp chamber is a low UV attenuating, high-quality, ES grade quartz window. The collector is formed by electro-depositing a thin translucent film of chrome on the outside of the window. The benefit of this PEF geometry is that the electric field from the collector is more uniform over the illuminated surface. An annular ring of opaque chrome with a one inch inside diameter is deposited around the outer edge of the window to provide a sharp, well defined illuminated region on the measurement surface.

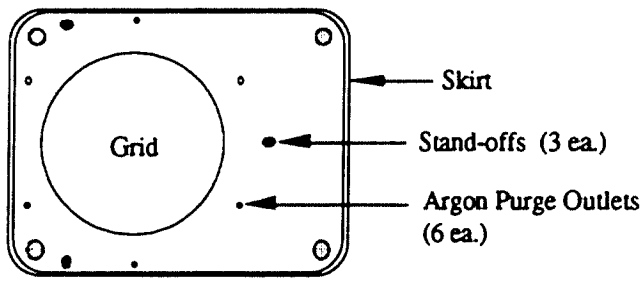

Figure 4. Bottom View of Probe

Argon Purge System

In order to minimize photo chemical production and to reduce UV absorption possible with ambient air, the lamp chamber and measurement region are purged with dry argon. For the purposes of OSEE argon is non-ionizing, chemically inert, and transparent to the UV wavelengths of interest. The argon begins its journey from a pressure vessel adjacent to the control station. The flow rate is regulated at the control station and fed to the probe assembly through the umbilical. Two independent lines are used; one to supply the lamp chamber and one for the measurement region. The outlets for the measurement region are illustrated in Figure 4. Argon flows into the lamp chamber whenever the lamp is operating. In fact, when the system is turned on, the lamp is not powered up until the argon supply line and lamp chamber are properly purged. This process occurs automatically and without any operator action required. In order to conserve the purge gas, argon flow to the measurement region is switched on only when a measurement is being performed. If the argon flow should be interrupted due to an exhausted supply tank or a disconnected supply line, the lamp is automatically shut off. In addition, a flexible skirt surrounds the bottom of the sensor head to help contain the argon and minimize in impact of external air currents on the measurement process. The argon flow is regulated to approximately 100 standard cubic centimeters per minute (sccm) in the lamp chamber while the instrument is on and approximately 600 sccm in the measurement region while and inspection is being performed. This rate of consumption allows the use of small portable argon containers for extended periods of operation.

Electrometer Circuit

The collector electrode is connected to the electrometer circuit through spring loaded contacts soldered directly to the electrometer printed circuit board (PCB). The electrometer circuit consists of an OPA-128 electrometer grade op-amp and several passive components. The input path from the collector electrode is less than one inch long. This reduces input capacitance and EMI pick-up into the 100MΩ input impedance of the circuit. The OPA-128 has a typical input bias current of only 75fA, well below the typical collector current of 500nA. This, combined with its wide gain-bandwidth product make the OPA-128 well suited for OSEE applications. The electrometer converts the OSEE current to a voltage relative to the collector bias and sends it to the isolation amplifier stage. The entire electrometer circuit is enclosed in a separate shielded compartment at the base of the probe, further reducing EMI pick-up.

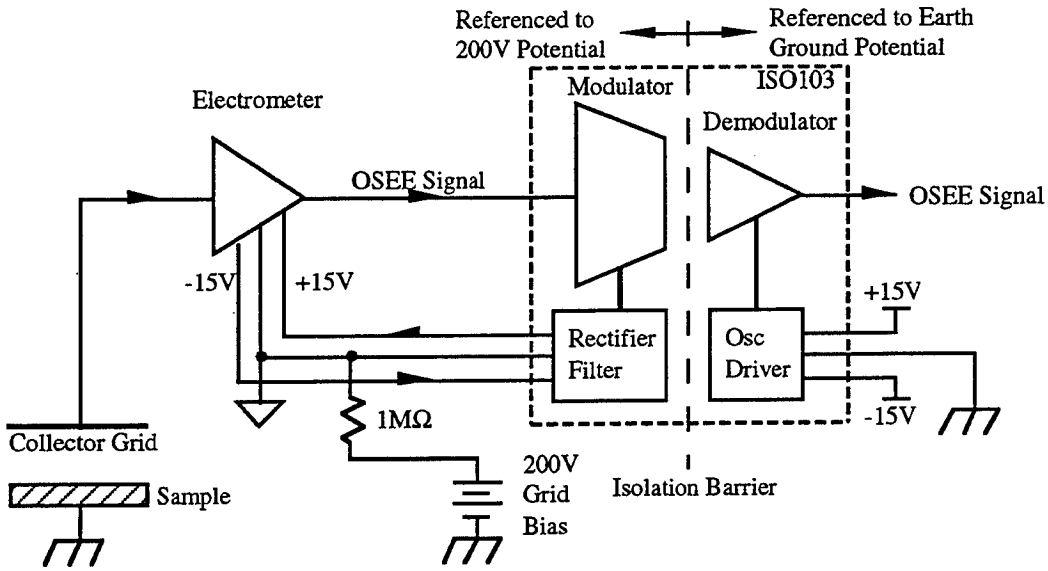

Figure 5. Block Diagram of Probe Front End Electronics

Isolation Amplifier and Driver / Receiver Circuit

Because of the common mode measurement required for OSEE, the high collector voltage must be decoupled from the OSEE signal while maintaining the proper potential between the collector and measurement surface. A Burr-Brown ISO103 isolation amplifier was chosen for this task. Figure 5 shows the probe front end electronics and illustrates the isolation amplifier theory of operation. The ISO103 provides both signal and power across a high impedance isolation barrier. The Integrated Circuit (IC) contains an 800Khz oscillator driver on the output side of the isolation barrier. The driver is transformer coupled to the signal input side of the IC where it is rectified and filtered to provide an isolated power source for the internal and external circuitry. The input signal is modulated using the oscillator, transmitted across the isolation barrier, and demodulated on the output side. The ISO103 has an isolation barrier rated to 1500Vrms. The IC can provide isolated power up to ±15mA at ±15V for the electrometer. The 200Vdc grid voltage is applied to common on the input side of the isolation amplifier through a 1MΩ resistor. The output signal from the isolation amplifier is low pass filtered to minimize any residual oscillator feed through. The OSEE signal is then transmitted over the umbilical by a balanced line driver/receiver pair. The Analog Devices SSM-2142/1 driver/receiver pair provide a total harmonic distortion (THD) of less than 0.001% and common-mode rejection (CMR) greater then 90 db over the pass band of the system.

Stand-off Monitor and Display

Although the OSEE measurement itself is non-contacting, the signal level is inversely proportional to the stand-off distance between the collector grid and the substrate. Consequently, some means must be employed to maintain a constant stand-off during the measurement process. For situations where a robotic system is used for inspection, a proximity sensor may be used. For a manually operated instrument where the operator is placing the sensor on the substrate, three short pins protrude below the collector grid in order to maintain the proper stand-off distance (refer to Figure 4). A circuit within the sensor head detects when the stand-off pins are in contact with the substrate and illuminates a LED when the sensor is properly positioned. If so desired, the system may be configured to disable the measurement process if the sensor is not properly positioned. This minimizes errors from erroneous readings. This function is controlled via an interlock switch on the control station front panel.

Just above the stand-off LED on the sensor head, a ten segment bar graph continuously displays the magnitude of the OSEE output signal. This provides the operator with a visual indication of contamination level without having to observe the front panel meters of the control station.

Control Station and System Operation

The control station is housed in a 14" D x 11" W x 7" H enclosure with a carrying handle. A diagram of the front panel layout is provided in figure 5. The control station has two "modes" of operation determined by a front panel switch; a scan mode and a manual mode. A second switch enables or disables the stand-off circuit interlock feature described previously. Calibration is provided by two multi-turn potentiometers which provide for adjustment of signal gain and offset. For signal display a 3 1/2 digit panel meter is used in both manual and scanning mode. An additional 20 segment bar graph meter is also enabled during scanning operation to provide contamination level trend information which would be difficult to observe from the numerical meter alone. Two indicator lamps are also mounted to the front panel; one illuminates when the 3 1/2 digit meter is updating the signal data, the other illuminates when the argon supply pressure drops below 10psi. In this condition the UV lamp is powered down in order to minimize the build-up of possible contaminants in the lamp chamber and on the collector grid due interactions between the UV light and the atmosphere. When the argon pressure is restored, the argon umbilical line and lamp chamber are purged and the UV source is automatically powered back up.

To manually measure surface contamination, the operator places the unit into manual mode and positions the probe over the substrate until the three stand-off pins are in contact with the surface. For metal surfaces, the interlock switch is generally enabled and the operator verifies the proper position via the illumination of the stand-off LED on the sensor probe. At the operator's discretion, the trigger on the sensor handle is pressed which initiates a measurement cycle. First, the measurement region is purged with an argon "burp". Next the optical shutter below the reflector is opened and the system allowed to stabilize. The OSEE signal is then sampled and the 3 1/2 digit meter is updated to reflect the latest reading. The display remains fixed until another measurement is taken. The entire process is performed in approximately two seconds and is independent of the duration of the trigger time, although another sample cannot be taken until the cycle is complete and the trigger released. The OSEE signal is also present at the "signal out" jack at the rear of the control station. A "trigger out" signal on a second output indicates to an external data acquisition system when valid data is present at the output. In addition, an "external trigger" input is provided at the rear to allow for an alternate means of generating the trigger signal. This would allow for a robotic system attached to the probe to perform spot check measurements on the surface under inspection.

When the system is placed in the scan mode, argon is continuously supplied to the measurement region and the shutter is opened indefinitely. This allows the probe to be mounted in a continuous scanning system for overall mapping of the substrate. A proximity sensor may be attached to the probe to

maintain the correct stand-off distance. The interlock signal is ignored by the control station and the stand-off pins may be removed with conventional pliers. In scan mode the 3 1/2 digit meter is continuously updated at the maximum sample rate of the meter (approximately 2 samples per second), and the bar graph meter, which updates at greater than 200 samples per second, is turned on. The OSEE signal is again available at the rear of the control station.

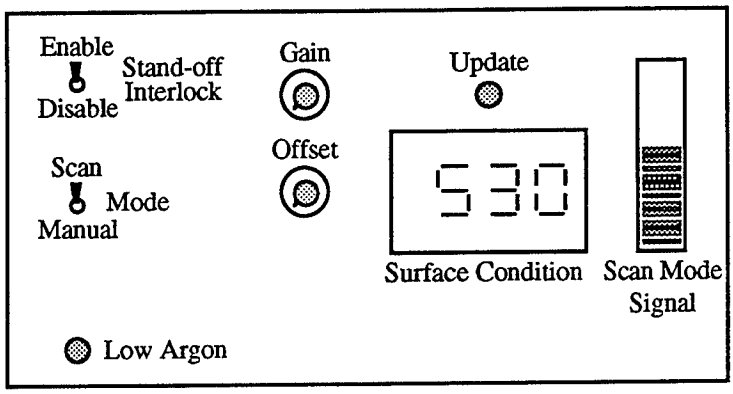

Figure 6. Front and View of Control Station

Safety Issues

Because of the potential shock hazard from the high voltage lamp and grid power supplies, several safety features have been included in the design. First, the 200V DC grid bias is resistively decoupled from the exposed collector grid through a 1 MΩ resistor. This, together with the very low input capacitance of the electrometer circuit eliminates the potential for electric shock from accidentally touching the collector grid. However, fingerprints and other foreign matter on the collector grid will result in erroneous readings. For the lamp power, an interlock system is employed which automatically shuts off the lamp power supply if lamp power connector to the umbilical is removed.

Acknowledgments

The development of this instrument was funded by the NASA Office of Safety and Mission Quality. The author wishes to thank B. H. Nerren and H. D. Burns of MSFC, O. Huddleston of Thiokol Corp., and R. E. Booth and C. K. Caldwell of AC Engineering for their assistance in the development of the system requirements; C. S. Welch of the College of William and Mary, E. Scales and T. M. Goodman of Analytical Services and Materials, and J. Bly of Lockheed Martin Co. for their assistance in the design, fabrication, and testing of the instrument.

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August 9, 1996 Huntsville, Alabama

STUDY OF SRM CRITICAL SURFACES USING NEAR INFRARED OPTICAL FIBER SPECTROMETRY

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ABSTRACT

The measurement and control of cleanliness for critical surfaces during manufacturing and in service operations provides a unique challenge in the current thrust for environmentally benign processes. Of particular interest has been work performed in maintaining quality in the production of bondline surfaces in propulsion systems and the identification of possible contaminants which are detrimental to the integrity of the bondline. This work requires an in-depth study of the possible sources of contamination, methodologies to identify contaminants, discrimination between contaminants and chemical species caused by environment, and the effect of particular contaminants on the bondline integrity of the critical surfaces.

This presentation will provide an introduction to the use of Near Infrared (NIR) optical fiber spectrometry in a nondestructive measurement system for process monitoring and how it can be used to help clarify issues concerning surface chemistry. In a previous conference,(1) experimental results for quantitative measurement of silicone and Conoco HD2 greases, , and tape residues on solid rocket motor surfaces were presented. This paper will present data for metal hydroxides and discussthe use of the integrating sphere to minimize the effects of physical properties of the surfaces (such as surface roughness) on the results obtained from the chemometric methods used for quantitative analysis.

INTRODUCTION

Optical fiber spectrometry offers unique capabilities for detection and identification of contaminating species on aerospace flight hardware and other critical surfaces, either stand-alone or in conjunction with other inspection processes. Much progress has been made in understanding spectral features observed from surface films with optical fiber probes, yet the interpretation of spectral features on surfaces continues to be the major challenge for this spectrometric tool. The complexity of the interactions due to thin film reflection/absorption phenomena still requires some chemical and physical knowledge about the surface being analyzed. In addition considerable expertise is still required to sort through the spectral features obtained, to pick out the significant features and determine the origin of these features. It is anticipated that the evolving methodologies resulting from the work presented here, will become more easily absorbed into the production arena with increased emphasis on the development and implementation of NIR systems.

This paper results from continuing work with the Surface Contamination Analysis Team (SCAT) at NASA/MSFC and with Thiokol RSRM group, providing the opportunity to apply the capabilities of optical fiber NIR techniques to the following cases:

- HD2 and silicone films on D6AC steel and 7075 aluminum
- Mixtures of HD2 and silicone films on D6AC steel and 7075 aluminum
- D6AC steel, 7075 Aluminum and Lithium Aluminum plates in controlled temperature and humidity environments for extended periods of time.

The primary results of these observations was been to show that NIR spectrometry is able to:

- Discriminate between HD2 and silicone greases in single or mixed applications, both qualitatively and quantitatively.

- Detect the various water/hydroxide species that occur on both D6AC steel and aluminum alloy surfaces under variable humidity and temperature conditions.
- Detect levels of contamination by tape residues used in the manufacturing operations of the RSRM.

Optical Fiber Spectrometry Considerations:

Optical fiber spectrometry is a very flexible analytical tool which provides a number of challenges for accurate surface analysis. A number of the factors which can affect the signals observed, and correspondingly the interpretation of its chemistry, are shown in Figure 1 below.

Figure 1. Factors affecting the interpretation of spectra observed from surfaces.

FACTORS AFFECTING OPTICAL FIBER SPECTRA

- **REFLECTION-ABSORPTION RELATIONSHIPS**
- **CHEMICAL ENTITIES - Molecular, Chemisorbed, or Reaction-Products**
- **SURFACE FEATURES**
- **PROBE CHARACTERISTICS**
- **SPECTRAL SCAN PARAMETERS**
- **DATA PROCESSING ROUTINES**

The underlying physics associated with the reflection/absorption characteristics of the many types of films which may occur on a surface are always going to be part of the unknown in any analysis performed on solid rocket motors. Objectively, the data processing techniques used in this work, have been oriented such that these phenomena can be categorically factored to provide spectral features associated with both the chemical species and/or physical parameters represented on the surface. These chemical entities can be oxides, hydroxides, or any other materials. In the spectral region in which this work has been performed, 1.0 - 2.5 microns, -OH stretching vibrations are the major peaks observed for species which result from hydrolysis or hydration. These spectral bands represent the second harmonic or combination bands of features normally observed in the mid-IR using FTIR or other infra-red instruments. In most cases, -CH stretching vibrations are also observed in this region as combination bands. This observation, for example, allows us to differentiate between HD2 and silicone greases. Spectral observations in the mid-IR can not always do as well in differentiating between similar species.

In this work, the chemical entities which are observed in the spectral scans are primarily hydrated species which result from the presence of water on the surface of the metal or contaminants purposely placed on the surface. The chemistry associated with hydrolysis of D6AC steel and aluminum 7075, obviously becomes a very important part of the interpretation of the spectra observed in these experiments. In the case of D6AC steel, very little work on hydrolysis at ambient temperatures has been found in the literature so far. Aluminum; however, provides a large number of data presented in the literature which makes the interpretation of the spectral observations somewhat easier.

The obvious goal of any spectral analysis is to obtain a quantitative measure of the interaction between the material being analyzed and the light used for interrogation. The physical features extracted in the factor analysis can be difficult to interpret with non-uniform surfaces, presenting another set of problems in the quantitative analysis of films on surfaces. Since the light may specularly reflect off the surface of the film or the surface of the metal more than once, one may obtain spurious intensity relationships from the spectral analysis. Also if the light reflected off the surface has passed through the film more than once, then one has difficulty providing a quantitative measurement of the properties of the film. In the case of the materials used in this study, solid rocket

motor case materials were not intended to have mirror finishes, hence, diffuse scattering from randomly oriented surface features encompasses the primary thrust of this work. In general most the panels provided for spectral analysis had varying surface roughness and reflectivity, making calibration one of the more difficult tasks in the study.

Since optical fiber spectrometers normally operate in a single beam mode, much use is made of signal enhancement methods for precise work. A summary of the path used to optimize upon the analytical approach used are presented in figure 2 below. In addition to the enhancement of the desired signals using physical improvements related to the optical and scan parameters, improved software approaches have also been used during this work, primarily in the use of chemometrics techniques to extract the useful information contained in a series of spectra acquired from the various samples under test. These methods fall under the category of multivariate analysis techniques and are used very successfully in a number of chemical and process industries. For example the idea is to analyze all the relevant spectral data at once and extract features which dominate the behavior of the data set. This is shown in figure 3 on the next page, in which the accumulated spectral data is analyzed by a multivariate analysis technique and the loadings (spectral features) and scores (influences) are extracted to determine how the system is changing chemically. This analysis is currently being performed with the Unscrambler II™ software developed by CAMO.(2)

Figure 2. Data analysis concepts used in this work

DATA ANALYSIS CONCEPTS

- Experimental Contraints
  - Low signal levels
  - Variable reflectivity among samples
  - Silica spectral domain
- Digital Filtering
  - Savitsky-Golay Smoothing Routines
- Principal Component Analysis (PCA) and Partial Least Squares (PLS)
  - Provide number of factors that influence the observed spectra
  - Identify the real factors
  - Detect clusterings of data
  - Identify spectra due to each factor
  - Predict new data and/or verify model

The procedures followed in obtaining spectral data and performing the analysis were fairly consistent. Deviations in the use of specific routines for data smoothing or to bring out certain anticipated features were implemented as required. Once a series of NIR spectra were obtained from the experiments described in this report, a variety of of chemometric techniques were employed to isolate significant spectral features as facators using either Principal Component Analysis (PCA) or Partial Least Squares (PLS) techniques. Iterative smoothing routines were sometimes performed back-to-back to improve the S/N ratio of the observed spectra. Complementary analysis techniques were used in order to trade off advantages over disadvantages of various techniques. For instance, optical fiber spectral scans were performed with the Guided Wave 260, which can obtain the highest resolution possible either by reducing the spectral bandwidth or by signal averaging. Either choice requires relatively longer scan times. Hence trade-offs between resolution and scan time had to be used in optimizing spectral scans with scans of other instrumentation in the studies performed in the environmental chamber. At the level of resolution used, sequential smoothing routines allow for good spectral definition.

The major software used to support this work included SpectraCalc and Unscrambler II. Typically spectra were recorded in units of watts and transformed into absorbance using the relationship:

$$A = \log \frac{I}{I_{ref}}$$

Much work was spent in the beginning of the research in determining what reference surfaces to use for calculating absorbances. The major problem that arises in this type of analysis is when a spectral feature goes negative; i.e. $I < I_{ref}$ then most of the matrix multiplication techniques are not applicable. In practice, a negative absorbance is undefined, which means that the reference is not valid. Several reference surfaces used in this work include an aluminum or gold mirror; i.e. totally or specular reflecting; barium sulfate i.e., diffuse reflecting, and native surfaces such as D6AC steel or aluminum alloys.

Experimental Results:

The results of three different experiments are reported here. The occurrence of either a contaminating substance or a naturally occurring process film, such as oxides and hydroxides, that can degrade a critical bond need to quantitatively determined. The three experiment reported here are concerned with the quantitative identification of hydroxide and oxide films on D6AC steel, 7075 Aluminum, and AlLi alloy . Since the manufacturing facilities for RSM's provide a number of opportunities for these films to occur on critical bonding surfaces, an inspection technique to quantify both of these films will be beneficial for determining the effect of these films on bonding. For each of the alloys, a set of panels were vapor degreased and grit blasted prior to placing in the environmental chamber. The D6AC and 7075 panels were processed using two grit blast angles, 90° and 20°. This variation was included in the test matrix to determine the effect of grit blast angle on bonding for a Thiokol in-house project. NIR spectra of the panels obtained and analyzed with the PLS1 methodology.

Another series of experiments looked at the surface chemistry of D6AC steel and 7075 Aluminum plates in controlled temperature and humidity for extended periods of time to determine the effects of relative humidity, temperature and grit blast angle on the bonding characteristics of both D6AC steel and Aluminum 7075. In both sets of experiments, spectra subtraction between any two spectra showed peaks in the -OH vibration region that varied throughout the experiments. In the case of the D6AC steel, the lack of knowledge of what spectra l features to expect made evaluation difficult. Aluminum has been studied substantially more and does provide spectral features which can be predicted from the literature.(3-11) The chemistry of the aluminum-water system has been studied substantially more than that of the D6AC-water system. Hence there is a considerable amount of information available in the literature on the various oxides and hydroxides associated with aluminum and its alloys.

The Alcoa report(12) contains considerable information about the chemistry associated with this system. Of the various hydroxides which form in the presence of water, bayerite is considered by most to be the most stable form of $Al(OH)_3$ which will persist as a crystalline surface film. On the other hand Boehemite or psuedo-Boehemite (consisting as an amorphous film) is recorded to the precursor in the reaction kinetics with aqueous environment. Consequently, in order to interpret the spectral results of the aluminum alloy system, one needs to take into account the known chemistry of aluminum hydroxides and oxides. In addition one can then determine the bonding characteristics associated with the presence of these films for use in optimizing the bonding processes in production. A complete analysis of the chemistry cannot be provided at this time due the need to perform a number of other experiments to substantiate these results.

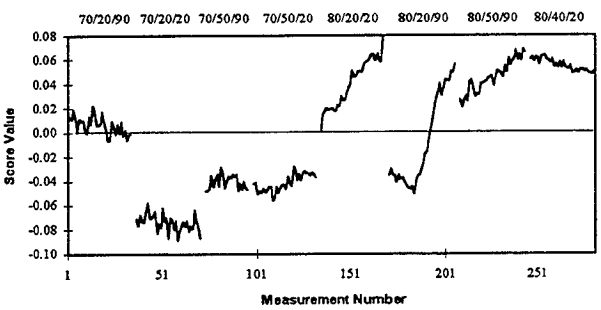
Consequently more substance has been given to the PLS analysis in trying to interpret the observed spectral features. In each case the total collection of spectra for one substrate has been amassed into one data set to generate a PLS model. In both cases, the principal components which appeared as the primary factor was grit blast angle, showing that surface features had the most influence. In the D6AC experiments temperature and relative humidity showed up nicely as factors 2 and 3, with prominent spectral features assigned to double harmonics of OH stretching bands. These spectral features varied throughout the test to provide information about the kinetics

of hydroxide formation as shown in the scores plot in Figure 3a. The three numbers across the top of the chart define the variable conditions in the order: grit blast angle/ temperature/relative humidity. The corresponding spectral features shown in Figure 3b, have been reproduced in several data sets where OH formation is possible. For the aluminum data set, the temperature and relative humidity did not separate out quite as nicely, indicating that the interpretation for the aluminum-water chemistry is obviously quite complex. Fortunately; however, the chemistry has been well studied and the literature does provide more information than the D6AC chemistry. For instance, the growth kinetics of bayerite is fairly well reproduced by the NIR data obtained in the environmental chamber studies.(9)

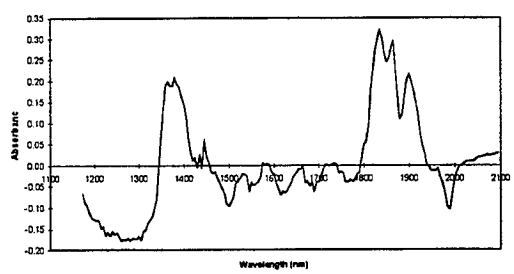
As mentioned above, the early experiments on the environmental effects of D6AC and AL7075 were run with optical fiber pick-ups that were very sensitive to surface topology because the area coverage per scan was very small (~ 5 mm^2) The most influential feature obtained in that experiment was the grit blast angle. Recent experiments used an integrating sphere (~6 mm^2) to pick up the surface reflections and eliminated the grit blast angle as an experimental variable. Since the formation of hydroxides and oxides is kinetically controlled by both temperature and humidity, these experimental variables are still prominent. The scores for factor 3 show that the spectral features contained in the loadings for factor 3 increase progressively throughout the experiment. Hence the kinetics of the OH formation can be obtained from these loadings.

Figure 3. Scores and loadings for D6AC steel obtained during temperature and humidity experiments.

a. Scores for Factor 3.

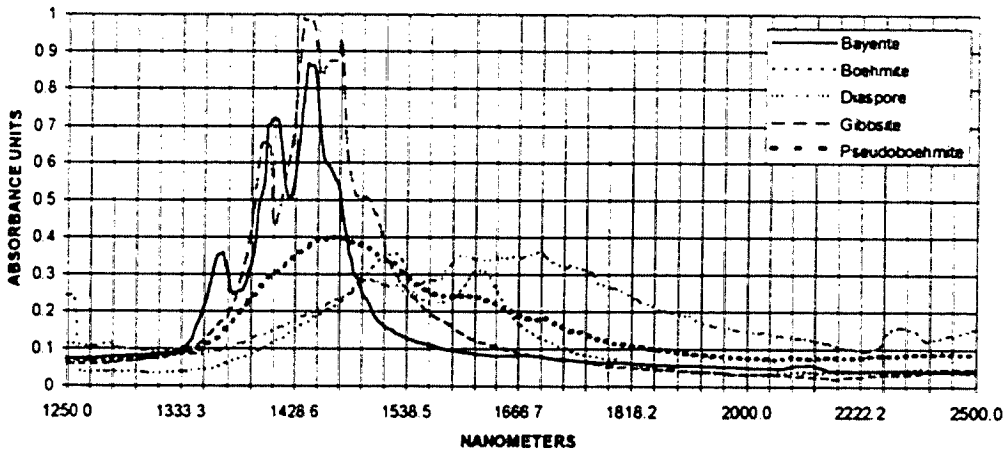


b. Loadings for Factor 3.



Identification of these spectral features were attained through frequency doubling of mid-infrared spectra obtained in the literature. The spectral features around 1.4 microns previously assigned to bayerite compare favorably in band shape and band energies when compared to the loadings for factor 3. The frequency doubled bands for the various aluminum hydroxides is given in Figure 4 below. Note that the spectral feature around 1.8 microns could be

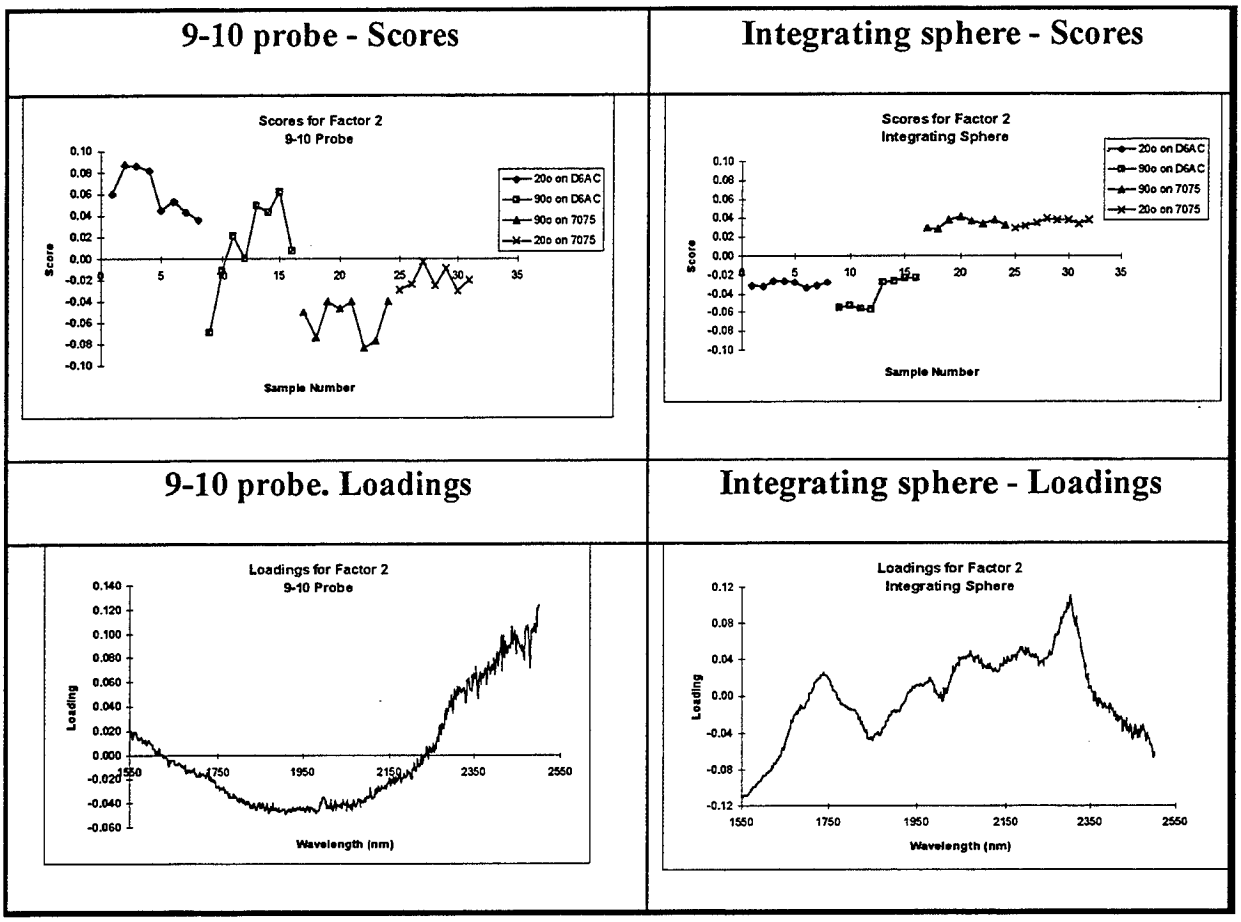
Figure 4. Frequency doubled bands for aluminum hydroxides.



the second order Gibbsite peak, indicating the presence of a mixture of hydroxides.

A major improvement in the ability of the system to work with grit blast surfaces was attained through the use of an integrating sphere. Multiple Scattering Correlation techniques were used to on the hydroxide data; but this technique did not reduce the influence of the grit blast angle significantly. The physics of scattering appeared to be better handled by physically reducing the importance of the diffuse scattering effect of the grit blasted surfaces with an integrating sphere approach. The differences noted by use of the integrating sphere are shown in the following graphs in Figure 5:

Figure 5. Comparison of scores and loadings with 9-10 probe and with integrating sphere.

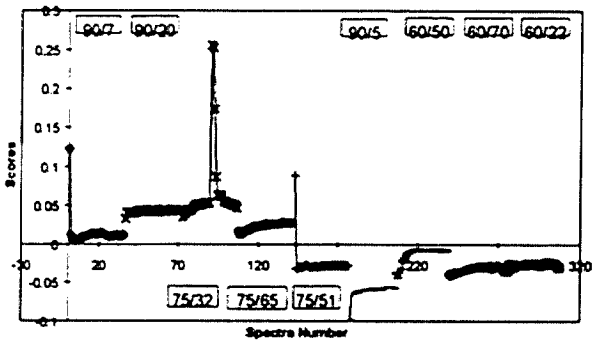


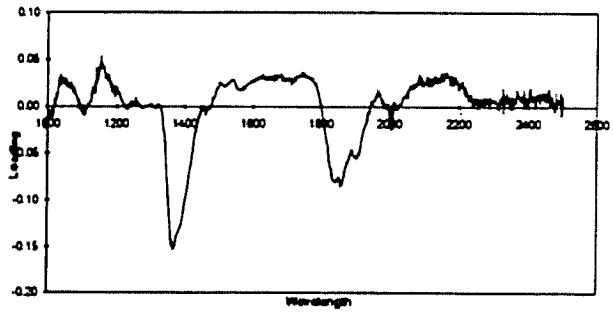
Note that the features using the integrating sphere resemble spectral peaks more closely than that from the 9-10 probe. The spectra obtained for the third factor is the same as originally obtained using the 9-10 probe. These comparisons show that the influence of the grit blast angle on the PLS model is significantly reduced by the use of the integrating sphere.

New experiments using LiAl alloys were run much recently. Similar environmental variables ere included in the test matrix as the Al7075 experiments, except only the one grit blast angle of 20° was used. Figure 6 shows the loadings appearing in factor 5 were similar to the Al7075 with virtually no increasing influence with time. The loadings from the PLS analysis quite often will be inverted, but that is just a manifestation of the mathematics. Hence the hydroxide layer was static during the time of the experiment. An anomalous event in the third experiment did occur and is still unexplained. Developing a PLS model of only the first readings gave a similar result, indicating that the main spectral features related to the hydroxyl formation were present at the time of the first scan. Hence the five to ten minutes that it took to grit blast the sample, take it to the environmental chamber and initiate the NIR spectrum was all that was needed to obtain the NIR features associated with the hydroxides. The effect of the Li in the Al matrix does provide a more reactive surface for the formation of the hydroxides.

Figure 6. Scores and Loadings for AlLi Alloy.

Scores for Factor 5 Loadings for Factor 5





Summary

NIR spectrometry can provide a useful tool for the inspection of critical surfaces and the quantitative detection of contaminating materials. The utility of optical fiber system allows for flexible approach to using NIR in untraditional applications. In conjunction with chemometric tools, like PCA or PLS, the on-line approach is quite feasible and can provide a useful supplement to other inspection techniques.

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Development and operation of a material identification and discrimination imaging spectroradiometer

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ABSTRACT

Many imaging applications require quantitative determination of a scene's spectral radiance. This paper describes a new system capable of real-time spectroradiometric imagery. Operating at a full-spectrum update rate of 30Hz, this imager is capable of collecting a 30 point spectrum from each of three imaging heads: the first operates from 400 nx m to 950 nm, with a 2% bandwidth; the second operates from 1.5 µm to 5.5 µm with a 1.5% bandwidth; the third operates from 5 µm to 12 µm, also at a 1.5% bandwidth. Standard image format is 256 x 256, with 512 x 512 possible in the VIS/NIR head. Spectra of up to 256 points are available at proportionately lower frame rates. In order to make such a tremendous amount of data more manageable, internal processing electronics perform four important operations on the spectral imagery data in real-time. First, all data in the spatial/spectral cube of data is spectro-radiometrically calibrated as it is collected. Second, to allow the imager to simulate sensors with arbitrary spectral response, any set of three spectral response functions may be loaded into the imager including delta functions to allow single wavelength viewing; the instrument then evaluates the integral of the product of the scene spectral radiances and the response function. Third, more powerful exploitation of the gathered spectral radiances can be effected by application of various spectral-matched filtering algorithms to identify pixels whose relative spectral radiance distribution matches a sought-after spectral radiance distribution, allowing materials-based identification and discrimination. Fourth, the instrument allows determination of spectral reflectance, surface temperature, and spectral emissivity, also in real-time. The spectral imaging technique used in the instrument allows tailoring of the frame rate and/or the spectral bandwidth to suit the scene radiance levels, i.e., frame rate can be reduced, or bandwidth increased to improve SNR when viewing low radiance scenes.

The unique challenges of design and calibration are described. Pixel readout rates of 160 MHz, for full frame readout rates of 1000 Hz (512 x 512 image) present the first challenge; processing rates of nearly 500 million integer operations per second for sensor emulation, or over 2 billion per second for matched filtering, present the second. Spatial and spectral calibration of 65,536 pixels (262,144 for the 512 x 512 version) and up to 1,000 spectral positions mandate novel decoupling methods to keep the required calibration memory to a reasonable size. Large radiometric dynamic range also requires care to maintain precision operation with minimum memory size.

1.0 INTRODUCTION

Over the past three years, Surface Optics Corporation (SOC) has developed extensive experience in the field of real-time imaging spectroradiometry. During 1992, SOC developed a visible/near-IR band imaging

spectroradiometer, capable of collecting a 30 point spectrum at each pixel in a 256 x 192 image in only 1/15th of a second. At the same rate that the instrument collects data, it also spectroradiometrically calibrates every point in the 1.5 million point cube of data; after data has been properly calibrated, each pixel's spectral radiance is then weighted by an arbitrary spectral response function and integrated spectrally, thereby allowing the instrument to emulate any VIS/NIR band sensor. Six such response curve convolutions can be performed simultaneously. Default curves produce the CIE tristimulus values on three channels, and RGB for display to a video monitor on the other three.

Building on the experience gained from this VIS/NIR imaging spectroradiometer, SOC has teamed with the Jet Propulsion Laboratory (JPL) to develop a second generation version of the VIS/NIR instrument. Capable of collecting up to 256 spectral points simultaneously from each of three spectral imaging heads covering the range from near-UV to long-wave IR, this new instrument implements real-time calibration and arbitrary response convolution, but also implements a much more powerful exploitation of the spectral data. A desired spectral radiance distribution may be entered into or measured by the instrument; by then selecting one of a wide variety of spectral-matched filtering algorithms, the instrument filters each pixel's spectral radiance against the sought-after radiance, showing matching pixels as bright, and mismatched pixel's as dim. Filtering algorithms range from very broad filters, requiring only basic similar shape for match, to very narrow filters, requiring close match of spectral features. The instrument is capable of collecting up to 30 spectral points from each head in only 1/30th of a second when using 256 x 256 imaging format, or up to 20 spectral points in the same time when using a 512 x 512 imaging format. Ultimate development of the instrument will also allow real-time compensation of atmospheric effects, and determination of temperature and spectral emissivity/reflectivity. SOC and JPL are currently working under contract with the U.S. Army Armament Research and Development Engineering Center (ARDEC) at Picatinny Arsenal to develop the first phase of this instrument, which will use one of the imaging heads to provide coverage from 1.5 μm to 5.5 μm.

2.0 INSTRUMENT DESCRIPTION

A detailed technical description of the instrument is presented below. Figure 1 presents a conceptual drawing of the ultimate 400 nm - 30 μm instrument, with three heads attached to a single processor. As illustrated schematically in Figure 2, basic design of a Multiband Identification and Discrimination Imaging Spectroradiometer (MIDIS) is straightforward, allowing construction of a compact, rugged, easily producible instrument. The instrument comprises four main sections. First, raw spectral images are gleaned by a continuously variable narrowband IR filter-based imaging spectrometer at up to a 1000Hz rate. Second, raw image data is collected, spectro-radiometrically calibrated, and processed by a high-speed processing section. Third, data is formatted as standard RS-170 analog video data or as high speed 12-bit digital data by an output processing section. Fourth, overall system operation is monitored and controlled by a system controller which also communicates to an external computer over standard serial or parallel busses.

All functions of the instrument, e.g, CVF speed, integration time, iris, have both an automatic and manual mode. In the automatic mode, the system controller determines the optimum settings for the instrument based on scene spectral radiances and dependent on other conditions already set by the operator, such as minimum allowable frame rate. In the manual mode, the operator sets the desired parameter to a given value through one of the interface busses, or through the back panel interface. These two modes allow for complete flexibility in instrument control, from fully autonomous operation, to completely manual control.

In either case, output from the instrument is fully spectro-radiometrically calibrated, unlike current spectro-radiometers which generally rely on an external computer for calibration and processing. Realizing that spectral images in-and-of themselves are only partially useful, SOC's instrument includes two very powerful processing modes. First, any desired spectral response function can be loaded into the instrument. Internal electronics will then integrate the product of the response curve and the measured spectral radiances to allow emulation of any type of SWIR/MWIR sensor system (or ultimately any VIS-LWIR sensor). Three such integrals can be performed and output simultaneously. Second is spectral matched filtering. In this mode, a desired relative spectral radiance to search for is either entered into, or measured by, the instrument.

Several internal matched filtering algorithms can then be employed to filter scene spectral radiances against the desired radiance; any objects in the scene possessing the desired relative spectral radiance will appear bright, while other objects will appear dim. Real-time preprocessing of the calibrated data will also allow determination of pixel temperature and spectral emissivity/reflectivity.

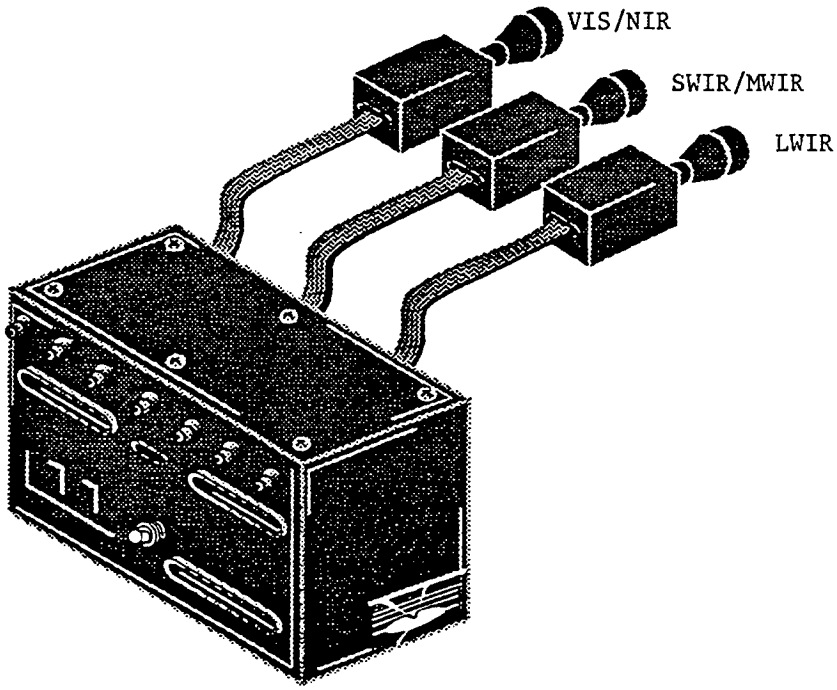

Figure 1. Multi-Band VIS-LWIR Imaging Spectroradiometer.

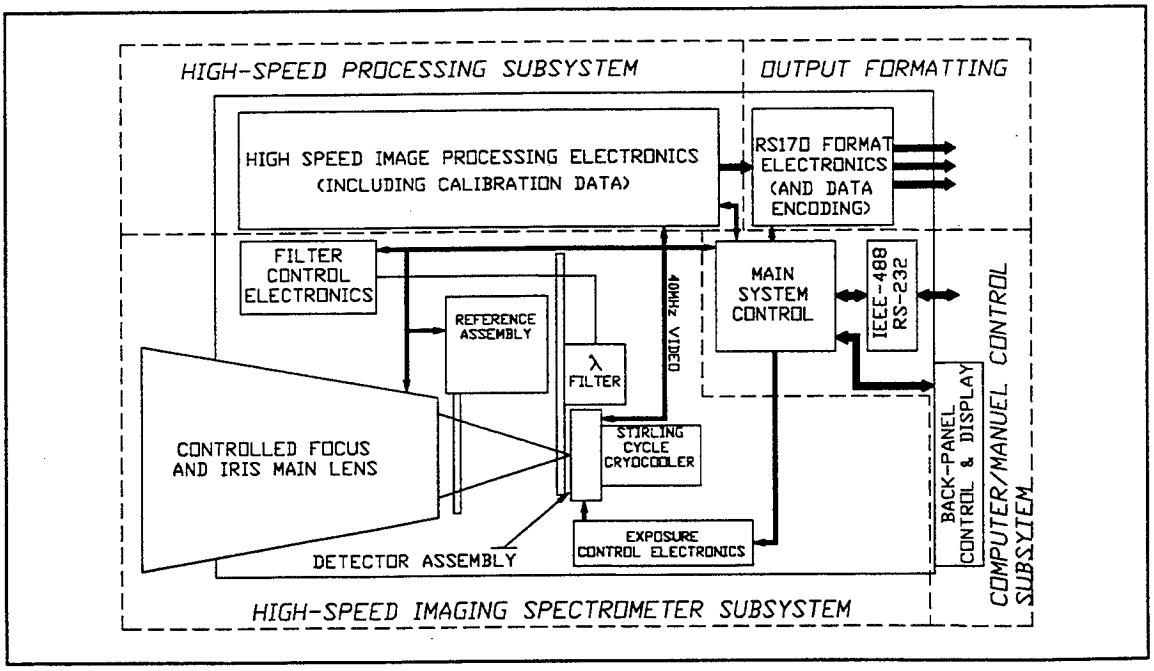

Figure 2. Schematic Overview of Imaging MWIR Spectroradiometer.

2.1 Imaging Spectrometer Detailed Description

The first step in generating and processing spectro-radiometric imagery is capturing raw spectral images. SOC and JPL are developing a circularly variable filter-based (CVF) spectral imager operating from about 1.5 μm to about 5.5 μm, analogous to SOC's already developed visible-band instrument.

2.1.1 Spectral Image Collection

Spectral information is gleaned by a narrow-band SWIR/MWIR circular variable filter. Comprising two segments, this filter varies its center wavelength from approximately 1.5 μm to 5.5 μm as it rotates 360°, and has a passband of approximately 1.5% FWHM of the center wavelength. Position of the filter is encoded to 4,095 points per revolution, ensuring accurate determination of exact wavelength being viewed. A 1.5% filter will see a negligible increase in its bandwidth when used in a fast F/1.8 system (cone angle =±15.5°). Hence, the imaging spectrometer portion of this instrument has tremendous light gathering capability. The CVF is also temperature stable, exhibiting a center wavelength change of only about 70ppm/°C, or only ±0.6% over the temperature range of -55°C to 125°C. This is less than half a bandwidth change, or only 15 nm at 2500 nm for extremely harsh environmental conditions.

Output from the CVF is imaged onto an area detector array, providing the spatial imaging of the system. The array is a 16-port 256 x 256, variable exposure, InSb array with a maximum exposure rate of 1,200 exposures per second. To compensate for band-to-band variances in spectral radiance and to effectively freeze the CVF's rotation, controllable integration time is necessary. Several different approaches can be used to effect variable integration time. In the visible band, this is simple task accomplished merely by gating on and off an image intensifier. In the infrared, such a technique can not be used since no photocathode material is available with a work function as low as a thermally-generated photon's energy. Mechanical shuttering could be used, but a shutter with the required aperture and response time (sub millisecond) would be extremely difficult to develop and likely unreliable; hence, this is not a viable option. Fortunately, electronic techniques can be used to effect variable integration time. The array is a random access photodiode array. Each photodiode integrates charge on an associated capacitor. Analog field-effect transistor switches then allow readout of each pixel. The array offers the ability to reset any sixteen pixels and read any other sixteen pixels in a 200ns clock cycle. Resetting pixels an appropriate number of clock cycles before reading them allows variable integration time. This can be visualized as a window moving through the array, with pixels at the leading edge of the window held in reset, pixels within the window integrating, and pixels at the trailing edge of the window being read out. Integration times are then variable from 1/4096th of the frame time up to the full frame time. At a frame time of 1.6 milliseconds, integration times are variable from 400 ns to 1.6 ms in 400 ns increments.

By placing the detector immediately behind the CVF, dramatic decrease in background noise is realized. Since the CVF achieves its blocking characteristics through reflection rather than absorption, emissivity of the filter is extremely low. Hence, background from the filter reaching the detector is minimal, since close proximity to the detector ensures that the detector sees its own reflection at only 77°K.

2.1.2 Internal Calibration Sources

To allow the instrument to maintain calibration with a minimal amount of laboratory calibration, MIDIS contains an internal reference. SOC is very familiar with the manufacture and use of blackbody sources, as much of our instrumentation employs these sources. For this instrument, a thermo-electrically controlled reference is employed. The reference consists of two blades connected to either side of the cooler; one cooler, then, produces both a hot and a cold reference, both of whose temperatures will be monitored to allow correct gain and offset compensation. Absolute spectro-radiometric calibration data is generated at time of assembly by having the radiometer view a source of known spectral radiance (blackbody). Immediately after this, the internal reference is viewed. By viewing the internal source later, calibration data can be appropriately scaled to compensate for any gain or offset variations.

2.1.3 Spectrometer Energy Throughput

In order to determine the expected performance of SOC's and JPL's proposed MIDIS, detailed analysis of the light gathering capability of the system was performed. Since such analysis is key to the expected performance of the instrument, a brief review of the throughput analysis will be conducted here. A short digression into radiometry will help to clarify how the instrument works. Assume that a detector of area A_p, linear dimension l_p, sits behind a lens of arbitrary focal length F and collecting area A_l, and is viewing a scene a distance D from the lens. Assume also that the scene possesses a spectral radiance $L(\lambda)$ in units of $W/(cm^2 \cdot sr \cdot \mu m)$. The lens will project the detector to an area A_{pp} on the scene. At a distance D from the scene, the lens subtends a solid angle Ω_l. Therefore, total power collected by the system and deposited, neglecting transmission or scattering losses, on the detector is $L(\lambda)A_{pp}\Omega_l$. Here, Ω_l was assumed small. If the angular distribution of radiance were to change significantly over the angle subtended by the lens, then explicit integration of spectral radiance over the lens's subtended angle would have to be performed. The preceding notation, however, is not easy to use since both A_{pp} and Ω_l depend on the distance D to the object. Introduce a new parameter, Ω_p, the solid angle subtended by the detector (pixel) at the focal distance from the lens. All these quantities are shown in Figure 3.

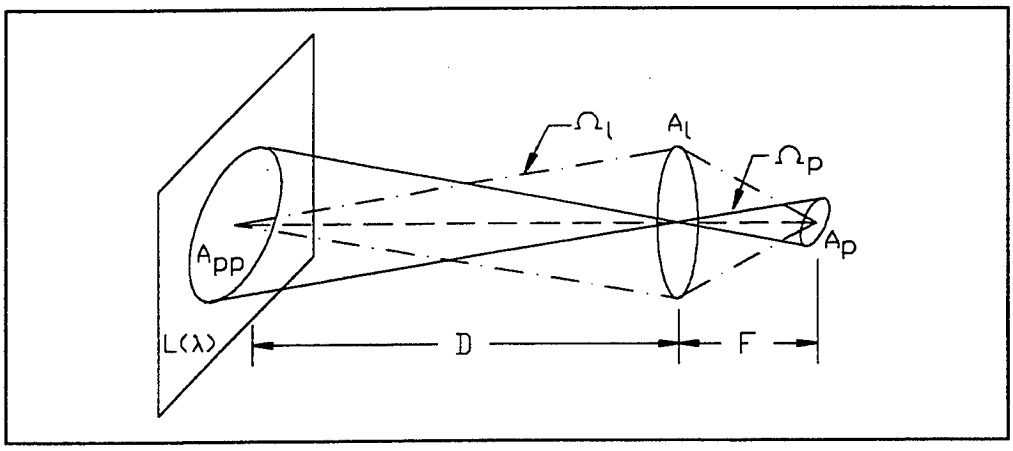

Figure 3. Definition of Terms for Energy Collection Analysis.

A simple derivation will show that given the condition of D >> F (i.e., image plane and focal plane of lens nearly coincident), and $l_p << F$, then the product $A_{pp}\Omega_l \approx A_l\Omega_p$, with the degree of approximation being dependent on the relative magnitudes of F, D, and l_p. For example, an F/1.8 lens with F = 55mm viewing a scene 1 meter away and illuminating a pixel 38 μm on a side, will have a $A_l\Omega_p$ product which is only .022% greater than the actual collection product of $A_{pp}\Omega_l$.

With the above description in mind, neglecting path radiance contributions for now, the spectral power incident on a given pixel in the imaging array, through an optical train of transmission $T_o(\lambda)$, through atmosphere of transmission $T_a(\lambda)$, but without any spectral filtering is

$$P(\lambda) = L(\lambda)\ \Omega_p\ A_l\ T_o(\lambda)\ T_a(\lambda) \qquad [\frac{W}{\mu m}] \quad .$$

If now a spectral filter with response function at λ_c of $F(\lambda,\lambda_c)$ is introduced into the optical train, the total power striking a pixel is

$$P(\lambda_c) = \int L(\lambda)\ A_l\ \Omega_p\ T_o(\lambda)\ T_a(\lambda)\ F(\lambda\ ,\ \lambda_c)d\lambda \qquad [W] \quad .$$

If the detector has a quantum efficiency $\eta(\lambda)$, and the pixel is exposed to the above power level for an integration time of Δt, then the total number of electrons collected by a pixel is

$$N_e(\lambda_c) = \int \frac{L(\lambda)\, A_l\, \Omega_p\, T_o(\lambda)\, T_a(\lambda)\, F(\lambda, \lambda_c)\, \eta(\lambda)\, \Delta t}{h\, \frac{c}{\lambda}} d\lambda \qquad [number] \quad .$$

Here, the division by hc/λ converts a spectral radiance to a spectral photon radiance. This is the desired throughput equation for a generalized spectro-radiometer. Also note that given a focal length F much greater than pixel dimension l_p, the product $A_l\, \Omega_p$ for a lens of f-number F/no can be rewritten as

$$A_l\, \Omega_p = \left[\frac{\pi\, l_p}{4\, F/no}\right]^2 \qquad [m^2 \cdot sr] \quad .$$

2.1.4 Spectral Imager Noise Levels

To correctly quantify system performance, an expression for the radiometer's noise level must also be generated. Four main sources were considered, namely signal shot noise, background shot noise, detector noise, and readout noise. Total noise, σ_{total}, is the RSS sum of these uncorrelated sources. By translating this RMS noise electron level back through the imaging system, a Noise Equivalent Spectral Radiance (NESR) can be generated as:

$$NESR(\lambda_c) = \frac{\sigma_{total}\, h \cdot c}{A_l\, \Omega_p\, \Delta t \int T_o(\lambda)\, T_a(\lambda)\, \lambda\, F(\lambda, \lambda_c)\, \eta(\lambda) d\lambda} \quad .$$

Figure 4 shows the target's spectral radiance and MIDIS's predicted NESR when viewing a 25°C sunlit grass field through a 1 km horizontal atmospheric path. Integration time is used as a parameter.

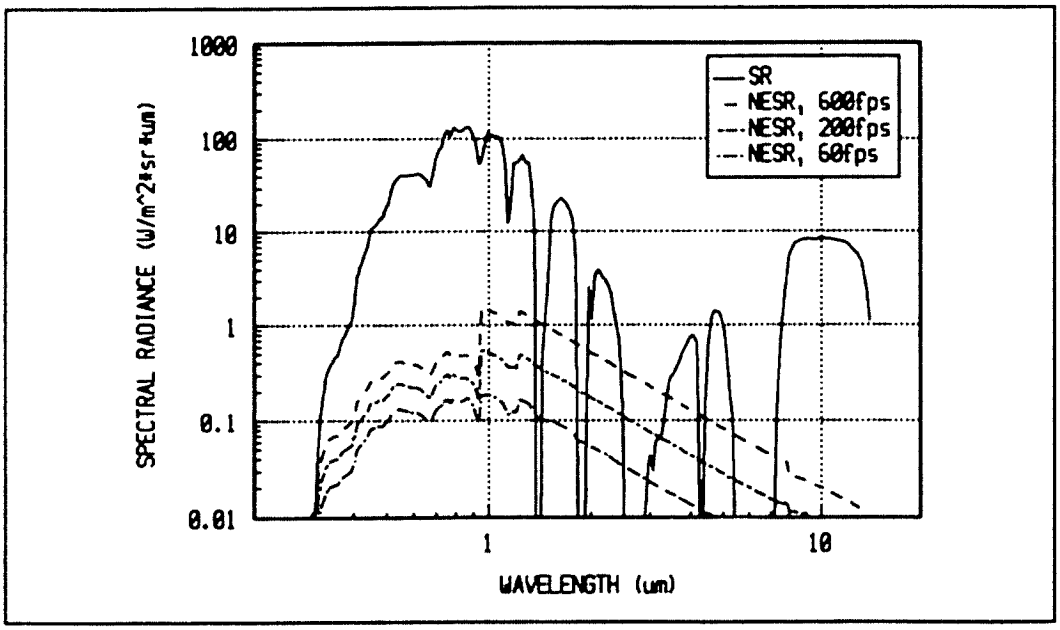

Figure 4. NESR and Target Radiance for Spectral Imager.

2.2 Processing Electronics

To this point, much explanation has been given to generating raw spectral images. Generation of images, however, is only a small part of the real goal of generating useful discriminants which can be used to classify, identify, track, or otherwise monitor a desired object. In order to generate useful discriminants from raw data, additional processing is necessary. Having a compact, high-speed spectral imager is of little use if a stand alone super-computer is necessary to process the data at the same rate as the imager generates it, or if a standard processor can process at only a fraction of the generation rate.

In order to effectively exploit the spectral images generated by MIDIS's imaging spectrometer, SOC's instrument includes a high-speed processing section. In addition to spectro-radiometrically calibrating each spectral and spatial pixel at the same rate that they are generated, the instrument further processes the spectrum for each spatial pixel, allowing real-time implementation of spectral response integration and spectral matched filtering. Pre-processing the calibrated data will ultimately allow real-time compensation for atmospheric effects and for determination of surface temperature and spectral emissivity/reflectivity. Spectral response integration allows the instrument to emulate any desired SWIR/MWIR imager by integrating the measured spectral radiances with any arbitrary response curve, so that the output at a given pixel, SE(p), is given by

$$SE(p) = \int L(\lambda, p)\, R(\lambda)\, d\lambda \quad ,$$

where $R(\lambda)$ is the spectral response curve of the sensor being emulated. SOC's visible-band instrument performs six such integrals simultaneously; MIDIS, however, performs three simultaneously. An even more powerful processing operation implemented by the instrument is spectral matched filtering. Here, a desired relative spectral radiance to filter for is loaded into the instrument, either by direct measurement or through an interface bus. Several different filtering algorithms with varying degrees of sensitivity can then be implemented to filter each pixel's spectral radiance against the sought after radiance, with matching pixels appearing bright, while mismatched pixels are dim. A few of the possible algorithms are described below.

The dot product is a very simple filtering algorithm that treats each spectral radiance as an N-dimensional vector and simply computes the dot product of the two vectors. Formally, this algorithm is given by

$$C_{DOT} = \frac{\sum L(\lambda_n) \cdot F(\lambda_n)}{\sqrt{\sum L(\lambda_n)^2 \cdot \sum F(\lambda_n)^2}} \quad ,$$

where $L(\lambda_n)$ is the measured spectral radiance at the nth wavelength, and $F(\lambda_n)$ is the filter spectral radiance at the nth wavelength. A major problem with this algorithm is that it is extremely broad. That is, the measured and filter radiances need only have roughly the same shape in order for the dot product to produce a high correlation value. The dot product generates the cosine between the two vectors acted upon by the algorithm. An N-dimensional vector can lie in any one of 2^N possible dimensional sectors, e.g., a three dimensional vector can lie in any one of 8 octants. Spectral radiances, however, are always positive, constraining radiance vectors to all lie in only one of their 2^N sectors. Hence, all vectors are necessarily forced to point in the same general direction, with the forced match becoming greater as more spectral points are added. How, then, can a tighter filter be implemented while still retaining spectral features?

The zero-mean dot product accomplishes this task. By removing the mean value from each spectral point, the shape of the spectral radiance curve is maintained, but the new zero-mean spectral radiance vector can now lie in any of the 2^N sectors of its N-space. Performing a dot product on the zero-mean radiance vectors then gives a tighter matching algorithm. This algorithm is given formally by

$$C_{ZMDOT} = \frac{\sum (L(\lambda_n) - \langle L(\lambda)\rangle)(F(\lambda_n) - \langle F(\lambda)\rangle)}{\sqrt{\sum (L(\lambda_n) - \langle L(\lambda)\rangle)^2 \cdot \sum (F(\lambda_n) - \langle F(\lambda)\rangle)^2}} \quad ,$$

where the spectral radiance mean is given by

$$\langle L(\lambda)\rangle = \frac{1}{N} \cdot \sum_{1}^{N} L(\lambda_n) \quad ,$$

and similarly for $\langle F(\lambda)\rangle$. Inspection of the above equation reveals that applying the zero-mean dot product to two spectral radiances is equivalent to treating those two radiances as sets of discrete random variables and computing the correlation coefficient between the two. Both the dot product and zero-mean dot product can also be applied to the derivative of the spectral radiances to further tighten their matching characteristics by simply replacing $L(\lambda_n)$ and $F(\lambda_n)$ in the above equations with $(L(\lambda_{n+1}) - L(\lambda_n))/(\lambda_{n+1} - \lambda_n)$.

In the infrared, the shape of the individual material spectral radiance curves is dominated by the shape of the Planck blackbody function, which reduces the efficacy of the spectral matched filter algorithms described above. To overcome this problem, MIDIS is being designed to ultimately allow real-time determination of surface temperature and spectral emissivity/reflectivity on a pixel-by-pixel basis. Using emissivity or reflectivity in place of true spectral radiance allows much more effective filtering based material characteristics.

These are but a few of the algorithms which SOC's MIDIS performs at the same rate at which image data is collected. Substantial computational power is needed to perform such processing. In fact, to spectro-radiometrically calibrated each pixel in a set of 256 x 256 pixel images 30 spectral points deep at each pixel, generated at 30Hz frame rate requires 131 million calculations per second. To calibrate the data and then evaluate three integrals of the form given by SE(p) above requires over 500 million calculations per second. To match filter using the most complex algorithm available to MIDIS and to perform response curve integration on three channels requires over 2.5 billion calculations per second. Compare this processing rate, albeit fixed-point, to a Cray 1S CFT capable of performing 23 million floating-point calculations per second and the magnitude of the challenge is evident. Electronics designed specifically to perform this task by using pipelined and paralleled processing yield the required processing speed.

3.0 MATCHED-FILTERING EFFICACY DEMONSTRATION

A major goal of the work performed during the phase I SBIR from ARDEC was to demonstrate the applicability and efficacy of spectral matched filtering to spatial contrast enhancement through exploitation of spectral features. Since all materials possess a relatively unique set of spectral complex indices of refraction giving rise to similarly unique spectral reflectances, emittances and transmittances, proper processing of spectral radiances allows material-based discrimination. If a material is to be uniquely identified, then explicit knowledge of the illuminant, of the material temperature, and of the transmittance of any intervening medium (such as the atmosphere) is required. In the case of laboratory or industrial measurements, these quantities can be controlled or directly measured. In the case of remote sensing, spectral distribution of illumination can be quantified fairly easily, and temperature and atmospheric transmittance calculated through appropriate processing. In the case of discrimination rather than identification, however, explicit knowledge of the material sought is not always necessary; rather, only a difference from another object is important. For instance, filtering for the measured radiance of, say, a grassy field will directly show all objects different from the field.

In order to demonstrate the increase in spatial contrast which can be obtained by matched filtering in the spectral domain, SOC procured material samples whose reflectances were measured to identify spectral

features that could be exploited using a spectral imaging camera. Computer simulations were performed to predict the performance of the imaging system and to develop and evaluate spectral processing algorithms. Two types of algorithms were evaluated: spectral matched filtering for spatially enhancing pixels with a desired reflectance spectrum in the image, and temperature and spectral emissivity determination from the pixel spectral radiance data in the image. Finally, a laboratory demonstration of infrared imaging spectroscopy was performed using a broad band, 3-12 micron, thermal imager and a series of discrete filters.

Through discussions with a firm that produces light weight, parabolic reflectors for space applications, graphite composite contamination was identified as an application that could benefit from use of spectral imaging. The manufacture of these reflectors requires surface preparation with chemical etching treatments. The residue left from the chemical etching process affects the adhesion and quality of the subsequent metal deposition on the reflector surface. An imaging spectroradiometer that could identify regions on the reflector surface that are contaminated with the chemical etch residue would be very valuable to quality control.

The composite manufacturer provided a number of samples of their graphite composite materials, some of which were known to be clean, and others known to be contaminated with a silica residue. Figure 5 shows a comparison of the 1.5 to 26 micron reflectance measurements of contaminated (FS6857) and clean (FS6855) samples of the graphite composite material, which shows significant variations in spectral emittance. A broad band, 8 to 12 micron, image of these samples is shown in Figure 6, and shows very little discernable contrast difference between the samples. Note that for display purpose, contrast of the printed image was increased four-fold. Using a spectral matched filtering algorithm, based on five experimental spectral points (4.4, 8, 9, 10.5, and 11.7 microns), demonstrated the capability for spatially enhancing features in the image with specific spectral properties. Figure 7 shows the filtered image using the five point filter derived from pixels on the contaminated sample (FS6857), which dramatically highlights the contaminated samples in the image; note that contrast of this image was not enhanced for printing, unlike the broad-band image. Also note that the two known contaminated samples show different distributions of contaminant; one shows blotchy contamination, while the other shows fairly uniform contamination. The sample on the far right was an unknown sample that also shows signs of contamination.

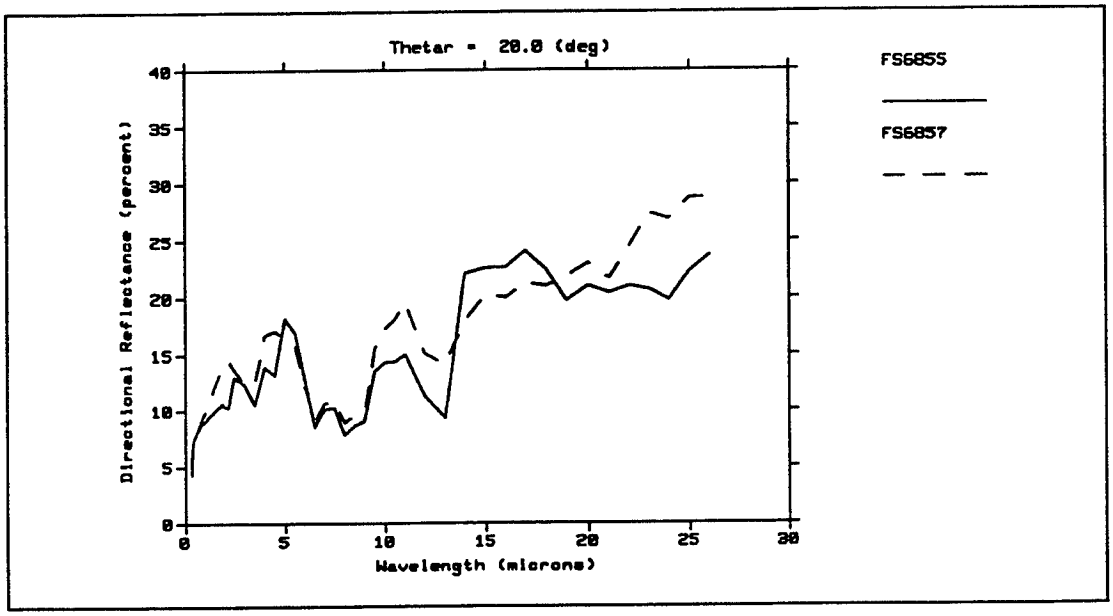

Figure 5. Comparison of a Clean (FS6855) and a Silica Contaminated Graphite Composite Sample (FS6854).

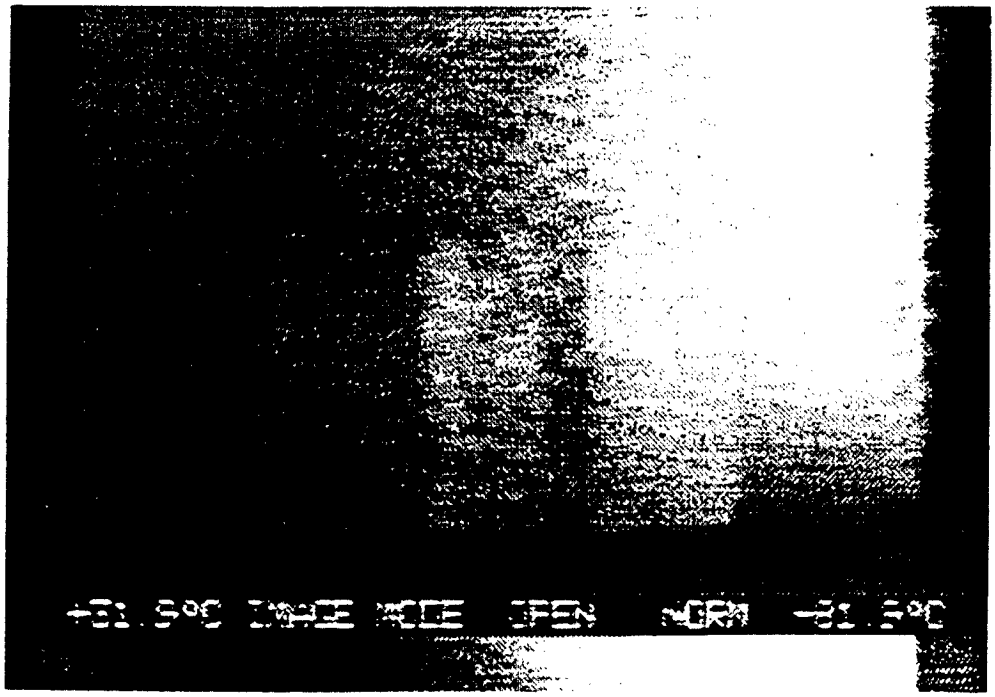

Figure 6. 8 μm to 12.0 μm Broad-Band Image of Graphite Composite Material.

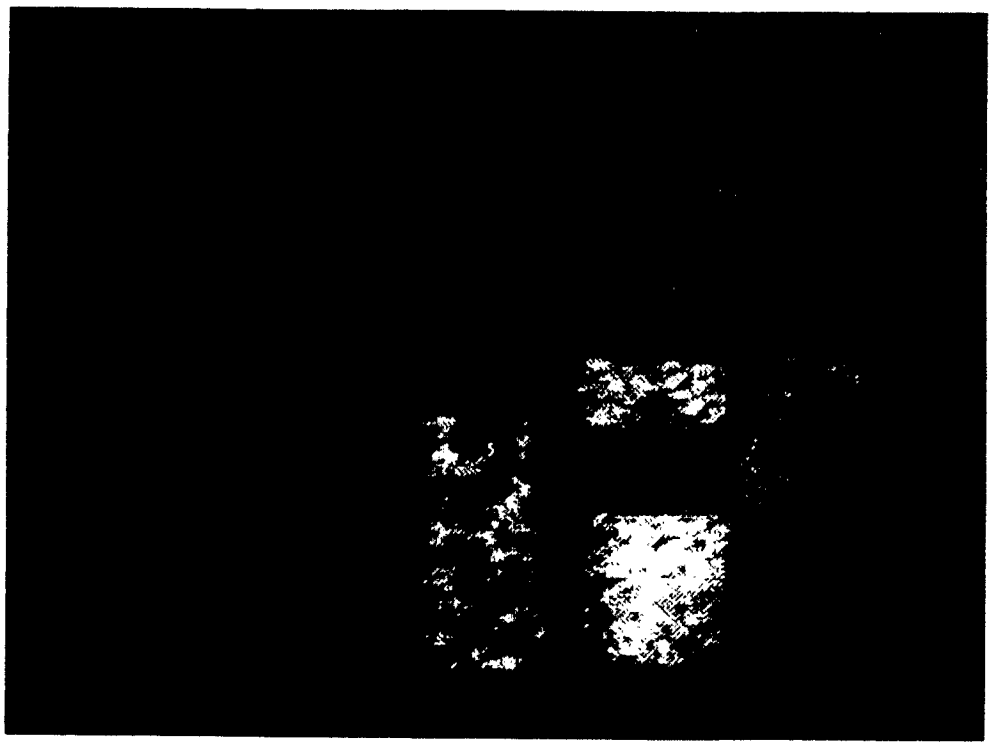

Figure 7. Filtered Image using FS6857 as Filter Spectral Radiance.

The laboratory demonstration of the use of infrared imaging spectroscopy for NDI applications that was performed during this Phase I program shows promising results. The spectrally filtered images, using one detector, five spectral points, and taking many hours to acquire and post process, clearly identified the regions in the image which matched the spectral filter. These results demonstrated only a small fraction of the capability of the proposed instrument with 256x256 detectors, 30 to 60 spectral points, and real-time processing and display.

4.0 CONCLUSIONS

Surface Optics Corporation and the Jet Propulsion Laboratory, under a phase I SBIR from the Armament Research and Development Engineering Center, have demonstrated the power of exploiting spectral features to enhance spatial contrast, allowing materials-based identification and discrimination. Embodied in a newly designed multiband, identification and discrimination imaging spectroradiometer (MIDIS), such capability will have broad benefit to any discipline requiring real-time remote identification of materials. For medical diagnostics, non-invasive identification of surface or near surface tissues will be possible without biopsy; with appropriate use of an endoscopic attachment, minimally invasive identification of internal tissues will also be possible. Remote monitoring of mineral deposits, crop type and health, or forest health will be possible more readily than with current instruments. Monitoring of industrial effluent discharge, or of toxic vapors from chemical spills will aid in protection of our environment and health. Similar monitoring could add another weapon to the arsenal in the war on manufacture of drugs. Any industry wanting to monitor processing of a product to increase quality and minimize cost would also benefit from the technology explored during this research and development, and currently being constructed.

5.0 ACKNOWLEDGEMENTS

Surface Optics Corporation is very grateful to the U.S. Army Armament Research and Development Engineering Center at Picatinny Arsenal for funding the Phase I SBIR under which the described research was performed. ARDEC's continued support in award of a Phase II SBIR to produce the MIDIS instrument researched during the Phase I effort will advance the state-of-the-art in real-time collection and processing of spectral imagery. SOC also thanks JPL for their support as subcontractor on this effort, lending their renowned experience and expertise in the field of spectral imaging.

DIFFUSE REFLECTANCE MID-INFRARED SPECTROSCOPY AS A TOOL FOR THE IDENTIFICATION OF SURFACE CONTAMINATION ON SANDBLASTED METALS.

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ABSTRACT

The SOC 400 Surface Inspection Machine/Infrared (SIMIR) is a small, ruggedized Fourier transform infrared spectrometer having dedicated diffuse reflectance optics. The SOC 400 was designed for the purpose of detecting (qualitatively and quantitatively) oil stains on the inside surface of solid rocket motor casings in the as-sandblasted and cleaned condition at levels approaching 1 mg ft^{-2}. The performance of this instrument is described using spectral mapping techniques.

INTRODUCTION

Reflectance mid-infrared spectroscopy is a very useful tool for the determination of surface contamination in manufacturing applications(1). Diffuse reflectance is a particularly useful method for obtaining spectral data from surfaces of a host of practical materials. Metal surfaces that have been sandblasted in preparation for coating applications and bonding are examples of such a material(2). The inner surface of solid rocket motor casings is such a material and certification of the cleanliness of this surface prior to applying primer coatings and adhesives is essential to the reliability of the motor.

A collaboration involving Lockheed Martin Energy Systems, Inc., the NASA Surface Contamination Analysis Technology Team (SCATT), the Army Environmental Center, and Surface Optics Corporation has resulted in the development and commercialization of a hand-held (or remotely positioned) Fourier transform infrared (FTIR) spectrometer that uses diffuse reflectance optics to interrogate surfaces. The Surface Optics Corporation SOC 400 Surface Inspection Machine/InfraRed (SIMIR)(1) weighs less than 8 Kg and may be manipulated into any orientation during operation. The SIMIR is based on barrel ellipse diffuse reflectance optics(3) having a focal point located in the plane of an opening in the face plate of the instrument. This "point-and-shoot" type of instrument allows rapid in-field analyses to be made with sensitivity comparable to sample compartment accessories in laboratory instruments; allows dedicated scanning, collection, and analysis routines; and has the robust characteristics of the barrel ellipse focal point with respect to sample positioning. The spectrometer software can instruct positioning devices in a noncontact mode(4). Applications to inspecting (both qualitatively and quantitatively) sandblasted metal surfaces for oil contamination are described using spectroscopic mapping techniques for the determination of the calibration factors for sandblasted D6AC steel surfaces as a function of contamination level.

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THE SOC 400 SURFACE INSPECTION MACHINE / INFRARED (SIMIR)

The SOC 400 Surface Inspection Machine/InfraRed (SIMIR) shown in Figure 1 weighs less than 8 Kg, occupies less than 14 L, and may be operated at any orientation. The focal point of the barrel ellipse diffuse reflectance optics is located in the plane of an 12-mm D opening in the center of the face plate of the instrument. The barrel ellipse optical configuration is located behind the black circular (85-mm D) face-plate shown in Figure 1. The SIMIR uses the MIDAC FTIR spectrometer, but the components have been reconfigured to reduce the size and weight of the system, the optical throughput has been increased, the barrel ellipse is half-scale, and the detector performance has been improved. The system is supported by either 12 VDC or 120 VAC and a computer (Pentium and 486 laptop are used interchangeably) using MIDAC GRAMS/386 software for the operating system. The SIMIR operates at <40 W, slightly less than the power requirements for the laptop computer. Normally, the

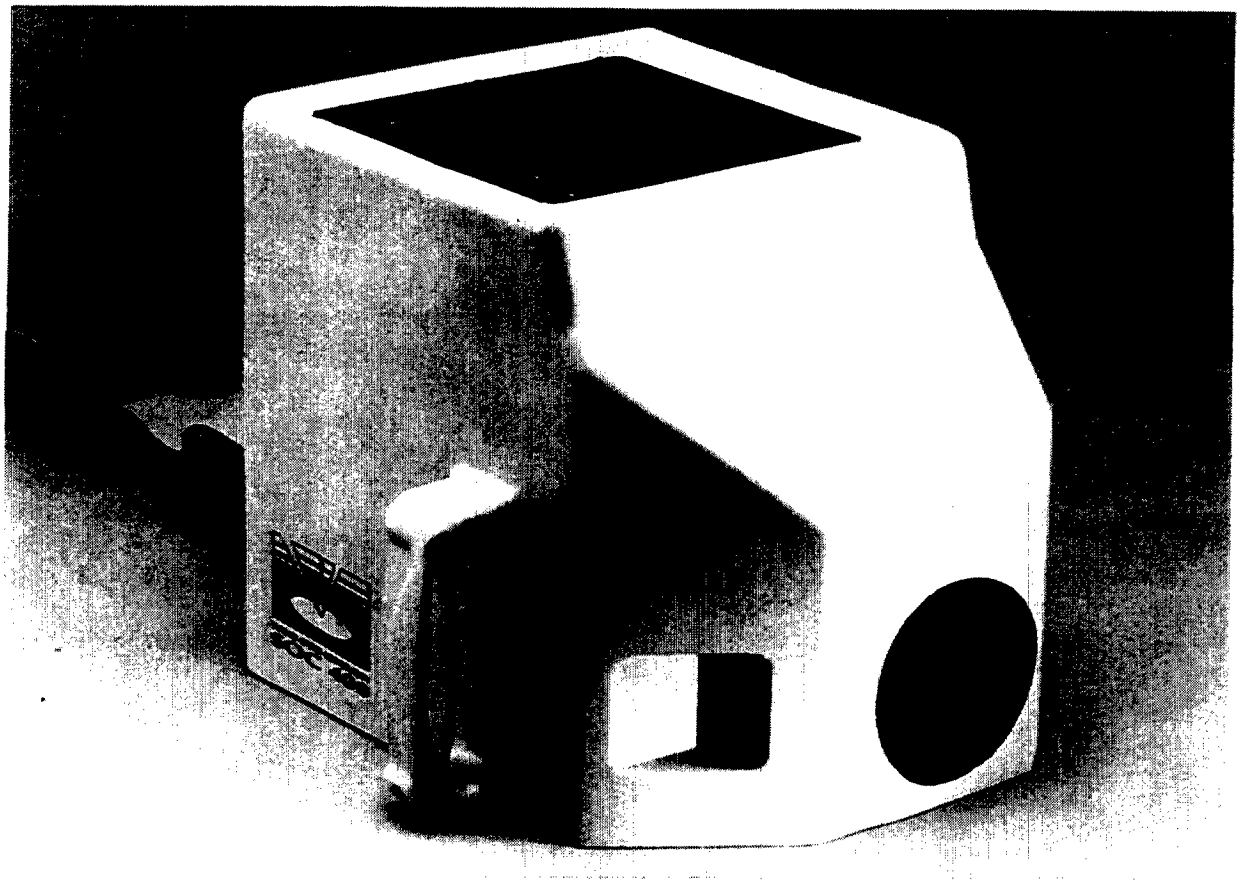

Figure 1. The SOC 400 Surface Inspection Machine/InfraRed (SIMIR).

specimen may be located within a millimeter of the face plate without loss in calibration or sensitivity. The operating system may also be customized using MIDAC/Grams386/Array Basic or MIDAC Visual Basic software for dedicated inspection operations. This is done to make the inspection operation user friendly, hardened against accidental loss of data and changes in operational parameters, to introduce dedicated post processing of data, and to instruct external devices by serial communications to reposition the specimen and execute other operations. When the capability for having the spectrometer software instruct positioning devices in a noncontact mode is utilized, dramatic increases in productivity and utility are achieved. For this purpose Velmex Unislides (3 slides

oriented for X, Y, and Z positioning) with a Velmex NF90 serial controller are used. At the completion of the collection of a spectrum, the operating software instructs the NF90 controller to move to the next position. Surface mapping is a powerful tool for approaching the difficult task of establishing calibration factors for relating the amplitudes of the spectral bands to the quantity of film that contaminates the substrate. Mapping is also important in inspection operations for determining the distribution of a stain over a surface.

The SOC 400 operates in a similar fashion to most laboratory FTIR spectrometers, a characteristic that makes its operation and data evaluation very familiar to most experimental chemists. The principal difference with respect to laboratory instruments is that the aligning of accessories and the waiting for the spectrometer to purge after loading no longer exist. The SIMIR and the specimen surface are brought into appropriate proximity, made easy by the contact face plate, and the spectrum is collected while observing the spectrum develop in nearly real time (1.3 s phase lag). As with all FTIR spectrometers, the measurement is a comparative one. A reference spectrum is obtained as an interferogram and fast-Fourier transformed to a "single-beam" spectrum (i. e., light intensity as a function of energy). Subsequent single beam spectra are ratioed to the reference spectrum and represented as the fraction (or %) of light lost (in units referred to as %T) or further processed to the negative base 10 logarithm (Beer's Law) in absorbance units (a. u.), where the spectral bands, under the most ideal conditions, increase with the areal density of the absorber. Spectra presented in this report were typically the result of 48 coadded scans (1 min. collect time) ratioed to a reference spectrum of an equal or greater number of scans at 16 cm^{-1} resolution and 2 times zero filling..

The achievement of a particular signal-to-noise level for a given collection time interval (typically one minute) is the best method for defining performance in an FTIR spectrometer. Indeed, the performance of the spectrometer, perceived by the operator as the rate at which a spectrum of a particular quality can be obtained, goes as the square of the signal-to-noise since multiple spectra are usually averaged to yield a final spectrum. With respect to certifying the cleanliness of metals, the inspector must know that the reference spectrum substrate is clean within the detection limits of the method. Contamination must not be transferred from one substrate to another, an event that may be avoided by operating in a noncontact mode. In the process of cleaning metals, this is the technique intensive process of keeping a clean part clean. The substrate may also have spectral features related to the inherent reflectivity of the metal, oxide films on the metal, and adsorbed moisture that may complicate spectral interpretation.

Sandblasted gold is the optimum substrate material for metal cleanliness studies because gold is easily cleaned, and if necessary, by very harsh chemical methods. Freshly sandblasted gold that was ultrasonically cleaned in Micro detergent, rinsed under a stream of distilled water, and dried in a stream of high-purity nitrogen was used in following experiments. Gold is one of the most reflective of metals and displays no features related to oxide films. Thus, sandblasted gold returns to the infrared detector a true representation of the spectral distribution of the incident beam. Sandblasted aluminum is also a good substrate, but the aluminum oxide film can significantly contribute to the spectral features. Highly anodized aluminum strongly absorbs over much of the mid infrared spectral range. Sandblasted stainless steel is also a good substrate in that it is very durable and cleanable, but does contribute some oxide film features to the spectra. D6AC steel is the steel that is used on rocket motor casings and is the primary substrate of interest in this work. Again, the emphasis is on this form of surface inspection as a comparative technique suggesting that the background spectrum for surface cleanliness approximate as closely as possible the clean substrate of the surface being analyzed.

In Figure 2, the spectrum of sandblasted gold referenced to the same location on the same gold specimen defines the performance of the SOC 400. This spectrum could be fit to a fourth order polynomial over the 3100 cm^{-1} to 500 cm^{-1} range with a standard error of 0.00007 a. u. or to a straight line over the 3100 cm^{-1} to 2700 cm^{-1} range with a comparable standard error. The design intent of the SOC 400 was to have ultimate detection limits of 0.0001 a. u. The upper curve in Figure 1 shows the spectrum of a clean D6AC steel sandblasted specimen referenced to clean gold showing that the light scattered from the steel specimen is attenuated by a factor of at least 2.5 with greater losses at the energy extremities of the spectrum, and a metal oxide absorption band near 1000 cm^{-1}. The middle spectrum in Figure 1 shows the effect of these D6AC steel factors on the spectrum of steel referenced to steel. Note that the band near 1000 cm-1 is present (although inverted) and the baseline noise is

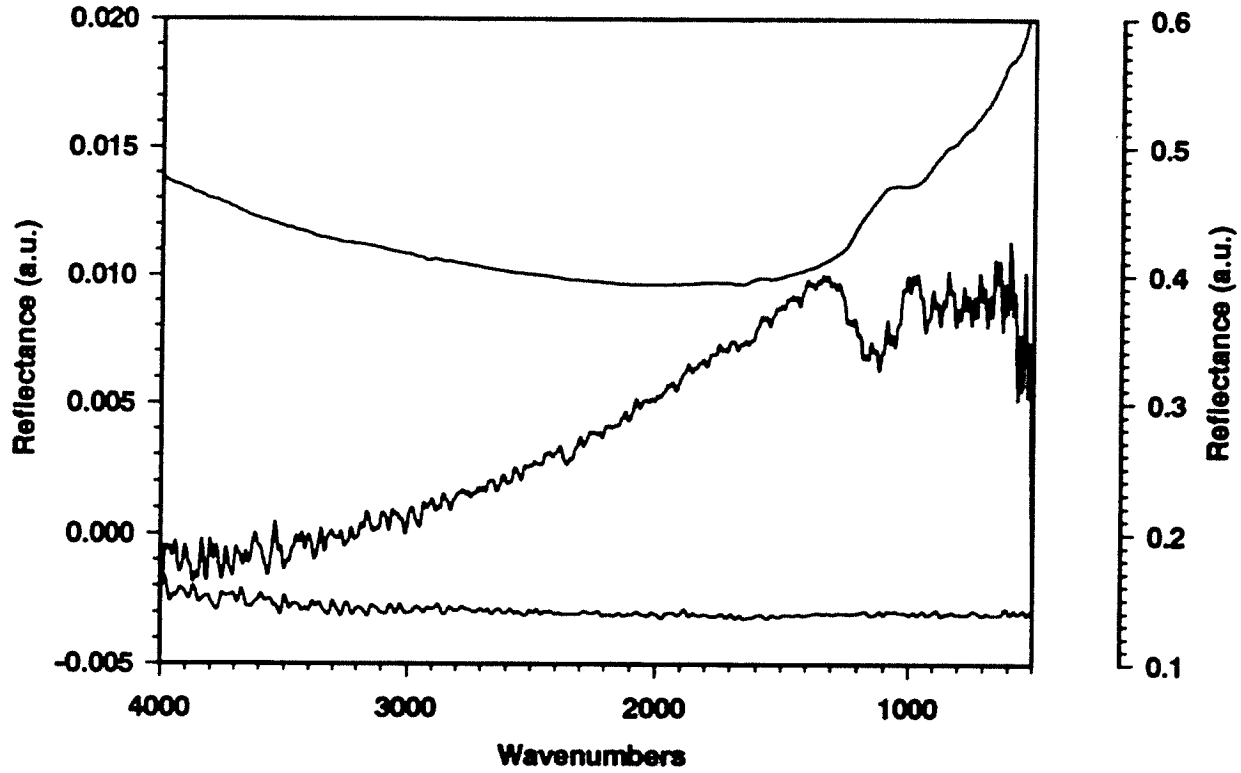

Figure 2. Spectra of sandblasted substrates obtained using the SOC 400 SIMIR. Lower spectrum; gold versus gold, Upper spectrum (right ordinate): D6AC steel versus gold, Middle spectrum: D6AC steel versus D6AC steel at a second position.

higher (standard error of 0.0002 a.u.). It will later be shown that part of this noise is a consistent feature of this D6AC steel reference spectrum.

Figure 3 shows spectra of CRC silicone oil, paraffin, and HD2 grease, at nominally the 50 mg ft^{-2} level of contamination, that are anticipated contaminants on solid rocket motor casings demonstrating the unique patterns of the spectra that are used for qualitative analysis. Both the paraffin and the HD2 grease spectra are that for aliphatic hydrocarbons with the latter having features below 1500 cm^{-1} due to a carbonate additive for pH control. The paraffin has somewhat sharper CH_2 stretching bands than the HD2 grease. For quantitative analysis, the baseline-corrected peak heights of unique peaks are measured and converted to mg ft^{-2} using a previously determined calibration factor. Baseline-corrected peak heights were determined for the hydrocarbon stretching region (3100 cm^{-1} to 2700 cm^{-1}, the universal signature of organic contamination) by establishing a line based on the average value of the spectrum over the 3075 cm^{-1} to 3100 cm^{-1} range and the 2700 cm^{-1} to 2725 cm^{-1} range, and measuring the maximum peak height relative to that line within that range. The spectrum for aliphatic hydrocarbons is dominated by the CH_2 stretching frequency near 2925 cm^{-1}, and silicones usually show only CH_3 stretching frequencies near 2965 cm^{-1}. For the CRC silicone oil, the base-line corrected peak height used the line based on the averages over the 1300 cm^{-1} to 1325 cm^{-1} range and the 1200 cm^{-1} to 1225 cm^{-1} range, with the maximum being found near 1260 cm^{-1}. The two bands below 1200 cm^{-1} could also be used for CRC silicone. However, on D6AC steel these bands can be confused with the oxide bands at the lower limits of detection.

The analysis region of the SOC 400 (i.e., the size of the focal point of the beam at the sample) is approximately 1 mm in diameter. Since noncontact analysis of clean surfaces is required to assure that the analysis does not contaminate the surface, the manner in which the distance between the contact face plate of the SOC 400 and the surface affects the calibration factor must be understood. For this purpose a clean gold substrate was placed against the contact face plate. A reference spectrum followed by a spectrum in units of %T were obtained. The spectrometer was operated in automatic spectral mapping mode so that, after this spectrum and each

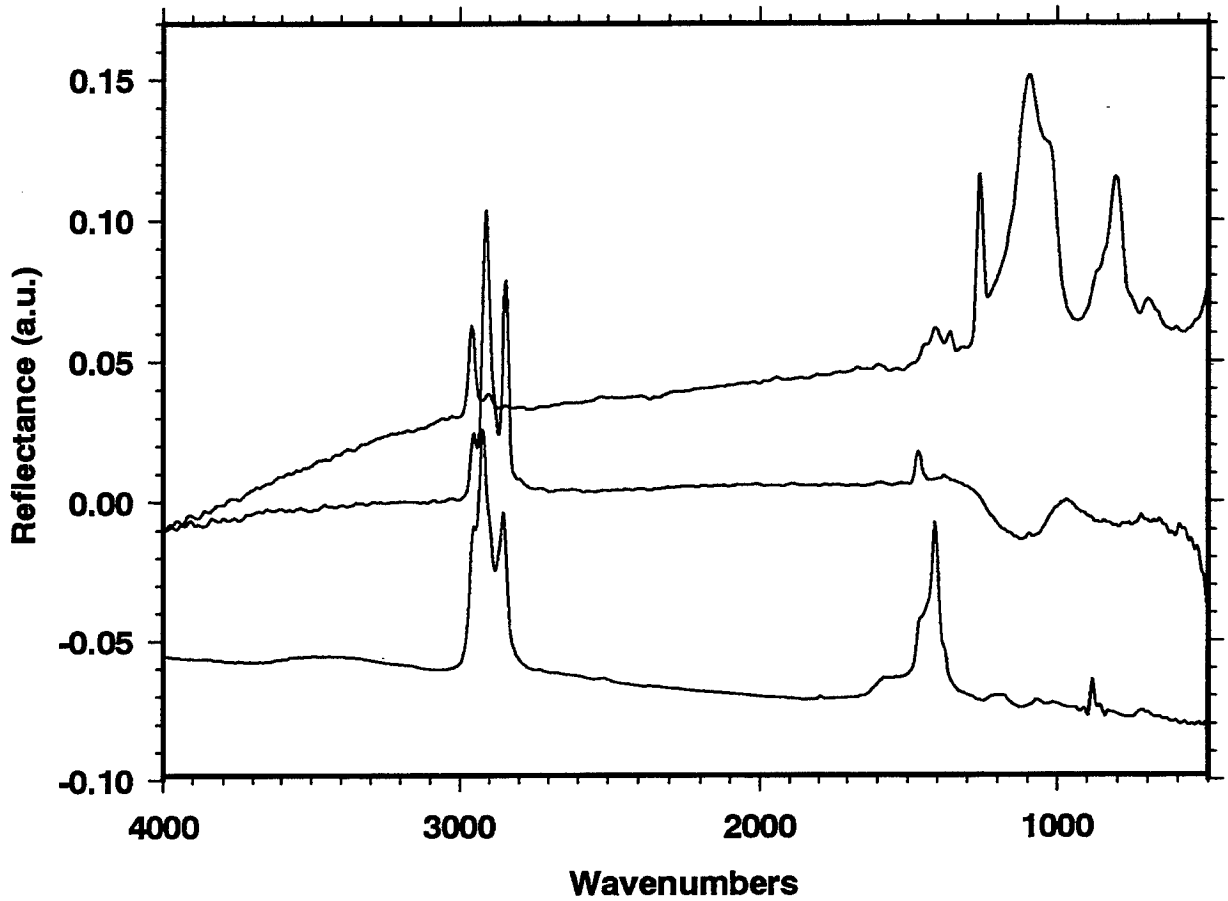

Figure 3. Spectra of potential oil stains at approximately the 50 mg ft^{-2} contamination level on D6AC steel referenced to clean D6AC steel. Lower spectrum: HD2 grease, Upper spectrum: CRC silicone, Middle spectrum: paraffin. The upper and lower spectra have been offset from near 0.00 for clarity.

succeeding spectrum, the surface was moved away from the face plate by 0.1 mm. This experiment was repeated using the established reference spectrum and a gold specimen stained with approximately 100 mg ft^{-2} of vegetable oil. Figure 4 shows that the signal level from the clean gold specimen increased over the first millimeter away from the contact face plate and dropped precipitously after passing the 2-mm distance. The baseline corrected peak height in absorbance units of the vegetable oil stain remained constant within 5 % over the first two millimeters of the noncontact range and gradually increased in sensitivity by as much as 30 % over the 2-mm to 6-mm range accompanied by a growth in the noise level that follows the loss in signal. The result indicates that the SOC 400 has a zone between 0.5 mm and 1.5 mm that is the optimum location for the surface to be inspected and that, over a range of several millimeters, the calibration factor, but not the detection limit, is unaffected by the standoff distance. This is probably due to the fact that the detector, on the scale of the focal point spot size, is a complex device with the sensitive region recessed inside a tube behind a window.

D6AC STEEL STEP-PLATE CALIBRATION STANDARD ANALYSES

Two D6AC steel step-plate standards were prepared by NASA SCATT using the technique described by Boothe(5). One plate used paraffin as an aliphatic hydrocarbon contaminant and the other used CRC silicone oil. The plates were 114 mm (4.5 in.) on a side with contamination steps 19 mm (0.75 in.) wide ranging from 0 to 50 mg ft^{-2} contamination in steps of 10 mg ft^{-2}. The spectral mapping technique was used to obtain spectra at millimeter intervals from 1 mm from the edge of the plate on the clean side to 112 mm on the 50 mg ft^{-2} paraffin

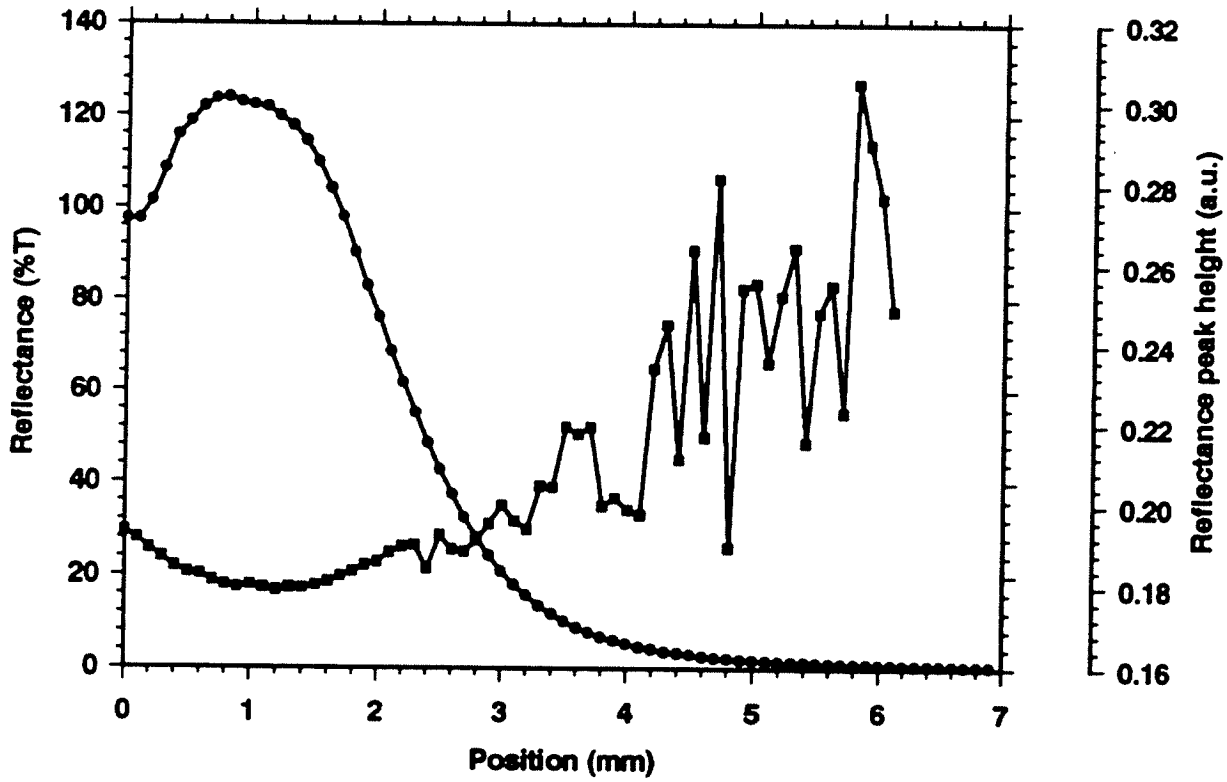

Figure 4. The sensitivity of the SOC 400 SIMIR to the specimen distance from the contact plate. Circles: the 2000 cm^{-1} value of clean gold versus clean gold spectra in % T, Squares (right ordinate): baseline corrected peak height of a vegetable oil stain.

side. Figure 5 shows the individual hydrocarbon stretching bands for the paraffin step-plate over the clean and the 9 mg ft^{-2} step including a bit of the transition zone to the 20 mg ft^{-2} region. These spectra are referenced to the spectrum obtained at the 3 mm distance from the edge on the clean side. At the 9 mg ft^{-2} level of contamination on sandblasted D6AC steel, the spectra obtained for paraffin is of high quality and obviously interpretable as an aliphatic hydrocarbon, even when observed as a 1.3 s single scan update (a 7X loss in sensivity). Figure 5 also shows a systematic ripple in the baseline on the 0 mg ft^{-2} step indicating that the standard error of 0.0002 a. u. in the baseline noise described earlier, results in part from the choice of a reference spectrum.

Figure 6 compares line maps across the step plates for the paraffin (2910 cm^{-1}) and the CRC silicon (1260 cm^{-1}) baseline corrected peak heights with the step contamination level at the time of application. There are several obvious differences between the paraffin and the CRC silicone step plates. The paraffin clearly defines the steps mainly because it was selected for its high viscosity so that if would not flow after being deposited. At all but the lowest level, the CRC silicone has flowed to erase the step edges and at the highest level (adjacent to the edge of the plate) the CRC silicone has flowed off the plate. The data scatter for the CRC silicone is significantly less than that of the paraffin indicating that the paraffin may exist as small islands of variable concentrations on the scale of 1 mm. These islands are visually observable for the 9 mg ft^{-2} step of the paraffin/D6AC steel step-plate. The high values for the CRC silicone above 110 mm results from the mixing of the silicone with an aromatic compound with stronger absorbances than the silicone. This is probably an adhesive residue from tape that retains silicone rather than allowing it to flow off the edge of the plate.

Figure 7 shows an expanded view of the spectral line map of the 0 mg ft^{-2} and 9 mg ft^{-2} regions of the step plate. Figure 7 includes the baseline corrected peak height measurements of the 2960 cm^{-1} CH_3 stretching band that is weaker than the 2910 cm^{-1} CH_2 stretching band by approximately a factor of 4. This band corresponds to a ripple in the baseline yielding a negative value for the baseline corrected peak height of clean D6AC steel. Figure

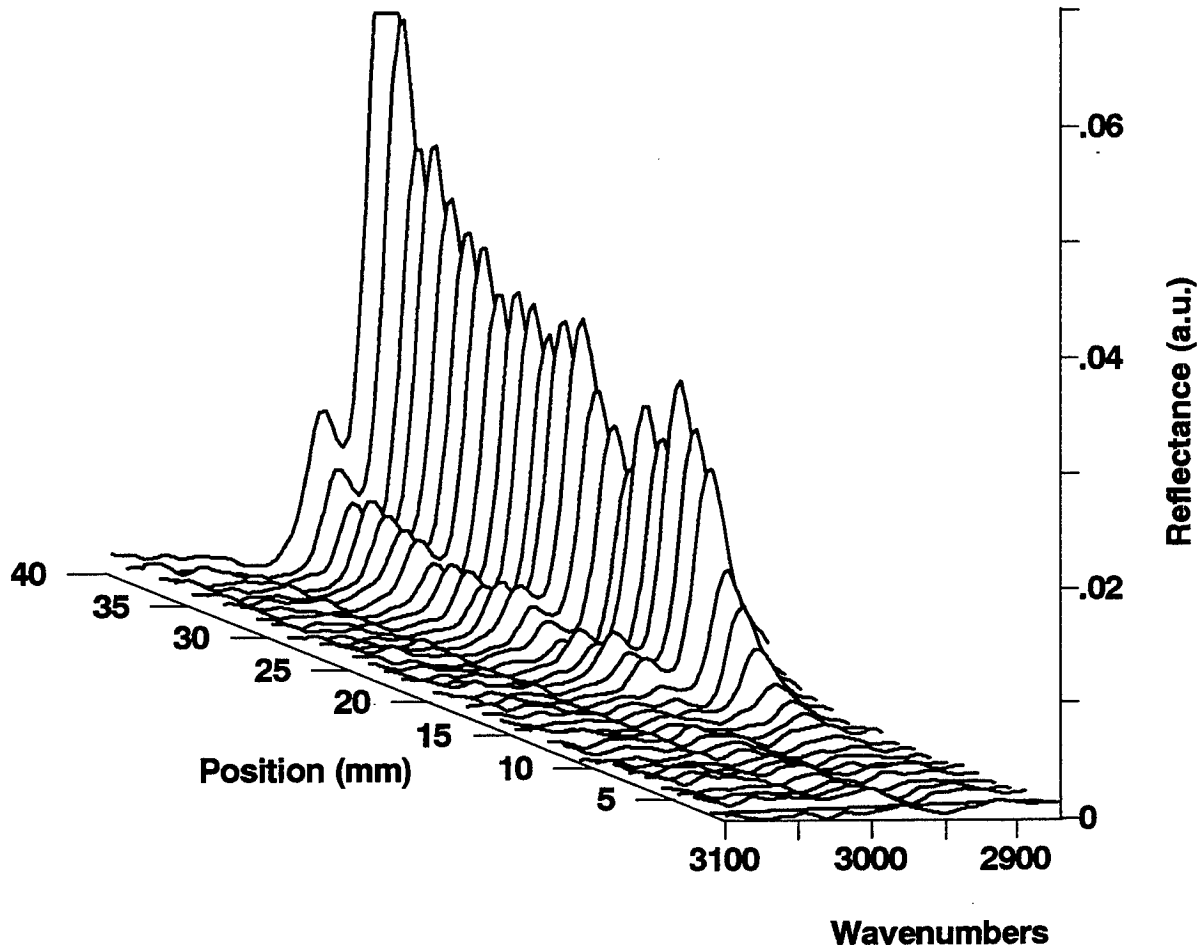

Figure 5. The SOC 400 spectral line mapping of the paraffin hydrocarbon stretching bands baseline corrected at 3100 cm^{-1} and 2700 cm^{-1}.

7 demonstrates the ability of the SOC 400 to detect hydrocarbon and silicone levels near the 0.0001 a.u. level. For both the paraffin and the CRC silicone, the average over the 3 to 13 mm region of the step plate was 0.00012 with a standard error of 0.00017 a. u. and 0.00012 respectively. Approximate calibration factors were 330 mg ft^{-2} /a. u. for the paraffin 2910 cm^{-1} band and 830 mg ft^{-2} /a. u. for the CRC silicone 1260 cm^{-1} band. At the 95 % confidence level the clean area was uniformly below 0.0004 a.u. (0.13 mg ft^{-2}) for paraffin and 0.0003 a. u. (0.25 mg ft^{-2}) for CRC silicone.

CONCLUSIONS

A ruggidized FTIR spectrometer dedicated to diffuse reflectance measurements in the form of the SOC 400 Surface Inspection Machine/Infrared (SIMIR) has been optimized to detect oil stains on sandblasted metals in order to address the solid rocket motor bondline contamination problem. This machine can operate down to the 0.0001 a. u. domain which translates into detection limits well below 1 mg ft^{-2} for hydrocarbons and silicones on D6AC steel in spectral acquisition times of 1 min. Above the 1 mg ft^{-2} level, spectra of sufficient quality may be obtained for qualitative analysis. At the 10 mg ft^{-2}, hydrocarbons are obvious in single scan spectra updating at 1.3 s. The sampling point of the instrument is approximately 1 mm in diameter and is very robust with respect sample position in noncontact mode. Little effect is observed on calibration or sensitivity when the specimen is placed within 2 mm of the contact face plate. When coupled with spectral mapping techniques, the critical capability of establishing contrast between clean and contaminated areas, and of observing the results of migration or island formation in order to establish whether data scatter results form real variation or instument variation, is straight

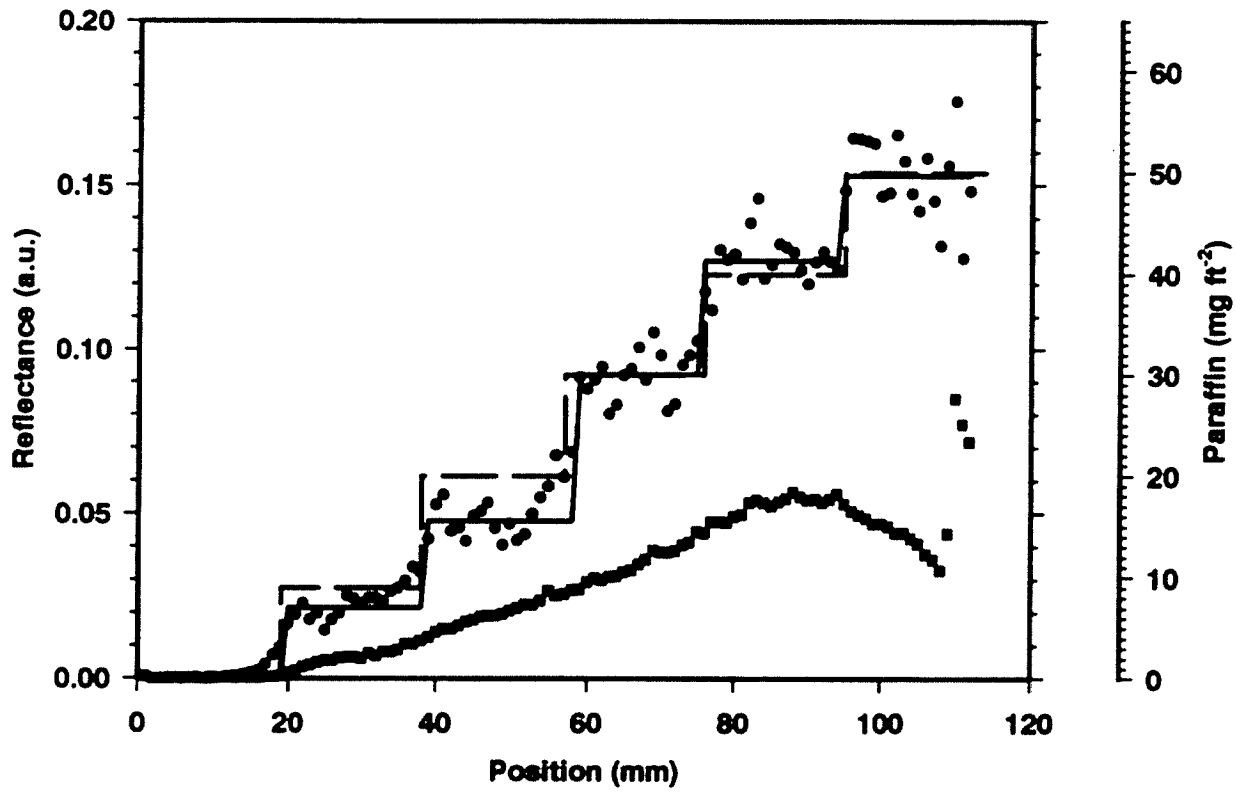

Figure 6. The SOC 400 spectral line mapping of paraffin (circles: 2910 cm^{-1}) and CRC silicone (squares: 1260 cm^{-1}) using baseline corrected peak heights. Solid line: average value of paraffin step height in a. u., Broken line (right ordinate): contamination level of the paraffin step plate scaled to match the middle step average a. u. level.

forward. The imaging of stains in terms of simple concepts such as peak height measurements or more sophisticated chemometric techniques such as partial least squares or spectral library analysis is just something to be done.

ACKNOWLEDGMENTS

The authors gratefully acknowledge E. R. Engberg, U. S. Army Environmental Center, Aberdeen Proving Grounds, Maryland forhis efforts to implement this inspection technology.

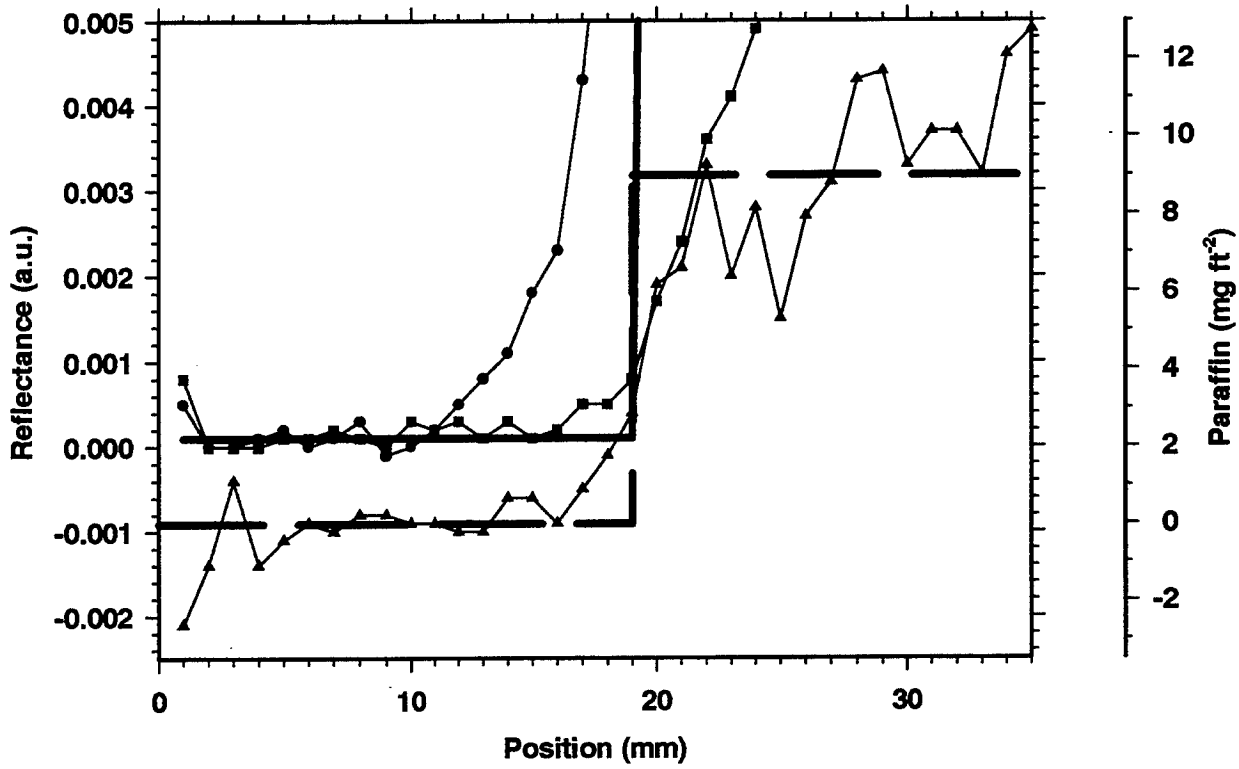

Figure 7. The SOC 400 spectral line mapping of paraffin (circles: 2910 cm^{-1}; triangles - 2960 cm^{-1}) and CRC silicone (squares: 1260 cm^{-1}) using baseline corrected peak heights. Heavy solid line: average value of paraffin step height in a. u., Heavy broken line (right ordinate): contamination level of the paraffin step plate adjusted to match the 2960 cm^{-1} band a. u. level.

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A New Tool for Contamination Analysis

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Abstract: The Contamination Analysis Unit (CAU) is a sensing system that facilitates a whole new approach to industrial cleaning. Through use of portable mass spectrometry and various desorption techniques, the CAU provides in-process, near-real-time measurement of surface cleanliness levels. It can be of help in significantly reducing hazardous waste generation and toxic air emissions from manufacturing operations.

Background

Most industrial activities require cleaning -- of both parts and equipment. These activities take time, cost money, and generate waste. Hazardous waste, air emissions, potential worker exposures, liabilities of waste management, transport and disposal -- all are factors adding to a company's cost of doing business.

The surprising thing is, how little "cleaning verification" has changed in the last century. In an age that can produce a palm-top computer, the cleanliness of a high tech part such as an airplane wing is still determined by such dated methods as the "waterbreak test," where when water sheets evenly off a part, it is declared clean. This method is common in many industries, even though serious contamination problems can be masked by the presence of surfactants in the water, which allow even dirty water to sheet off like it was clean.

The fact is that most manufacturing plants do not *know* how contaminated each part in its assembly line is. Shop foremen rely on procedures shown to generally clean parts well, rather than on real-time knowledge of just what's happening in their cleaning tanks.

This lack of real-time knowledge can be dangerous. It can lead to rejected parts when conditions change in a cleaning bath, and are not immediately detected. Rejected parts must be reworked or discarded, and both cost the company money in waste time and materials.

Until recently, there were few ways to tell *in-process* and to a high degree of accuracy when a part could move on to the next manufacturing step. So over-cleaning has become the rule. The thinking goes, if you clean and clean the parts far beyond what most of them need, few will get rejected.

Unfortunately, over-cleaning leads to another set of problems -- additional waste. Using three cleaning baths when two would do generates unnecessary solvent wastes, extra air emissions, and lower-than-optimal productivity. Overcleaning is common in such operations as electroplating, printed circuit board manufacture, aerospace and automotive parts manufacturing, and many other activities. In many shops, cleaning processes generate the majority of the waste volume.

Monitoring contamination levels on parts during cleaning operations can make such processes more efficient, and can provide useful feedback for reducing waste generation and air emissions caused by overcleaning, or under-cleaning and subsequent rework of the parts. Such real-time process controls could reduce reject rates, raise productivity, and reduce waste management expenses in a variety of high- and low-tech processes.

Objective of Study and Results

In response to this need, Lawrence Livermore National Laboratory has developed a sensor system that provides real-time cleaning verification feedback in an industrial production-line environment. The sensor system, termed a "Contamination Analysis Unit," or CAU, is robust enough to be used in a range of industrial applications, both in the private sector as well as in DOE operations. The CAU is portable so that it can quickly be moved from one part of an assembly line to another. The sensor generates highly precise data, and also identifies the type of contamination present. It can distinguish between different hydrocarbon species and detect other common contaminants, such as silicone oils. Finally, the sensor components are inexpensive; the CAU will soon be affordable to small-sized shops as well as to larger plants.

The CAU uses off-the-shelf mass spectrometry technology, as well as a probe designed to interface with parts surfaces and desorb trace amounts of contamination from the surface, using a combination of vacuum (as low as 10^{-7} atmospheres) plus surface heating (up to 225 degrees Celsius). The CAU contains data processing capabilities and a contaminant library for identifying the amount and type of surface contamination, and reads out in standard metrics such as micrograms of contamination per square centimeter of part surface.

The following table depicts how the key features of the CAU compare to existing products or technologies.

Comparison of CAU with Other Technologies

Technology:	CAU	Waterbreak Test	Laboratory Analysis	FTIR	MESERAN
Sensitivity	High (Nanometer range, or <1 micro-gram per/cm2 of contamination)	Low	High	High (Nanometer range)	High
Feedback time (including sample preparation)	Immediate	Immediate	Hours to Days	Immediate	Immediate
Able to analyze chemical compositions?	Yes	No	Yes	Yes , but requires thicker contaminant layers > 100 nanometers	No
Portable?	Yes	Yes	No	Yes	Yes
Type of contamination detected	Organics, Possibly Silicon oils and tritium	Organics, Silicon oils	All types (organics, particulates)	Organics, Silicon oils	Organics
Acceptable substrate composition	All compositions	All compositions	All compositions	Diffuse reflecting surfaces	All compositions
Comments		Surfactants can make a dirty surface appear clean			Contaminants must be doped with radioactive tracer prior to application

The CAU's big pluses are that it is both a highly portable and extremely sensitive instrument. Whereas waterbreak tests and similar technologies can also be applied *in situ*, they don't provide the accuracy and quantitative determination of contamination levels that the CAU does. Precise measurements of cleanliness levels can be made in the laboratory, but turnaround-times to get this data are typically hours or days. The CAU returns highly precise data in one minute.

MESERAN can also return precise data in short amounts of time, but MESERAN requires that contaminants be doped with a radioactive tracer before being applied to the surface. In industrial settings, contaminants often cannot be especially "prepared." The CAU requires no such doping of the contaminants.

Fabrication of the CAU currently costs considerably less than FTIR equipment, and an order of magnitude less than lab-based technologies such as ESCA and Auger analysis equipment.

Future miniaturization of the CAU's interface with parts surfaces will allow the equipment's sensors to be light enough to be held in one hand (the sensor is currently 17 pounds), which will increase its portability. The miniaturization is also expected to drastically reduce the cost of the unit.

Conclusion

In summary, industrial cleaning of parts and equipment is a widespread manufacturing operation that, in many plants, is in need modernization and increased efficiency, and a reduction in its impact on the environment. Modern sensor and analysis techniques such as the one described above provide the real-time feedback on the performance of a cleaning operation that is vital for process optimization. The Contamination Analysis Technology will allow cleaning times to be shorter, unnecessary operations to be eliminated, and reject rates to be reduced. It will also cut down on both hazardous waste generation and air emissions that originate from both undercleaned, and overcleaned parts. Optimizing industrial cleaning operations is a "win-win" strategy that reduces manufacturing costs, increases product quality, and helps protect both worker health and the surrounding environment.

QUANTITATIVE MEASUREMENT OF OILY AND GREASY RESIDUES FROM 1 TO 100,000 NANOGRAMS

Submitted by

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ABSTRACT

This paper describes a new microcomputer-based analytical method carried out at ambient temperature and pressure for the direct quantitative measure of microorganic residues (e.g. oils and greases) to nanogram levels--ca 2 orders of magnitude below current technology and ca 1 order of magnitude below the lowest level specified in MILSTD 1246C (A / 100 = 0.01 ug--10 ng / cm^2). Calibration to these very low levels is based on a series of volumetric dilutions of typical residues with depositions of a 10 uL aliquot onto each 'clean' reference surface. The solvents used in the volumetric dilutions have non-volatile organic residue levels (NVOR) of less than 10 PPB.

The amount of residue is measured when observing the evaporation of an added high-boiling-but-volatile Carbon-14 labeled compound (U S Nuclear Regulatory Commission EXEMPT) with which the microorganic residue forms a chemical solution. The log count vs time relationship is monitored by detecting beta particles emitted from molecules retained at the interface as a function of time. The slope of the evaporation curve, expressed as a positive integer, is an orderly inverse measure of the amount of residue--the higher the slope the less the residue and *vice versa.*

The work reported represents a significant increase in the sensitivity of the Evaporative Rate Analysis (ERA) method This advance is the first analytical method for the quantification of nanogram levels of microorganic residues at ambient conditions.

INTRODUCTION

Verification of the efficacy of cleaning procedures has remained a largely elusive goal despite the very high levels of technical achievement in other areas. There are few methods for quantifying microorganic residues (particularly oils and greases) other than those employing high vacuum technology. Such instrumentation employing high vacuum technology fails to monitor those surface oils and greases that have sufficient volatility literally to disappear from view during preparation for testing. Furthermore, it is difficult to measure relatively large areas or even to sample them statistically under these conditions. Even the measurement of non-volatile residue (NVR) in rinsing solvents remains troublesome at all levels and particularly at low PPM levels. There are no easy answers and all methods including the one presented herein have limitations for general and/or routine use.

BACKGROUND

The work reported in this paper is an extension of a development program carried out at the Research Triangle Institute during the summer and fall of 1991. In the exploratory program, RTI scientists (cf. ACKNOWLEDGMENTS) measured very small amounts of dipentyl phthalate (an analog of dioctyl phthalate herein reported) deposited from volumetric dilutions onto ultraclean watchglasses and other surfaces using a MESERAN Model 1200 Surface Analyzer. The RTI study showed significant differences at and above 23 nanograms but failed at 2.3 nanograms. The effort was contracted by Roger Hoffman of IBM Corporation , Rochester, MN.

The methodology of the RTI investigation is similar to that employed by the authors as described below. One of the authors (JLA) was a consultant during a portion of the RTI work. A limited number of the RTI results were

reported by JLA in an oral presentation at the American Vacuum Society meeting in Baltimore in the Spring of 1992.

The work described in this paper is based on a recently uncovered variation in the analytical technique known as Evaporative Rate Analysis (hereinafter ERA).[2] Another paper by two of the authors was published in the May 1996 issue of PRECISION CLEANING.[3]

In this paper a number of abbreviations, special words, and trademarks are employed:
(1) *uCi* means *microCurie*, a unit of radiation which corresponds to 3.7 E 4 (37,000) disintegrations per second.
(2) *Carbon-14 (C-14)* refers to the radioactive isotope of the element Carbon, an isotope which emits only soft or low energy beta particles; most C-14 beta particles are stopped by a sheet of paper.
(3) USNRC *EXEMPT* means the very low level of Carbon-14 that is not regulated by the U. S Nuclear Regulatory Commission. No license is required for possession or use. Only USNRC licensed companies are permitted to distribute EXEMPT quantities not to exceed ten 100 uCi C14 (or combinations of smaller quantities that added up to 100 uCi C14) at one time. Multiple quantities may be stored by the user. Shipments may be made to anyone in the US under USDOT *excepted package* rules.
(4) *ng* means *nanogram* (1 E -9 grams); *mg* means *milligram* (1 E - 3 grams).
(5) *uL* means microliter (1 millionth of a liter).
(6) *ca* is the abbreviation for the Latin *circa* which means 'approximately'.
(7) GM detector refers to a thin end-window Geiger Mueller detector tube which detects the C-14 beta emissions which penetrate through the 1.4 - 2.0 mg/cm^2 mica window.
(8) One nanomole (*nmole*) is 1 E -9 moles which equals ca 6 E 14 molecules (from Avogadro's ca 6 E 23 molecules per gram mole); one micromole (*umole*) equalsca 6 E 17 molecules.
(9) 1 square centimeter (sq cm) with a 'roughness factor' (RF) of 3 is equal to 3 E 16 square Angstroms.
(10) *Monolayer* refers to the number of molecules of a material which covers 1 sq cm in a conventional non-closepacked configuration. For example each molecule of n-tridecane covers ca 60 sq. Angstroms -- which equates to ca 5 E 14 molecules per sq cm (r.f. of 3).
(11) *NVR* means non-volatile residue; NVOR means non-volatile organic residue.
(12) *MESERAN*, *MicroOrganicResidue*, and *MOR* are trademarks licensed to E R A Systems, Inc.

The standard microcomputer-based ERA (or MESERAN) technology involves deposition using a 'clean' precision microsyringe onto a flat or concave surface of ca 18 ul of a test solution comprising a low boiling solvent or solvent combination (in the cases described - cyclopentane) and a high-boiling-but-volatile Carbon-14 labeled compound (in a ratio of ca 60,000:1). The amount of radiochemical per single test (< 0.06 uCi) corresponds to ca 6 E 14 molecules which equates to ca one *nmole*, the *equivalent* of ca one molecular layer over one sq cm. Metered air or nitrogen gas is then permitted to flow across the surface and between the surface and a GM detector positioned directly above the surface. The evaporation of the low boiling solvent and then the radiochemical is observed as a function of time by recording the detected emissions per second *arising from the radiochemical molecules remaining on, or retained by, the surface*--the vapor-phase, already-evaporated molecules having been swept out from under the detector by the metered gas. Figure 1 illustrates the GM detector / test surface configuration.

Each test takes only 2 minutes; the amount of radiochemical employed is classified as EXEMPT under U S Nuclear Regulatory Commission and/or 'Agreement State' licensing regulations due to the very low level of C-14 involved.

The method has two major applications which are based on separate and distinct mechanisms, namely:
(1) The quantification of micro-organic residues on surfaces which is described in more detail below and
(2) The measurement of the level of crosslink density in polymers through a variation of the classical *solvent swell* method. The evaporative response is best described as a second order process. The method requires preselection of an optimal solvent or solvent blend based on a suitable cure ladder (undercure, cure, overcure) for the particular polymeric material being tested as is described in another paper being delivered at this conference.

Applied to the measurement of microorganic residues, the ERA method may be used:
(1) Directly on a flat or concave surface and any microorganic residue thereon or
(2) Indirectly using an extracting solvent followed by depositing and evaporating an aliquot amount onto a 'clean' reference surface. Subsequent deposition and evaporation of the radiochemical solution permits measurement of the amount of deposited residue by comparing the results with previously obtained standards similarly deposited from volumetric dilutions. One of the major advantages of the nanogram sensitivity is the capability to measure solvent NVOR to 0.1 PPM based on only 10 ul of solvent.

For non-polar and/or hydrocarbon type residues, tridecane-C14 in cyclopentane (designated BK) is employed. For more polar residues, tetrabromoethane-C14 in cyclopentane (designated AK) is used. In order to provide a high number of detected emissions for the minimal amount of radiochemical deposited, the tridecane-C14 has a specific activity of ca 57 uCi/umole (one carbon atom is essentially pure C14 isotope) while the tetrabromoethane has both carbon atoms labeled (ca 114 uCi/umole). Ca 200 nanograms of radiochemical is deposited in each test.

The ERA method assumes that the test solution solvent substantially dissolves the residue within the time period of the solvent evaporation, that the particular radiochemical employed is chemically compatible with the residue, and that the test solution droplet covers all of the deposited residue. *Attention to the avoidance of inadvertent contamination and the maintenance of reasonably constant temperature and pressure are required for optimal reproducibility from test to test.*

The classic methods of ERA data interpretation are total counts under the evaporation curve or, more recently, the slope of the evaporative process following the evaporation of the low boiling component of the test solution (the peak of the curve). Figure 2 illustrates three typical experimentally derived curves of log count per second (less background) vs time in seconds representing a high level of residue for the upper slope, an intermediate level for the middle slope, and a low level for the lower slope. The scatter particularly noticeable at the lower values is due to the inherent randomness of radiation. The rationale for the initial increase in counts / second is that the C-14 soft beta emissions are partially absorbed by the solvent molecules--the final evaporation of liquid solvent correlates with the peak of the curve.

For determining the amount of microorganic residues, the total count method of analysis is valid from ca 100 - 200 ng (2 E -7 g) to at least 40,000 ng (4 E -5 g). Several differing methods of defining the slope of the evaporation process as discussed below provide quantitative measures of the level of residue from less than 1 ng to more than 100,000 ng.

MECHANISM OF THE ERA METHOD

When a homogeneous chemical is permitted to evaporate, the classical mechanism of the process (normally measured by monitoring the already evaporated portion) follows first order kinetics - the plot of log count vs time is a straight line. This mechanism applies to pure materials as well as to solutions of chemicals in which the components are chemically compatible. In the ERA technology however, the amount of radiochemical retained by the surface system as a function of time is measured. In this discussion the factors of temperature and pressure are assumed constant and the concentration of already evaporated molecules in the adjacent gaseous phase approaches zero due to the flowing air or nitrogen referred to above. The molecular weight of each evaporating molecule and the intermolecular forces among the molecular near-neighbors are thus the primary factors in determining the tendency of each molecule to remain in solution or conversely to escape from the liquid portion of the air / liquid (or semisolid) interface. As applied in ERA technology which employs only ca one monolayer *equivalent* of the radiochemical, the observed rate of evaporation is thus a function of the residual concentration of the non-evaporated molecules of the Carbon-14 radiochemical.

A solution of the high-boiling-but-volatile tridecane-C14 in higher boiling hydrocarbons follows a similar but slower path than does the evaporation of the tridecane itself since the non-volatile 'residue' molecules occupy increasing portions of the liquid (or semi-solid) interface. The observed rate of evaporation--the slope expressed as a positive integer--thus is an inverse measure of the amount of non-evaporating residue. The lower the slope, the more the residue and *vice versa*.

The constancy of the observed rate of evaporation in the log/linear relationship requires that the intermolecular forces remain substantially constant--the forces between and among molecules at the vapor / liquid interface are those in the approximate plane of the interface as well as those directly below and adjacent to the evaporating molecule.

However when examining the data obtained from extremely clean surfaces, the plots of logarithmic values of single second count accumulations vs time in seconds almost always exhibits a marked deviation from the expected straight line behavior with a much steeper slope as the curve approaches the lowest log values. This observation is contrary to the textbook thesis described above.

When a small quantity (eg 18 ul) of the test solution evaporates on a surface, the area occupied is normally only ca 0.7 sq cm and during evaporation most of the residual component ends up in a smaller mound of material. Thus the area covered by the radiochemical in this case is routinely only a fraction of a sq cm and evaporation of the earlier portion is similar to the evaporation of a bulk system.

The rationale for these observations is that the number of molecular interactions between and among similar evaporating molecules significantly decrease as the amount of radiochemical evaporates towards and approaches a monolayer and then to very low fractions of a monolayer: The rate of evaporation thus increases dramatically. In this discussion the effect of surface/evaporating molecular interactions is disregarded.

Applied to the analysis of micro-organic residues, the use of the much faster evaporation associated with monolayer / submonolayer conditions extends the sensitivity of the ERA method by at least two to three orders of magnitude since even extremely low amounts of non-volatile residue grossly affects the faster slope associated with the lower portion of the evaporative process. The values associated with the calibration of dioctyl phthalate (DOP) using AK shown in Figure 3 and Sun Quench Oil (reported to be a proprietary mixture of C_{18}-C_{35} linear hydrocarbons) using BK shown in Figure 4 at the levels below approximately 100 nanograms are illustrative of the change in the mechanism in the overall curve plot. The plot of the slopes associated with those lower levels of residue provide a decidedly different shape--apparently almost a linear relationship with a smoothed junction to the logarithmic relationship which applies to higher levels of residues. The positions of NVR and 'clean' are arbitrarily placed one and two orders of magnitude, respectively, below the 2.3 and 1.9 values *for plotting purposes only*. The true or absolute position in each case with respect to the deposited residues is not fully defined at this time although the slopes shown tend to justify the positioning. The NVR levels represent the residue deposited from 10 ul of the same pure solvent as that used in the volumetric dilutions as well as that used in the test solution original formulations. The levels shown by the slopes indicate that the NVR purity of each solvent is less than 10 PPB (0.01 PPM) and it may be as low as 1 PPB.

The slope values *expressed as positive integers* are plotted in Figures 3 and 4. Smoothing of data was based on logarithmic values of counts-per-second-less-background and involved adding five immediately prior and five immediately subsequent logarithmic data values to each logarithmic data value followed by dividing by the net degrees of freedom (in this case 10). The resultant smoothed values were analyzed by computer by selecting the slope based on minimal variance.

In Figure 4, slope values vs amount of residue were also calculated based on logarithms of raw-data- less-background. Also in Figure 4 the relationships of slope values based on the maximal differences between successive six second data accumulations expressed as logarithms. For each calculation of slope, the six differing accumulations starting with the first through sixth data points and extending through the data sets were analyzed for the maximal difference between successive values. These maximal differences were then totaled and divided by three. The values plotted in Figure 4 represent the center three of five tests in the calibration series while the NVR and 'clean' values were based on all four tests in each case.

The one standard deviation errors for the data points used in plotting Figure 4 are shown in Table 1.

EXPERIMENTAL DETAILS

The microcomputer-based MESERAN MicroOrganicResidue Model 400 MOR together with current operating software was used for all the measurements. This analytical instrument provides a highly regulated high voltage power supply for the GM. detector and also provides a internal nozzle directing the air or nitrogen flow between the surface being tested and the adjacent GM detector. Count data is obtained during each second and is recorded by the computer for analysis directly following data acquisition.

The surfaces employed in the *DOP* (dioctyl phthalate) calibration were 40 mm watchglasses of soft glass which were cleaned in a hot sulfuric/nitric acid mixture followed by copious rinsing with distilled water. The surfaces were encased in hest cleaned aluminum foil (which acts as a 'getter' for contaminants) during oven drying at 102 C.

The surfaces employed in the *Sun Quench Oil* calibration were 38 mm borosilicate glass dishes with a 1/8 in by 1.25 in conical depression with a faired bottom on one side cleaned and dried as described in the paragraph above.

The *DOP* calibration solutions were made using redistilled chloroform starting with 19.4 mg of *DOP* in a 'clean' 10 ml volumetric flask followed by four successive 1 ml to 10 ml dilutions (namely 1.94 mg, 194 ug, 19.4 ug, and 1.94 ug.). In each case significant care was exercised to avoid inadvertent contamination. These solutions were then deposited using a precleaned syringe in 10 ul quantities starting with the lowest level of 1.94 ng. and proceeding to the highest level of 19,400 ng. In each case all the lowest depositions were carried out before progressing to the next higher order of magnitude. Each deposited 10 ul quantity was permitted to evaporate while protected from atmospheric fallout and were stored in precleaned closed plastic containers.

The *Sun Quench Oil* calibration solutions were prepared using double distilled methylene chloride for the first 230 mg solution and triple distilled cyclopentane for all the lower levels. The five order of magnitude dilutions resulted in deposition of 10 ul containing 2.3 nanograms at the lowest level.

DISCUSSION

The ability quantitatively to measure microorganic residues to well below the nanogram levels described herein will depend on the ability to reproduce clean surfaces and to prepare and maintain the radiochemicals and the solvents employed to even greater levels of purity than the present methods permit.

The authors are not aware of any reference in the published or unpublished literature with respect to the significantly increased rates of evaporation of monolayer / submonolayer molecules or to the method of analysis of very low nanogram levels herein described. The ability quantitatively to measure to such levels of oily or greasy residues is described herein and in the cited publication (Ref. 3) for the first time.

A broad reevaluation of residues and contamination at subnanogram levels as well as studies of improved cleaning procedures is now underway in the authors' laboratories to extend the current methodology toward its absolute limits.

SAFETY AND ENVIRONMENTAL ASPECTS

A few comments on the safety aspects of the use of the carbon-14 labeled materials are appropriate. The Material Safety Data Sheets provided with the preformulated and precalibrated test solutions provide --in addition to the conventional information--comprehensive surveys of the use of the materials with respect to release to the atmosphere and the actual levels of exposure of individuals. These levels are compared to OSHA and EPA recommended limits of both solvents and radiochemicals as well as the USNRC limits of release based on the limit to unrestricted areas of 3 E -9 uCi /ml, a value which is, strictly speaking, applicable only to USNRC licensed activities whereas the levels distributed as EXEMPT from such licensing have no such limit.

In all cases the release to the environment of vapor phase solvent and the chemical aspect of the radiochemicals are invariably many orders of magnitude less than the applicable OSHA and/or EPA limits. Even in the event of accidental breakage or spillage of a standard 1.6 ml quantity of test solution, no limits are exceeded with respect to the exposure of an individual.

One calculation shows that release to the atmosphere of the vapor phase radiochemical during maximal testing of ten tests per hour with exhausting to the outside atmosphere using a hood of only 100 CFM never exceeds the 3 E - 9 uCi / ml level at the release point. Another calculation shows that release of all the vapor phase material directly into a working area of 5 m x 4 m x 3 m with only six air changes per hour will never exceed any of the applicable limits of either solvent or radiochemical although release to the outside using a small hood is recommended.

CONCLUSIONS

Significantly improved statistical analyses of ERA based tests of deliberately deposited microorganic residues have provided quantitative measures from greater than 100,000 ng to very low nanogram levels.

Application of the improved analysis of microorganic residues in the real world of ambient temperature and pressures should materially improve cleaning procedures and the methodology of cleaning.

ACKNOWLEDGMENTS

The authors are deeply appreciative of the pioneering work in quantifying microorganic residues using MESERAN technology by R. P. Donovan, E. A. Hill, P. A. Lawless, and K. D. Carter, Jr. of the Center for Aerosol Technology of the Research Triangle Institute, Research Triangle Park, North Carolina in 1991. They also thank Roger Hoffman and IBM ROCHESTER for sponsoring the RTI effort.

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Figure 1

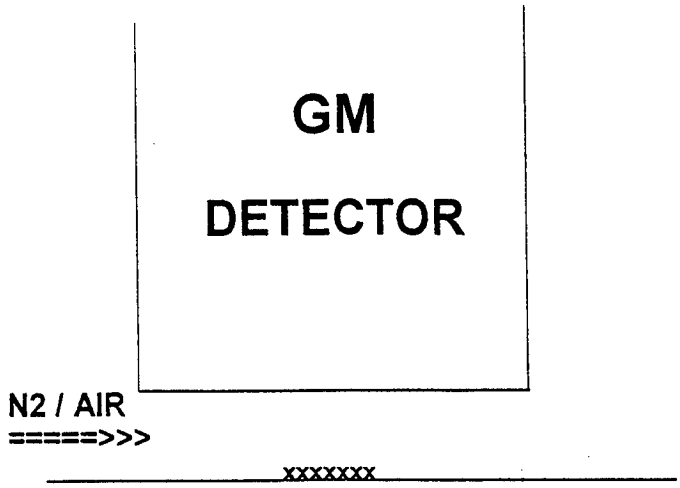

Figure 2
Plot of Ln (Counts - Background) Showing
Low, Medium, and High Levels of Organic Contamination

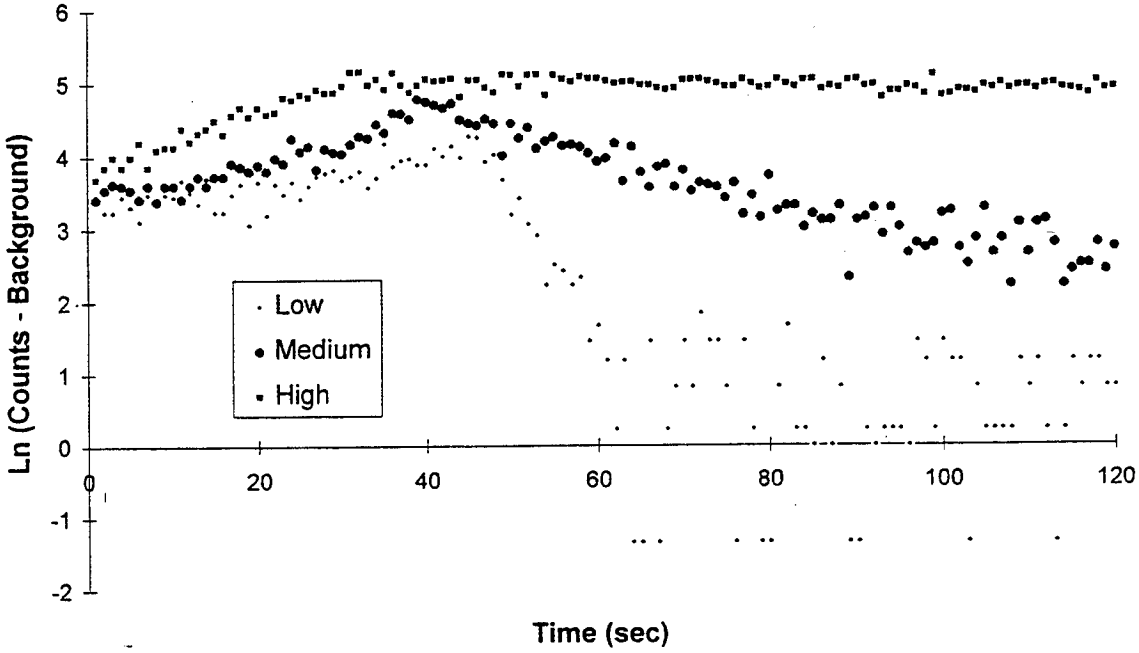

Figure 3

Calibration Curve For Dioctyl Phthalate (DOP) on Watchglasses (Ln Smoothed MESERAN Slope Values)

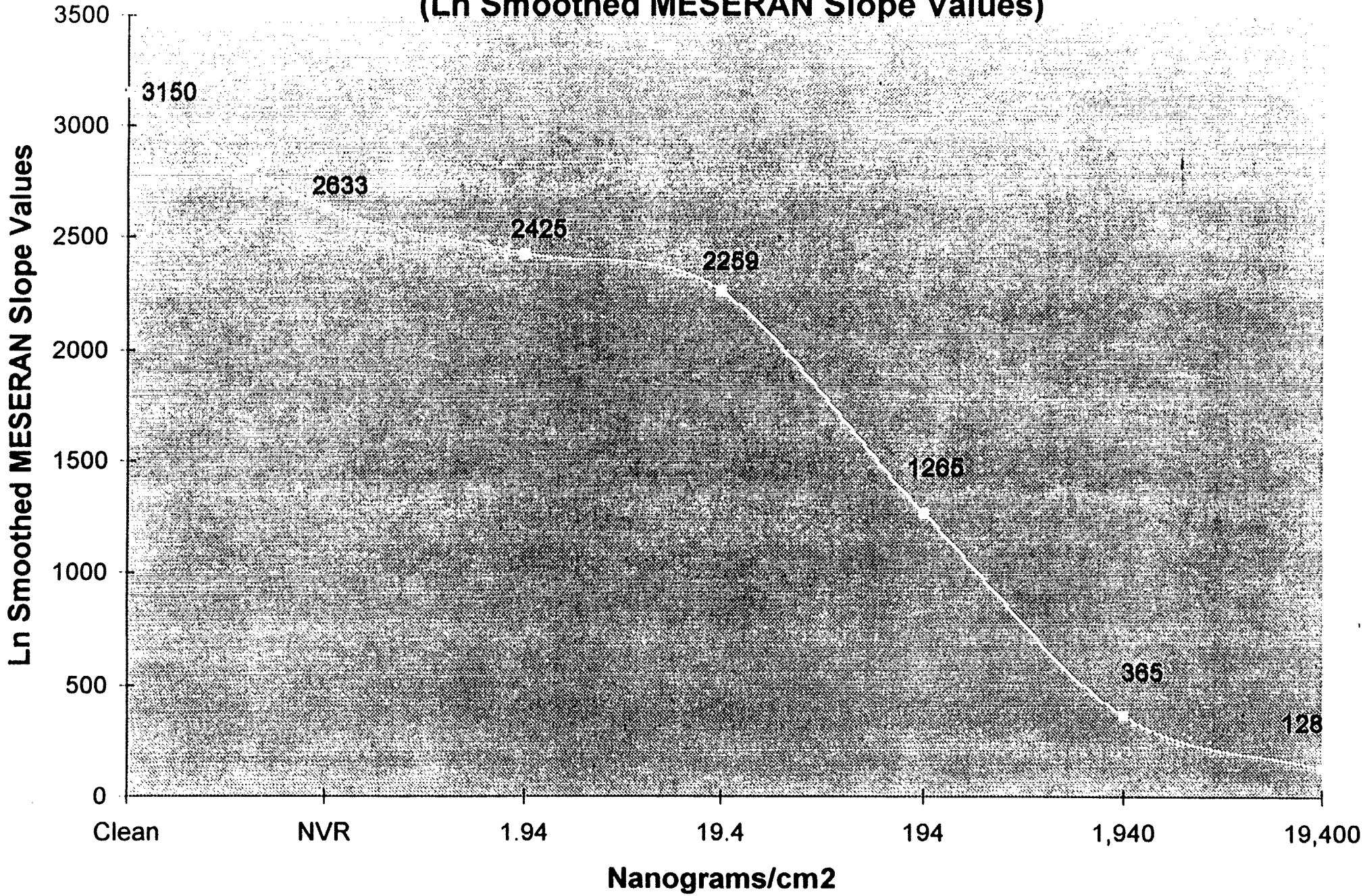

Figure 4

Calibration of Sunquench Oil on Glass Cones (Using Three Different Analysis Methods)

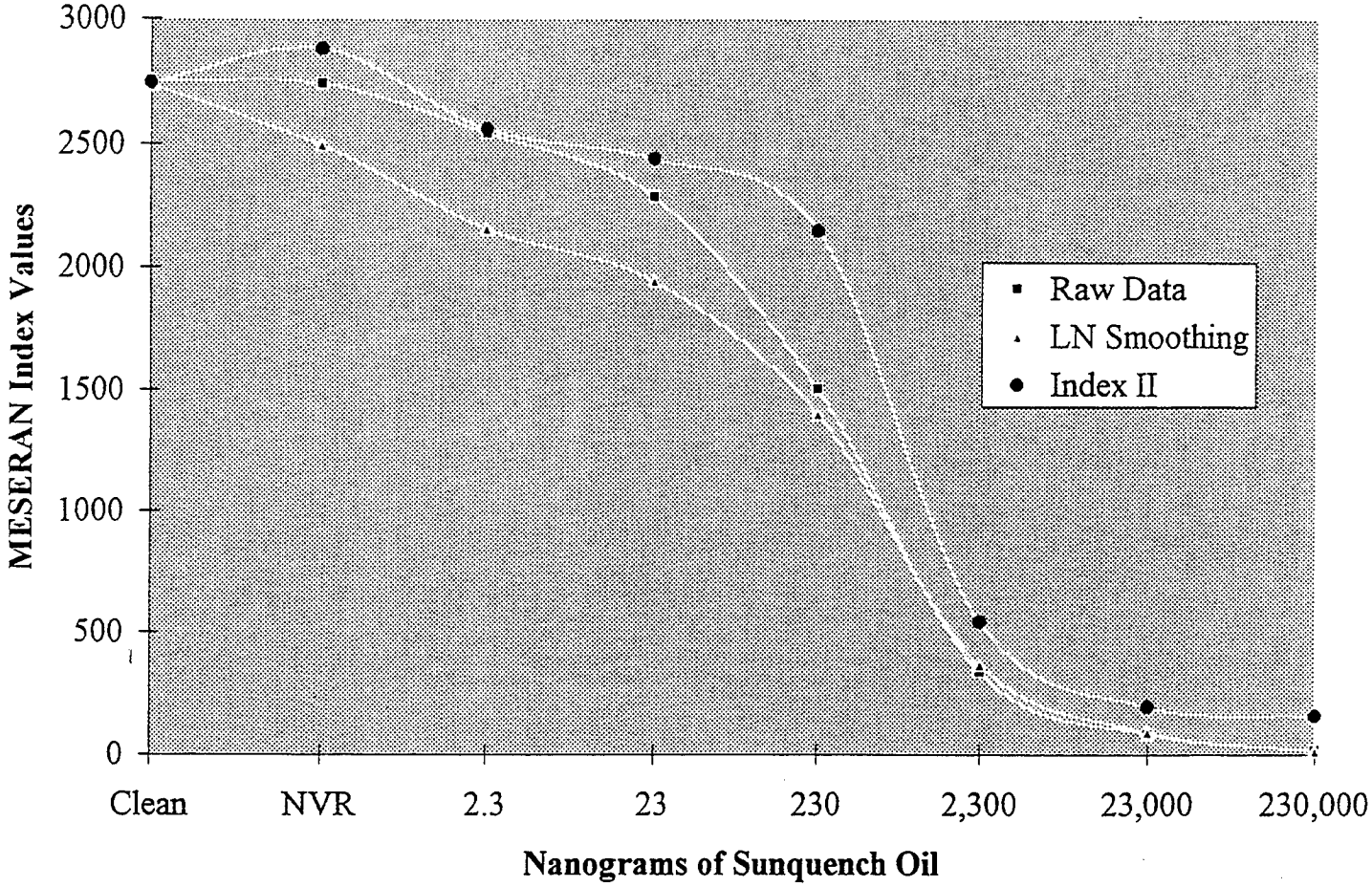

TABLE 1
CALIBRATION DATA FOR SUNQUENCH OIL

DEPOSITED IN 10 uL QUANTITIES ONTO 'CLEAN' GLASS CONES

NANOGRAM AVERAGES OF FIVE TESTS WITH HIGH AND LOW VALUES DISCARDED
NVR AND 'CLEAN' AVERAGES OF ALL FOUR TESTS IN EACH CASE

Nanograms	Smoothed	1 SD	Raw	1 SD	MAX DIFF	1SD
230,000	15	3	17	7	158	17
23,000	91	2	84	2	196	9
2,300	366	4	338	12	542	20
230	1399	103	1501	125	2146	78
23	1941	29	2283	108	2437	121
2.3	2154	112	2541	147	2557	216
NVR	2492	122	2739	156	2877	122
'CLEAN'	2734	87	2751	211	2744	42

AIR EMISSION REDUCTION AND CONTROL

THE DESIGN OF A SMALL TRANSPORTABLE SOLID ROCKET MOTOR EXHAUST SCRUBBER

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ABSTRACT

The Naval Surface Warfare Center, Indian Head Division (NSWC/IHD) is being funded by CNO45 to develop a system to scrub rocket motor exhaust gases from test firings. NSWC/IHD has initiated a pilot program to design and fabricate a transportable system to perform this scrubbing without adversely affecting static testing results. This effort will also provide data for future scale-up design efforts . This paper addresses previous scrubber design efforts, current design requirements and constraints, our design approach, and elements of the final design.

INTRODUCTION

Rocket motor static test firing is an integral part of many Navy and non-Navy installations. These installations static fire thousands of solid propellant rocket motors each year for new motor development, qualification, Lot Acceptance Testing and Surveillance Testing. In anticipation of tighter environmental regulations that would apply to all static testing installations, NSWC/IHD, as a Navy center of excellence for energetic material technology, rocket motor development and propulsion, has initiated a pilot program to develop a scrubber for rocket motor exhausts. This pilot scrubber design utilizes concepts from work done at other installations, in addition to several NSWC/IHD innovations. This program involves design, fabrication and testing of a complete scrubber system.

The scrubber system design effort will begin with a system designed to scrub exhausts from a small rocket motor (up to 7 pounds of propellant), then larger sizes as the design and operational aspects are verified. The system will serve as an economical and flexible development tool - providing efficient production scrubbing for the smaller motors while serving as a vehicle to confirm performance calculations and provide design data for other scrubber units. The pilot system has the flexibility to vary air flow, spray quantity, solution and concentration, and the nozzle location, which will allow the optimization of scrubbing effectiveness for different sizes of motors, while having no effect on the static test data. The resulting data should be of benefit to the rocket motor test community within and outside the Navy. The first unit has been designed, is in fabrication, and is scheduled for testing in the fall of 1996. The overall system configuration is shown in Figure 1.

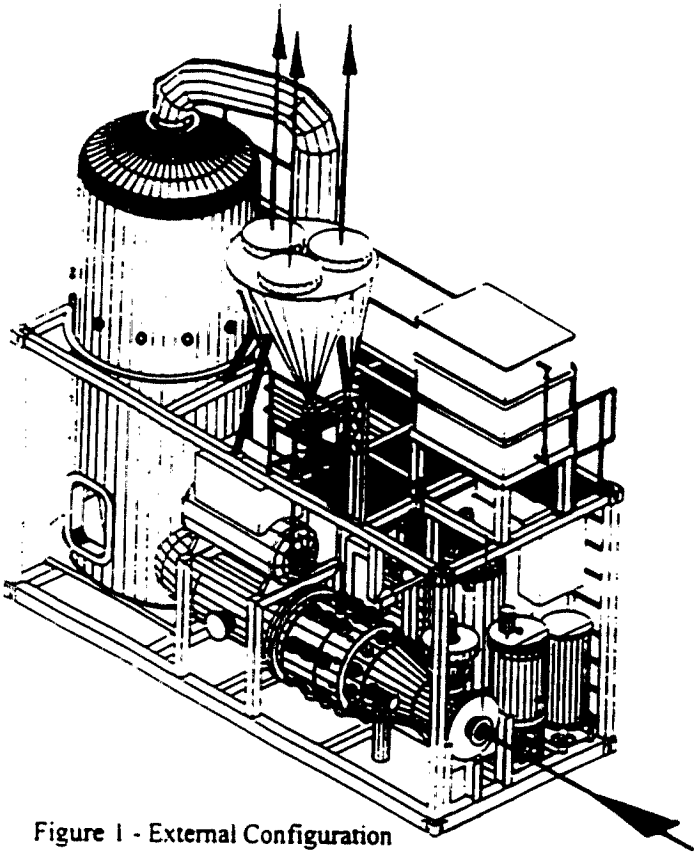

Figure 1 - External Configuration

DISCUSSION

Previous Systems

The cleaning, filtering, or scrubbing of the harmful emissions from rocket motor test firings has for many years ,been a major subject for discussion and deliberation. Agencies concerned with rocket motor development have tried to develop means of meeting emission requirements but no single method has been universally satisfactory. In earlier years Atlantic Research Corporation built a fully enclosed facility for Beryllium based rocket motors, batch cleaning the collected exhaust in slow time after the firing was complete. Edwards Air Force Base (AFB) built a pilot "straight through" scrubber for 5,000 pound thrust motors in the 1970s, but damage caused during test operations, and concern over future similar problems, halted any future development.

Design Requirement

The overall requirement is for NSWC/IHD to comply fully with future Clean Air Act regulations while inhibiting the efficiency of rocket motor testing as little as possible. This will entail the scrubbing of the exhausts from rocket motors of up to 1000 pounds mass, not a simple problem as there must be no impact on the test data being captured, e.g. thrust measurements, nor the turn-round rate or cycle time of testing (NSWC/IHD fires up to 40 small motors per day from a single test bay).

The specific requirement addressed here is the design of a proof of concept scrubber for test firings of small rocket motors (maximum 7 pounds of propellant for up to 7 seconds firing time). The performance and the dynamics of the scrubbing process will be analyzed to provide data for scaling up the design for larger rocket motors. The prototype scrubber is planned to be used in day-to-day test firings of small slab motors and will be capable of scrubbing the exhaust gas from rocket motors fired every 12 minutes. The design objective is to remove 98 percent of the hydrochloric acid and 98 percent of particulates greater than one micron. The system is transportable and is mounted on an 8 foot by 20 foot skid.

Design Approach

A thorough literature search was carried out to establish whether any data was openly available on systems, processes and technologies which could materially meet the design requirements. The prime references were reports on the Edwards AFB exhaust scrubber which was developed, built and tested between 1970 and 1977. Atlantic Research Corporation provided information on their Beryllium rocket motor exhaust scrubber; and the following databases were carefully searched: CPIA, AIAA, DTIC, NTIS, Epilog. The result of this search was that no successful rocket exhaust scrubber had been built, and operated, and the details published in the open literature.

Due to the fact that the Edwards AFB scrubber appeared to be the only system and configuration that would be applicable to the NSWC/IHD requirement, a detailed analysis of the relevant reports was made. Simply put, in the Edwards AFB design, the rocket motor fired into a diffuser which led to a chamber where the high velocity, high temperature exhaust was deluged with water sprays that penetrated to the core of the exhaust stream; following intimate mixing of the entrained scrubbing solution with the gas stream, the exhaust entered an expansion area where the exhaust was slowed and passed through a demister. No provisions were made for burning the combustibles in the gas stream.

Constraints and Input to Design

The overall design requirements have been stated earlier; the major design constraint being the 20 foot by 8 foot sizing. Other design inputs were discussed and included as the project progressed. The primary inputs were as shown in Table 1 below:

Table 1 - Design Parameters

Parameter	Requirement
a. Size	Maximum 20 foot x 8 foot footprint, 8 foot max height desirable
b. Weight	No specific constraint (but transportable)
c. Firing Interval	12 minutes
d. Maximum Propellant Weight	7 pounds
e. Maximum Burn Time	7 seconds
f. Design Max Burn Rate	3 pounds per second
g. Design Propellant Composition	Double Base AA-2, N5 and Composite
h. Scrubbing Efficiency	98 percent of HCl; 98 percent of 1 micron particulates
i. Material	Low Cost (test & development only)
j. Test Motor Nozzle Height	36 inches above ground level
k. Diffuser Compatibility Accommodation	2.5 inch to 6 inch diameter diffusers

After set-up, the automated scrubber will require a minimum of operations personnel. All actions required to operate and monitor the scrubber will be possible using the test personnel already required in the block house (replenishing fluids, dumping spent fluids and changing filter bags will periodically require additional personnel).

Afterburning of Exhaust

The primary technical problem with the Edwards AFB design was associated with the unplanned afterburning of the exhaust as it exited the unit due to the mixing of the exhaust with the outside atmosphere. The design and the composite material used in this area resulted in afterburning which caused considerable damage to the system. Despite this, the scrubber was reported as being very effective in scrubbing hydrochlorides and particulates from the exhaust in its earlier trials.

During early design discussions on the planned configuration of the system, the question of how and where to burn the excess hydrogen and carbon monoxide was a primary consideration. Initially, it was decided that the design should encourage oxygenation immediately after the exhaust entered the scrubbing chamber from the diffuser. Several methods of providing sufficient oxygen were discussed:

- Entrainment of air at the annulus around the rocket nozzle inside the diffuser tube.
- Providing spring loaded ports at the front end of the scrubber/afterburner chamber to admit combustion air.
- Injection of pure oxygen into the scrubber chamber via high pressure bottles.
- Reliance on the large volume of resident air in the scrubber (compared with exhaust volume) for combustion.
- Utilization of a powerful centrifugal exhaust fan to induce a high flow rate of external air (oxygen) through suitable ports.
- Injection of liquid oxygen.
- Some combination of the above.

However, the constraint on the overall length of the scrubber system drove the decision to design for afterburning after the demisters but at the same time allowing for the exhaust being partially oxygenated at the exit of the diffuser. The decision was based on the loss of residence time in the scrubbing chamber and the greater importance of scrubbing out the HCl. Alternatives, including designing a 'Z' shaped scrubber chamber (to provide more length and residence time), were not found acceptable due to manufacturing difficulties and overall volume constraints. A further complication in arranging for full combustion at the diffuser exit is that the volume and temperature of the gas stream would rise considerably requiring a greater volume of scrubbing water for cooling and, due to the volume/velocity increase of the gases, less residence time within the scrubbing chamber. Despite the design intention to afterburn the exhaust just before exiting to atmosphere, the scrubber chamber section was designed for an internal pressure of 150 psig to allow for both local shock effects and fast combustion causing rapid increases in local pressure. A simplified exhaust flow diagram is depicted in Figure 2.

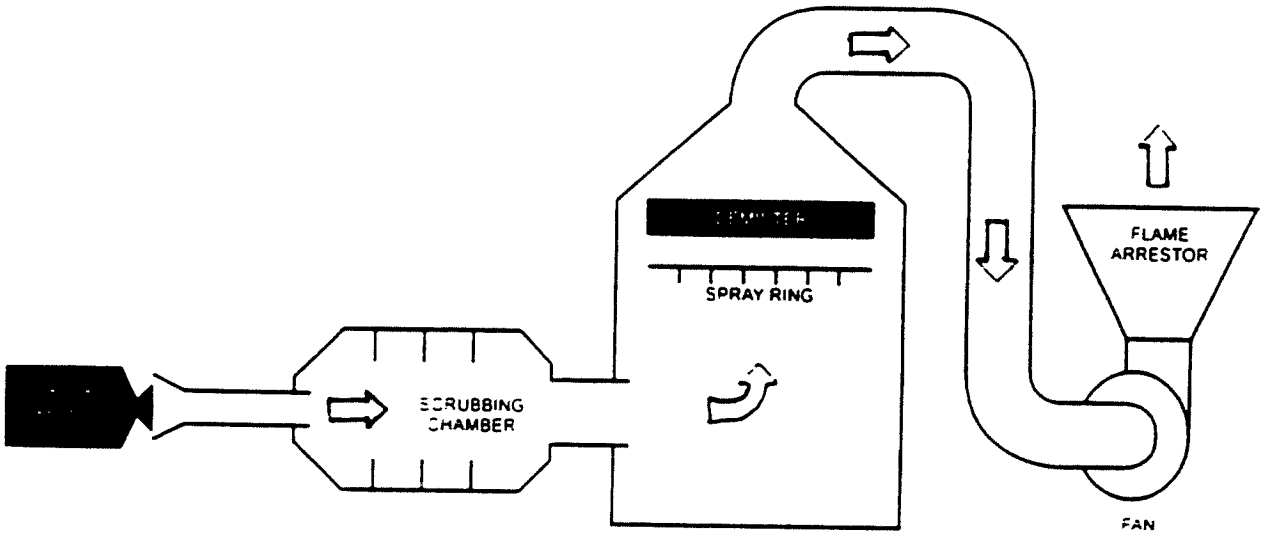

Figure 2 - Simplified Exhaust Flow

OVERALL CONFIGURATION AND OPERATION

Motor Exhaust Capture

The rocket motor exhaust, including approximately 10 percent of the mass of the motor exhaust drawn in as entrained air via the annulus between the motor nozzle and the diffuser, exits into the scrubber chamber via an adjustable (exchangeable) flanged diffuser tube. Diffuser tubes outfitted with reducer flanges allow for diffuser tubes of 2.5 inch to 6 inch in diameter to match the characteristics of the motor being tested. For initial tests, a diffuser diameter of 2.5 inches was assessed appropriate for a [illegible] pound motor and 3 pounds per second burn rate.

Scrubber Chamber

The calculated static pressure in a 2.5 inch diffuser pipe which is transferring the exhaust gases from the 3 pound per second rocket motor burn to the scrubber is calculated to be about 45 psig just before it discharges into the scrubber. On entering the scrubber, it expands rapidly. Just downstream of its entrance, the static pressure is calculated to be about 2.5 psig on the scrubbers centerline, decreasing to about 1 psig at the scrubber wall. Following injection of the spray solution into the 30 inch diameter chamber, its pressure just upstream of exiting into the large diameter demister chamber is predicted to be essentially uniform and about 1 psig (see Figure 3, below).

Since the exhaust flow is far from steady, accurate thermodynamic calculations were not practicable. Steady flows and normal shocks were therefore assumed to establish approximate gaseous conditions of state. With regard to the thermochemical aspects, a stoichiometric program was written to take account of different rocket motors and compositions, dimensions of the unit, and KOH concentration and flow rates to arrive at the constituents of the resultant exhaust to the atmosphere.

Essentially, all of the cooling of the gas stream results from the vaporization of part of the spray solution. The gas stream becomes saturated with water vapor at about 195° F. Very little conductive/convective cooling of the gas stream occurs beyond this to reduce it below the saturation temperature. About seven times the volume of water required for evaporative cooling is sprayed into the 30 inch chamber to assure an abundant volume is available to scrub the acid from the gas stream.

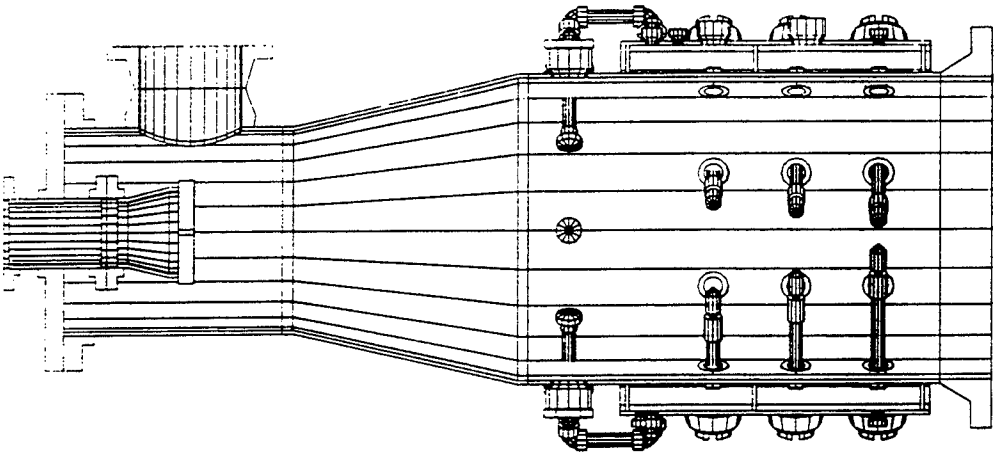

Figure 3 - Scrubber Spray Chamber

Demister Chamber

The scrubber chamber opens out into a large demister chamber which was sized to slow the flow rate to about 7 feet per second for maximum demister efficiency within scrubber module constraint dimensions. The exhaust is subject to further sprays in this chamber which de-entrain small liquid droplets as well as particulates. Three mechanisms effect de-entrainment of the moisture droplets (demisting) in the gas stream:

1. The reduced gas velocity permits larger droplets and particulates to gravity settle to the bottom of the chamber.
2. The large droplets sprayed down from the nozzles mounted near the top of the chamber capture (on impact) smaller entrained droplets and particulates carried by the gas stream.
3. The knit mesh pad coalesces essentially all the droplets/particulates not removed by the first two mechanisms. It is anticipated that 99.99 percent of the entrained moisture in the gas stream will be removed in the demister chamber.

An allowance has been made in the design for the addition of a second demister unit.

Filtration Units

The scrubber water, or KOH solution, is drained into the spray chamber sump tank and passed through polypropylene bag filters in filter baskets to prepare the solution for further scrubber use. Control of this spraying solution regeneration process is totally automated, controlled by the Programmable Logic Controller (PLC).

Centrifugal Blower Unit

The purposes of this unit are: to draw in oxygenating air through the rocket nozzle annulus and the pressure/vacuum port; to maintain a negative pressure in the system in order to assist the exhaust flow at firing; to ensure a continued flow after firing to ensure all harmful constituents are scrubbed; to eliminate blow-back; and to clean out the system before and after maintenance. The exhaust fan was sized to handle the gas stream from scrubbing a rocket propellant burn of 3 pounds per second; the resultant gas stream is approximately 8.5 pounds per second, the greatest percentage being gaseous water (steam).

External Services Required

The rocket exhaust scrubber requires the following outside services for operation:

- 440 volt, 3 phase, 60 Hz, electrical power.
- Fresh water to make-up the water that vaporizes into the atmosphere during the scrubbing process and to recharge the system when the spent scrubbing solution is dumped.
- A waste water system to receive the discharged spent scrubbing solution.
- Potassium hydroxide, KOH, solution (5 Normal, technical grade) to maintain the spray solution at its required pH value.
- Removal of solid waste.

Solid and Fluid Wastes

The scrubber is designed to automatically process the gas stream from a 7 pound rocket motor every 12 minutes (40 firings per day). The commencement of the scrubber operation will be accomplished remotely from the rocket motor firing control room just prior to firing the tested rocket motor. A programmable logic controller automatically cycles the spray solution after each firing.

It is projected that the rates of replenishment of water and KOH solution, and discharge of wastes shown below in Table 2, will result from the scrubbing operation based on the rocket motor size and firing cycle described above:

Table 2 - Make-up Liquids

Stream	Make-up Rate	Recharging System Rate
Fresh Water	32 GPD	360 Gallons every 1½ Weeks
Concentrated (5 normal) KOH	17 GPD	5 Gallons every 1½ Weeks
Spent Scrubbing Solution Discharge	None	360 Gallons every 1½ Weeks

It is anticipated that the spent scrubbing solution waste stream to be drummed for disposal will contain a 12½ percent concentration of dissolved salts (primarily potassium chloride, KCl).

Solid wastes (metal oxides and salts) will be removed by polypropylene bag filters in the scrubbing process. Although the actual projected rate of solid wastes is small, less than 50 pounds per day, some of them (like aluminum hydroxide) are gelatinous and may clog-up filter bags frequently. The frequency of replacing filter bags will have to be developed based on early operating experience with the scrubber. Differential pressure sensors are provided on the filters to sound an audible alarm when the pressure drop through the filter gets too high.

Weight, Size and Transportability

The dry weight of the scrubber module is estimated at 11.3 tons, with a fully replenished wet weight of 12.8 tons. The scrubber was designed to conform with a 20 foot by 8 foot standard shipping container skid to ease transportation, and its target maximum height was 8 foot to conform with standard shipping container heights. This

height limit could not be maintained. Three of the process requirements drove the assembly to a module height that exceeded the 8 foot target:

- The scrubbing process - in order to provide an efficient scrubbing process and arrange the mist eliminating demister to be accessible for developmental modifications during test and evaluation, a 15 foot 1¼ inches module height was required.
- The flame arrestor on the blower discharge - a vertical flame arrestor has been designed and arranged so that its maximum height does not exceed the height required by the scrubbing process.
- Gravity filling the high pressure spray system - the spray solution storage tank had to be elevated for efficient gravity filling of the spray distribution system prior to commencing high pressure spraying.

For shipping purposes, take down joints are provided on the demister chamber and the flame arrestor stack which will reduce the module's shipping height to 9 feet 6 inches. The field erection effort required for reassembly will not be significant. The skid (baseplate) is fitted with standard container corner fittings to facilitate transportation and lifting. These fittings are also used with standard shipping container twistlock fittings to lock the scrubber in place at the test sites.

DESIGN FLEXIBILITY AND FUTURE DEVELOPMENTS

Although the scrubber has been designed to handle the exhaust from a 7 pound rocket motor burning double base or composite propellant at a rate of 3 pounds per second, its greater value is seen to lie in inherent design features that will allow processing the exhaust from other rocket motor sizes and propellant types. These flexible features include:

- A variable speed centrifugal blower. By varying the speed of the blower, it can be "tuned" to handle different gas stream flow rates.
- The spray chamber has 100 percent spare ports for additional or alternative spray nozzles. These spare ports have pipe plugs installed.
- The hydropneumatic tank is outfitted with a level sensor that can be adjusted to control the high pressure KOH solution feed pump to fill the tank to any level selected prior to commencing high pressure spraying.
- The scrubber is designed to accommodate diffuser pipe diameters between 2½ inch and 6 inch.

As discussed earlier, these features will allow NSWC/IHD to gather data on which to base the design of larger scrubbing systems, including those large enough to accommodate the Standard Missile SM-2 Motor of some 1,000 pounds mass.

TEST & EVALUATION

Data Acquisition

Multiple ports have been designed into this pilot scrubber to allow for flexibility in acquiring data. Pressures, velocities, temperatures and gas samples will be measured and recorded, and the ports are of standard design allowing any of these sensors/samplers to be used in any location. Gas samples will be extracted via double banks of evacuated 0.5 liter bottles which can easily be disconnected and replaced between firings. Since the exhaust flow will be transient, it will be important to gather data over time; at most cross-sections, therefore, three ports are located circumferentially and equispaced, so that the variation in gas content with time can be captured by sequencing the solenoid valves on the relevant ports.

Operation of the sensors/samplers will be controlled by appropriate programming of the PLC. The P, V and T data will be automatically recorded and time stamped to record the times of gas sampling so that correlation of the test measurements can be made.

Performance Testing

After the scrubber systems' functions have been individually tested over their full performance range, the full-up system will be given 'dry' runs (i.e., no rocket fired) to ensure sequencing and operation satisfactory, and to capture baseline data. One pound slab motors will then be used to gain initial data for comparison with design calculations particularly in regard to over-temps or over-pressures. Then the scrubber will be 'tuned' to standard one pound slabs by altering air flow rates, KOH flow, and diffuser diameter to optimize these parameters (for these particular motors); the resulting data will provide guidance for the settings for larger motors. Finally, rocket motors will be sequentially tested with higher thrusts and longer burn times until the limit of the scrubber's performance is reached. It is expected that this scrubber will accommodate (and scrub satisfactorily) the ubiquitous 2.75 inch rocket motor.

CONCLUSION

The major constraints on the design of the exhaust scrubber were the length and the transportability. Unlike the Edwards AFB scrubber which was built in an area without physical constraints, the NSWC/IHD requirement resulted in major design difficulties and compromises. On the other hand, these constraints provide NSWC/IHD with the very significant advantage of an exhaust scrubber that can be utilized at different test sites at NSWC/IHD, and could also be transported to other locations for test or demonstration.

The Pilot Rocket Motor Exhaust Scrubber provides the Navy with a mobile, flexible exhaust scrubber which will cleanse the exhaust of rocket motors up to 7 pounds in weight with exhaust flows up to 3 pounds per second. Particulates greater than one micron, and 98 percent of HCl, will be scrubbed out. The design has utilized the experience of all previously known systems and has been conservatively designed to provide for future development. The design allows for flexibility for test and evaluation and has the unique advantage of being transportable for demonstration and tests at distant sites.

ACKNOWLEDGEMENTS

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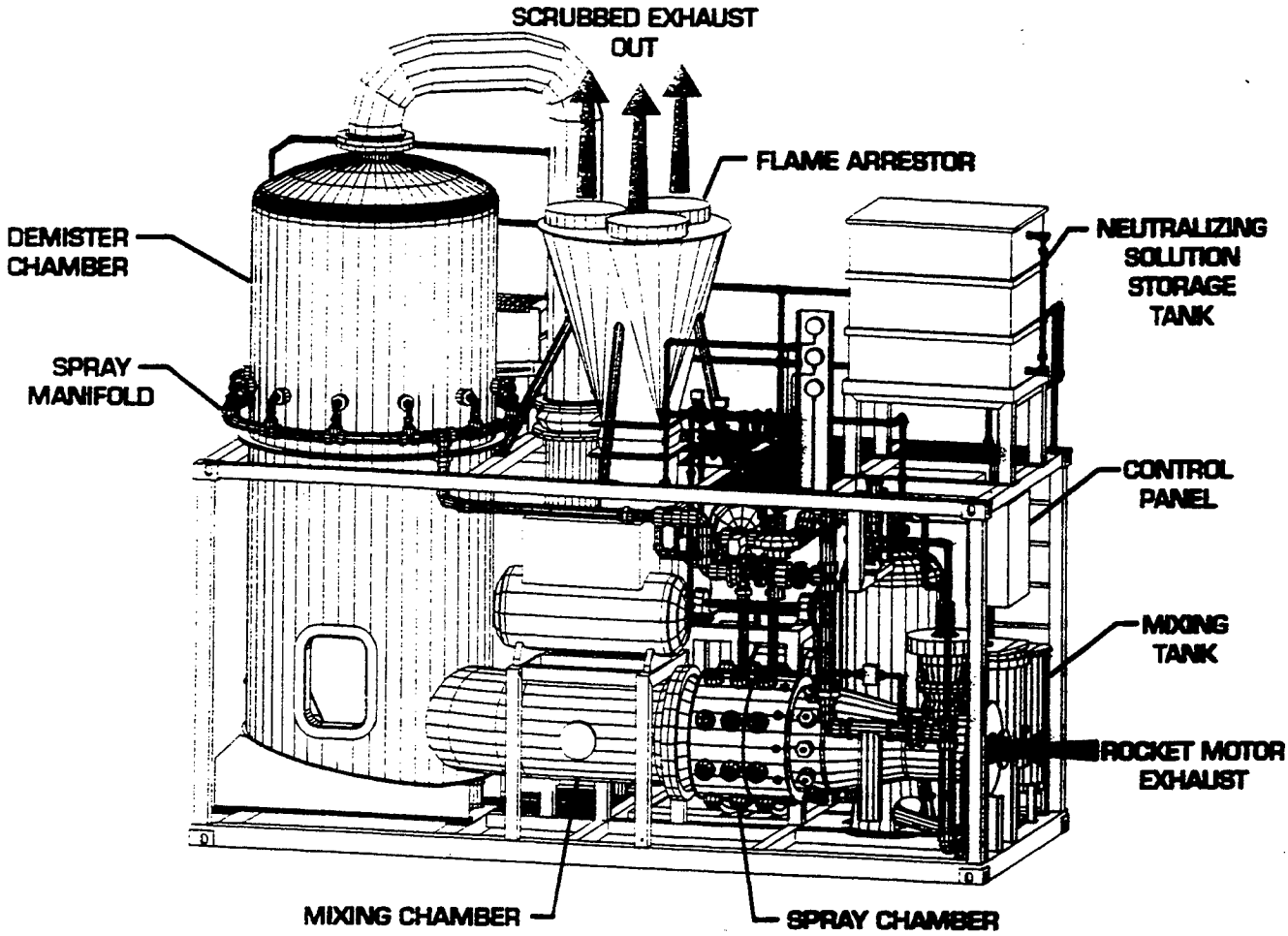

Rocket Motor Exhaust Scrubber

Experimental Studies on the Removal of Airborne VOCs By a Pilot Scale Hybrid Air Treatment System

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ABSTRACT

The Strategic Environmental Research and Development Program (SERDP) and the Marine Corps Logistics Bases (MCLB) have sponsored research on a 2500 cfm pilot scale hybrid air treatment system at The Applied Research Laboratory, The Pennsylvania State University. This hybrid system combines photolytic degradation, counter-current packed bed scrubbing, and carbon adsorption to treat a variety of airborne VOCs and HAPs at ambient temperature. In addition, the water and carbon are regenerated in-situ using advanced oxidation processes, eliminating secondary waste streams.

The pilot scale system has been in operation for over one year. Solvents typically present in Marine Corps coatings have been treated in the system. The performance of each individual system component has been determined for alcohols, hydrocarbons, ketones, and chlorinated solvents. System performance relative to a solvent's chemical functionality and physical attributes has been explored.

This work has shown that hybrid systems have a place in the treatment of exhaust air streams characterized by low concentrations of VOCs, high volumetric flow rates, changing VOC composition, and inconsistent flow rates. This paper will present the findings of these studies.

INTRODUCTION

The Marine Corps operates maintenance centers in Albany, GA, and in Barstow, CA. These centers are referred to as the Marine Corps Multi-Commodity Maintenance Centers, $(MC)^3$. At these centers, Marine Corps vehicles are serviced, repaired and maintained. This process generally includes painting and vapor degreasing operations which generate low levels of airborne volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), which are then exhausted to the atmosphere. Increasing Federal regulations, particularly the Clean Air Act Amendments of 1990, and state regulations, especially in California, require that these emissions be reduced and controlled.

Three years ago the Marine Corps Logistics Bases selected a 45,000 cfm hybrid UV-oxidation system for installation at their Barstow facility.

In early 1993, MCLB submitted a joint proposal with the US EPA to the Strategic Environmental Research and Development Program (SERDP) with the goal "to achieve rapid improvement in the quality of air emissions from paint spray booths and vapor degreasing tanks at the $(MC)^3$s and develop information on advanced air pollution prevention and control practices."

The research team for this project included the Marine Corps Logistics Bases (MCLB) and the US EPA Air and Energy Engineering Research Laboratory (AEERL). The Applied Research Laboratory at The Pennsylvania State University (ARL Penn State) provided technical and research support to the Marine Corps. Terr-Aqua Enviro Systems, Inc. was a commercialization partner through a cooperative agreement with ARL Penn State.

As a member of this project team, ARL Penn State's responsibility was to "perform modeling and experimentation to feed an iterative cycle of enhanced understanding of the [UV/radical oxidation air treatment] processes, [and] optimization of the field [air treatment] systems." This objective was to be met, in part, by defining baseline operation of a 2500 cfm pilot

scale air treatment system, and then comparing this baseline data with data on the same system after modifications were made. This paper discusses the results of the baseline pilot scale studies.

EQUIPMENT AND METHODS

A 2500 cfm pilot scale air treatment system was installed at The Applied Research Laboratory. This air treatment system is a hybrid system consisting of three independent units. Each unit is based on a unique VOC removal concept:

- two gas phase photolytic reactors which use UV radiation and ozone to initiate photolytic, photocatalytic and free radical reactions to oxidize VOCs,
- an aqua reactor which uses a counter-flow packed bed scrubber, a mist air dispersion unit, and an ozonating water treatment tank to absorb and oxidize VOCs, and
- a granular activated charcoal (GAC) unit which adsorbs VOCs.

Both the water and the GAC are regenerated within the pilot unit using advanced oxidation technologies. A schematic diagram of the pilot system is shown in Figure 1.

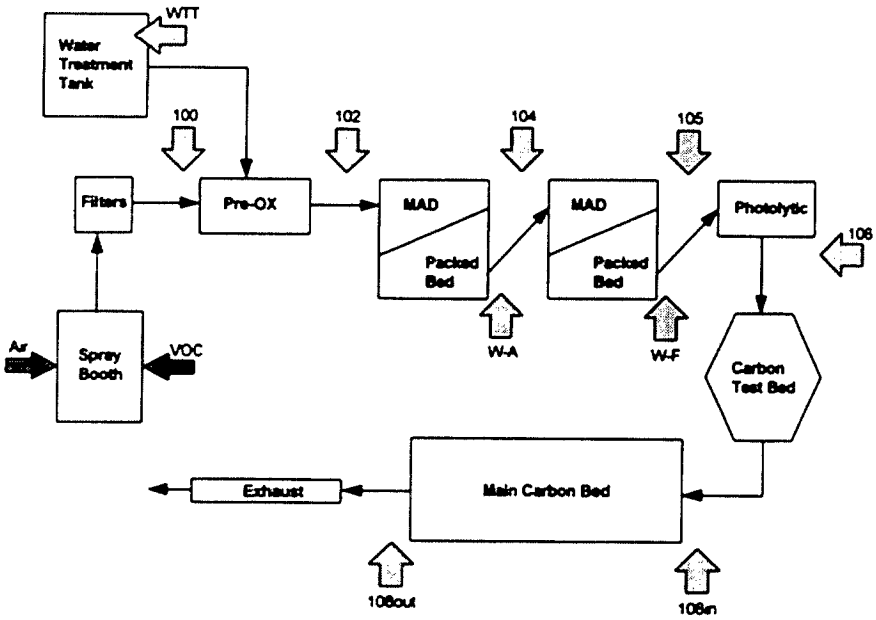

Figure 1. Schematic of pilot scale air treatment system showing air flow and air and water sampling ports.

Because it was designed as a research unit, the pilot scale system is flexible in a number of system parameters, so that investigations can include examination of changes in these parameters. Thus far, modifications of the following parameters have been studied: number of UV bulbs contained in each photolytic reactor (up to 7 bulbs), the volumetric flow rate of air to be treated (1300 cfm to 2600 cfm), height of packed bed scrubber, effect of mist air dispersion units, and residence time in the aqua reactor.

Samples of the air stream were taken from before and after each component of the system. This made it possible to examine the operation of each system component individually. All air and water sampling locations are indicated on the diagram in Figure 1.

All samples were tested by capillary gas chromatography using either flame ionization, thermal conductivity, electron capture, or mass selective detectors (FID, TCD, ECD, MS). Air samples were typically analyzed with the aid of cryoconcentration and cryofocusing. Water samples were typically diluted with a solvent containing an internal standard. All samples were quantitated using single point calibrations after linearity in the concentration range of interest had been validated.

Several VOCs were run in the pilot scale system for the purpose of collecting baseline data to establish a fundamental understanding of the physical and chemical functioning of the system. The solvents (VOCs) selected were chosen because they represented general classes of chemical compounds from polar to non-polar and chlorinated, and because they were representative of the solvents found in typical surface coatings used by the Marine Corps. The solvents which are the subject of this report are ethanol, ethylbenzene, methylethyl ketone, and trichloroethylene. Table 1 lists various chemical and physical data for these solvents.

Table 1. Physical data for solvents.

Solvent	CAS #	Chemical Formula	Molecular Weight (gms/mole)	Specific Gravity (gm/mL)	Boiling Point (°C)	Water Solubility
Ethanol	64-17-5	C_2H_5OH	46.1	0.785	78	Infinite
Ethyl benzene	100-41-1	$C_6H_5C_2H_5$	106.2	0.867	136	152 mg/L at 20°C[1]
Methylethyl ketone	78-93-3	$C_2H_5COCH_3$	72.1	0.805	80	353 g/L at 10°C[1]
Trichloroethylene	79-01-6	$ClCH{=}CCl_2$	131.4	1.464	87	1.1 mg/L at 25°C[1]

1. Verschueren, Karel; *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold, New York, 1977.

A typical run on the system consisted of spraying a VOC (solvent) into the incoming air stream to produce a solvent concentration of approximately 100 ppm. This concentration is similar to that experienced in the Marine Corps spray booths, 0-300 ppm (Ayer). Some data has been normalized to adjust for fluctuations in the actual air stream concentrations. Typical run times were 2 to 12 hours, with periodic sampling throughout the system over time. In general more samples were taken at early time periods, and around the dynamic aqua reactors. Fewer samples were taken around the steady state photolytic reactors and the carbon bed.

Findings for each technology - photolytic reactors, aqua reactors, and carbon bed - are discussed individually below. A summary discussion compares the complete system profiles for the four compounds tested.

RESULTS AND DISCUSSION

Photolytic Reactors

Reactor design. The pilot scale air treatment system contains two photolytic reactors. The first photolytic reactor (also called the pre-ox) is the first oxidation chamber that the air stream sees, located immediately after the inlet filters. The second photolytic reactor is located after a coalescer which separates it from the aqua reactors. (Figure 1).

The first photolytic reactor sees air at ambient humidity (relatively 'dry' air), particularly in actual production scale units where air from inside a building is exhausted out to the treatment system. In the pilot scale system, where outside air is pulled into the treatment system, there is no humidity control; humidity (and temperature) of the incoming air stream is dictated by ambient weather on the day of the run.

The second photolytic reactor sees only very humid air, after the air stream has passed through the aqua reactors. It is possible to install up to 7 bulbs in each photolytic reactor in the pilot scale unit; the bulbs used for these studies were 40 W low pressure mercury vapor lamps, which have about 90% of their light output centered at 254nm (Helz, et. al.). In all cases, the sampling port just prior to the specified photolytic reactor was sampled as the inlet, and the sampling port just after the specified reactor was sampled as the outlet.

One ethanol run, one ethylbenzene, three MEK, and two trichloroethylene runs provided information on photolytic reactivity in the system. Data for each solvent, and data at two system inlet air flow rates, and with both 3 and 7 photolytic bulbs have been analyzed.

Ethanol and ethylbenzene. The runs with ethanol and ethylbenzene showed no detectable degradation of either compound in the photolytic reactors. The inlet and outlet air concentration of the given VOC were within experimental error (RSD 5%) of each other, and no additional impurities (degradation products) were detected.

Methylethyl ketone. The run with methylethyl ketone showed the possible formation of a degradation product in the photolytic reactor, but we were unable to identify this product by gc/mass spec. With 7 bulbs in each reactor, the extra peak noted in the outlet samples was about 0.4% of the MEK response by FID; at decreased flow rates, this concentration doubled to 0.8%; with only 3 bulbs it was not detected. As for ethanol and ethylbenzene, the inlet and outlet air concentration of MEK were within experimental error.

Trichloroethylene. Trichloroethylene, as expected, showed significant photolytic activity (Helz, et. al.). Figure 2 shows the photolytic data from two separate runs of trichloroethylene. The data are presented as % degradation from the inlet to the outlet of each reactor. In the first run and the first half of the second run, where the system air flow rate was 2600 cfm, the average loss in the first photolytic reactor was 30%, and the average loss in the second photolytic reactor was also 30%. In the second half of the second run, where the flow rate was reduced to 1300 cfm, the average loss in the first and second photolytic reactors increased to 46%, and 48%, respectively. These data are consistent with expectations (Mallery) that at slower flow rates, where the time spent in the photolytic reactor is longer, degradation is increased.

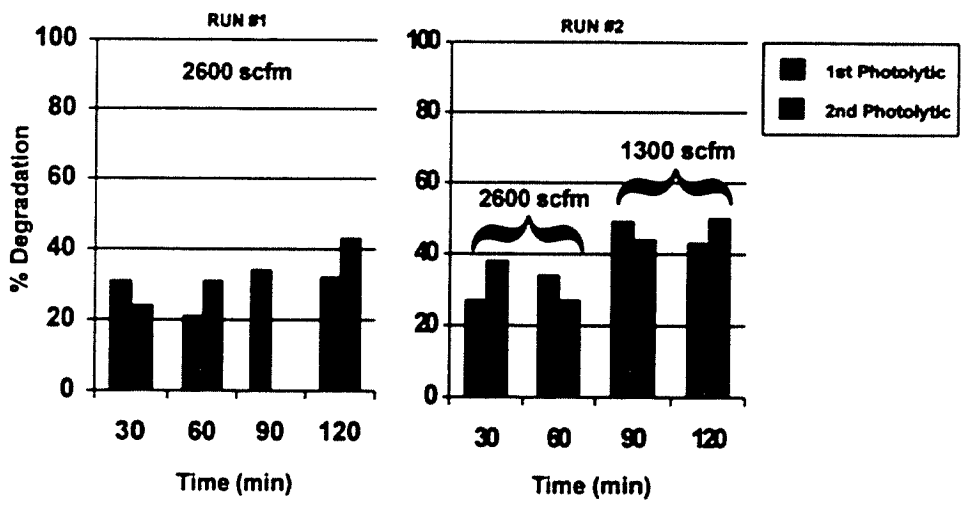

Figure 2. Trichloroethylene degradation in the photolytic reactors.

No by-products were detected in the analysis of any of the air phase TCE samples, but the pH of the water in the aqua reactors dropped very rapidly (15 minutes) from 6 to about 2, where it remained for the rest of the run.

The degradation pathway of TCE almost certainly led to the formation of hydrochloric acid (HCl). After the first photolytic reactor, much of the HCl was stripped from the gas phase into the water by the MAD/packed bed scrubbers, resulting in the noted pH drop. One proposed degradation pathway is given below (Helz, et. al.).

(1)

It was also determined that, over a concentration range of one order of magnitude (71 to 1117 ppm of TCE), relative degradation rates of TCE in each photolytic reactor remained consistent.

The photolytic findings are summarized in Table 2.

Table 2. Photolytic activity in the pilot scale air treatment system.

Solvent	Photolytic Activity
Ethanol	No change
Ethylbenzene	No change
Methylethyl ketone	0.5% impurity formed
Trichloroethylene	30% decrease in TCE No organic impurities seen Hydrochloric acid formed

Packed Bed Scrubbers

Reactor design. The pilot scale system has two aqua reactors in series. Each aqua reactor is composed of a mist air dispersion unit (MAD) and a counter-flow packed bed scrubber. In the MAD unit the air flows downward concurrent with a mist created by spraying water through nozzles; this is where water absorption and water initiated oxidations are claimed to initiate. After going through the MAD unit, the air stream then flows upward, counter current to the water flow of the packed bed scrubber; here further absorption of VOCs into the water phase takes place. The air then flows through a second MAD unit, followed by a second packed bed scrubber. This series of four units - MAD, packed bed, MAD, packed bed - is located after the first photolytic reactor and before the second photolytic reactor. Sampling ports are located as shown in Figure 1, before the first MAD units (ME-102), before the second MAD unit (ME-104) and at the outlet of the second packed bed scrubber (ME-105). This allows sampling of the air steam at the inlet, outlet, and halfway through the entire aqua reactor series.

The water which drains from the bottom of the first MAD and packed bed scrubber is collected, stored and treated separately from the water from the second MAD/packed bed scrubber. Each of these water basins may also be sampled (W-A and W-F).

The absorption of VOCs into the water phase by the aqua reactors is highly dependent on the vapor pressure and water solubility of the particular VOC. The solubilities for these four compounds are given in Table 1.

Ethanol. Ethanol, a highly polar VOC which is totally miscible with water in all proportions, absorbed readily into the water. At time periods up to 30 minutes after spraying of the ethanol began, about 90% of the ethanol in the air stream was absorbed into the water in the first MAD/packed bed aqua reactor; 90% of the remaining ethanol (another 9% of the original inlet ethanol concentration) was absorbed by the second aqua reactor. That is, if the inlet concentration of ethanol was 100 ppm, 90 ppm was absorbed in the first aqua reactor, and 9 ppm was absorbed in the second aqua reactor.

The amount of ethanol absorbed from the air stream decreased over time, as the concentration of ethanol in the water increased. After 6 hours of spraying, only 45% of the ethanol in the air stream was absorbed in first aqua reactor and 68% (of the remaining ethanol) in the second aqua reactor. The experiment was discontinued at this time, but it is expected that the amount of ethanol removed from the air phase by the water would continue to decrease until the system reached equilibrium.

Methylethyl ketone. Methylethyl ketone, which has a solubility of 353 g/L in water at 10°C, showed a similar, but accelerated, profile to that of ethanol. Figure 3 shows the concentration of MEK in the air phase at time periods from 5 minutes to 360 minutes after spraying of MEK was initiated. Assuming a 100 ppm concentration at the inlet to the first aqua reactor (ME-102), 76 ppm of MEK was absorbed by the first aqua reactor, and 16 ppm was absorbed in the second aqua reactor at 5 minutes; this accounts for a total of 92% of the MEK being absorbed by the two aqua reactors when the water was "fresh", early in the run. After one hour, the amounts dropped to 26 ppm and 31 ppm absorbed by the first and second

aqua reactors - a total of 57% of the inlet MEK. After 6 hours of spraying, no MEK was absorbed out of the air phase as it passed through the aqua reactors; the air and water concentrations of MEK for these conditions had reached equilibrium.

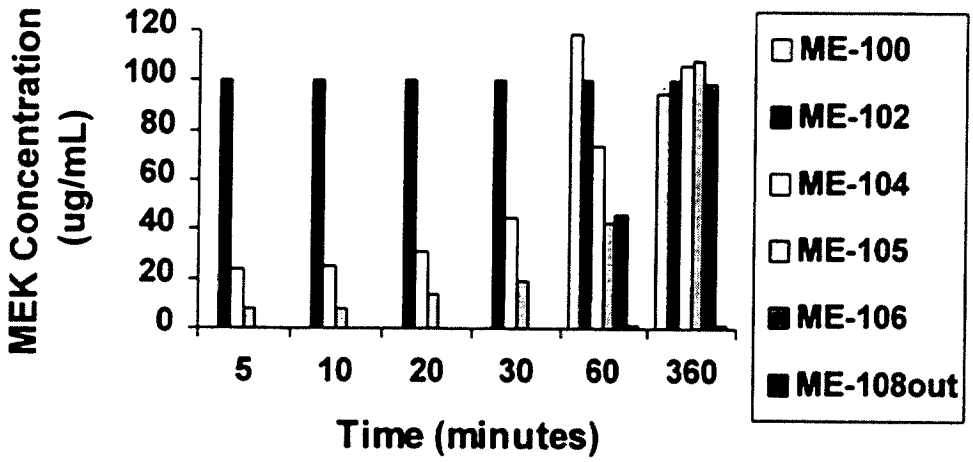

Figure 3. Concentration of MEK in air during pilot scale run.

Figure 4 shows the water data from the same MEK run. This shows increasing MEK in the water phase, increasing first in the first basin, then later in the second basin as would be expected from the air data. This graph also shows that after the MEK spraying is stopped, the concentrations in the water gradually fall as the MEK stripped out of the water and evaporated back into the air phase.

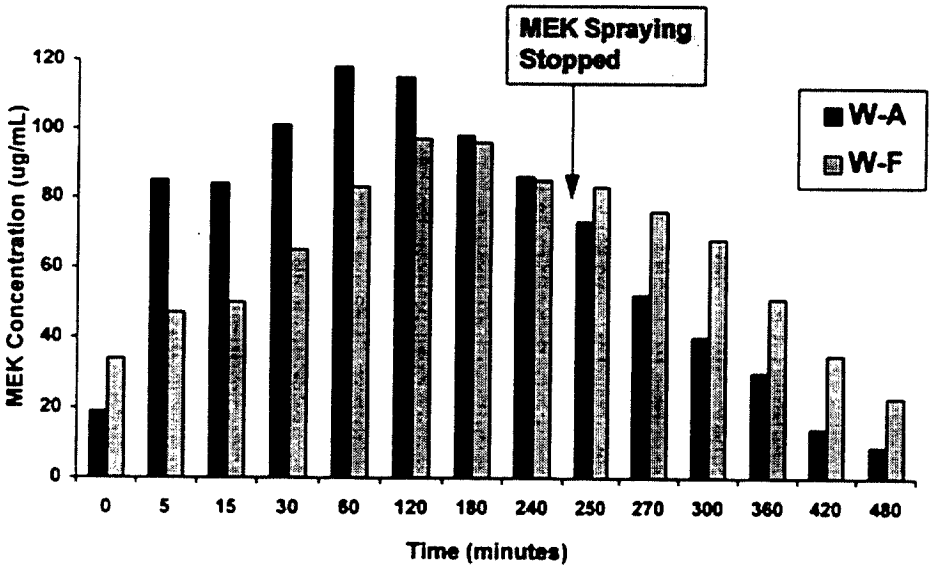

Figure 4. Concentration of MEK in water basins during pilot scale run.

Ethylbenzene. Ethylbenzene, which has very limited solubility in water (152 mg/L) exhibited a similar profile again, but on an even-shorter time scale. After 5 minutes of spraying, ethylbenzene had reached its maximum solubility in the water, and no more ethylbenzene was removed from the air stream by the aqua reactors.

Ethylbenzene concentrations were measured in the water basins and were found to average only 3 mg/L. This is expected based on the reported solubility of ethylbenzene in water. Figure 5 shows that when spraying commences the concentration of ethylbenzene in the water increases rapidly to its maximum solubility, then decreases rapidly to zero as soon as the spraying is stopped.

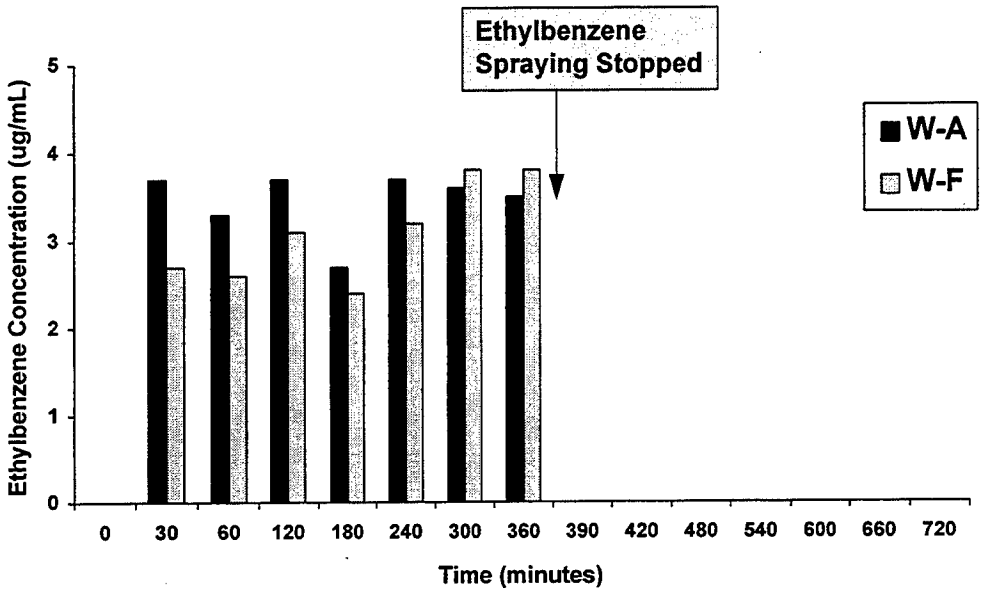

Figure 5. Concentration of ethylbenzene in water basins during pilot scale run.

<u>Trichloroethylene</u>. The profile for trichloroethylene was somewhat different even though it has the lowest water solubility of the four solvents discussed (1.1 mg/L). Figure 6 shows that in the second aqua reactor (ME-104 to ME-105), there was no significant removal of TCE from the air phase at any time interval tested. This is what would be expected based on our findings with the first three solvents. However, in the first aqua reactor (ME-102 to ME-104), there was a consistent decrease, averaging 23%, throughout the two hour run period. A possible explanation for this is that degradation of TCE continued into the first aqua reactor, caused by intermediates which had formed in the photolytic reactor.

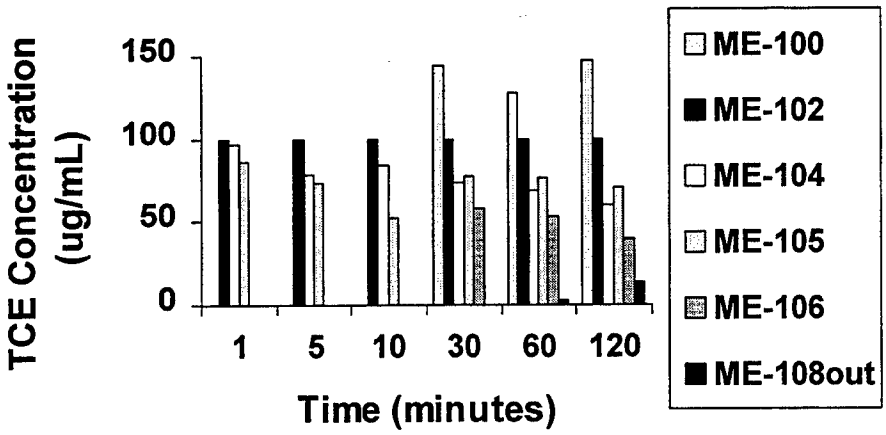

Figure 6. Concentration of TCE in air during pilot scale run.

Table 3 shows the highest water concentration attained for each solvent evaluated in these pilot scale experiments. The concentrations are consistent with the literature data (see Table 1) for these compounds.

Table 3. Maximum solvent concentrations achieved in scrubber water.

Solvent	Solvent Concentration	Time
Ethanol	610 mg/L	6 hours*
Ethylbenzene	4 mg/L	1 minute
Methylethyl ketone	120 mg/L	4 hours
Trichloroethylene	6 mg/L	1 minute

* End of run: concentration still increasing

Granulated Activated Carbon

All four VOCs that were tested were adsorbed by the granulated activated carbon bed. Outlet concentrations from the pilot scale system were determined for time intervals both early in the run (up to one hour after spraying of solvent was started), and late in the run (after 2 to 6 hours of continuous spraying of the solvent). Even after continuously spraying solvent for up to 6 hours, concentrations at the oulet of the carbon bed were on the order of 1 to 2 ppm for all solvents tested. This correlates to better than 95% overall removal/destruction by the pilot scale system, for polar, intermediate polarity, non-polar and chlorinated solvents. These data are presented in Figure 7.

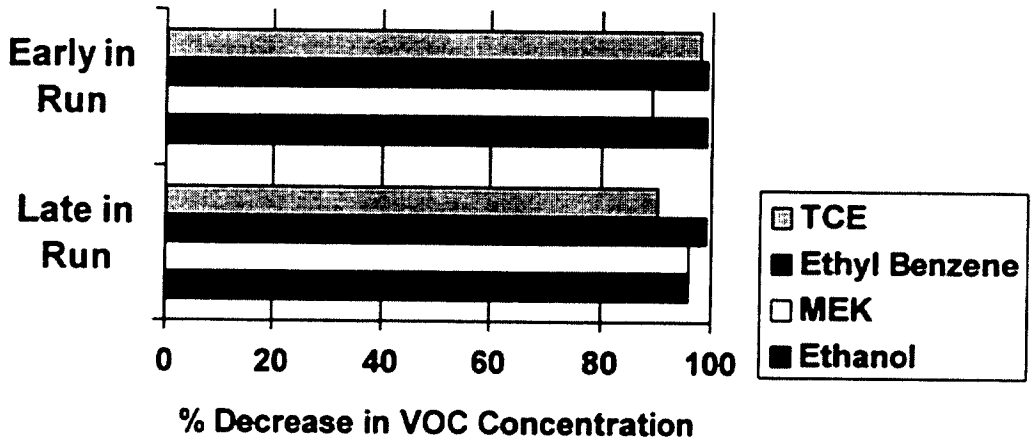

Figure 7. Overall decrease in VOC concentration from system inlet to system exhaust.

Additional studies on the activity of the carbon bed and its regeneration by ozone are underway at the bench scale level; detailed descriptions of these studies are the subject of other papers (Cannon, et al.).

CONCLUSIONS

Figure 8 summarize the data from the baseline studies for these four solvents. Each of these plots has been normalized to a 100 ppm inlet concentration of the given solvent. Air concentrations throughout the pilot scale system are plotted for three distinct time periods in each run.

For ethanol, a very polar solvent with unlimited water solubility, Figure 8 shows that early in the run (30 minutes), no destruction was seen in the pre-ox reactor, about 90% of the ethanol was removed by the first packed bed scrubber, about 9% was removed in the second packed bed scrubber, there was no destruction in the second photolytic reactor, and the remainder of the ethanol was removed by the carbon bed.

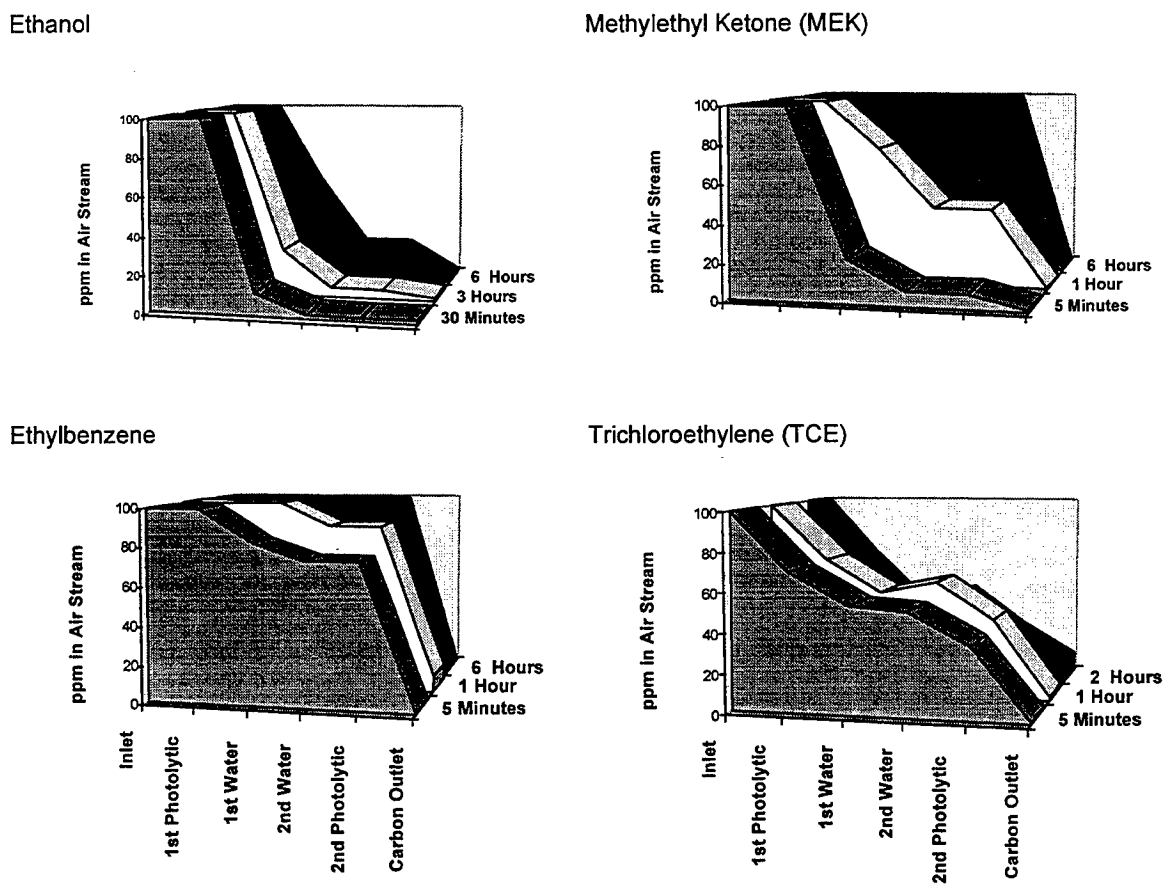

Figure 8. Pilot scale air treatment system profiles for four solvents.

A 3 hours and 6 hours, the profile for ethanol changes in the packed bed scrubbers. As the concentration of ethanol in the water increases, less ethanol is taken up by the water. At 6 hours, only 82% of the ethanol in the incoming air stream is taken up by the water. this is significantly less than the 99% taken up at only 30 minutes into the run.

For ethylbenzene, a very non-polar solvent with very low water solubility, the concentration profile throughout the system looks very different. At only 5 minutes into the run, the water has almost reached saturation and the first packed bed scrubber absorbs only 17% of the ethylbenzene in the incoming air stream; by one hour the first packed bed scrubber does not absorb any of the ethylbenzene out of the air stream. In this case, no destruction of the ethylbenzene was seen in either photolytic reactor. Therefore, in the case of ethylbenzene, most of the solvent is removed by the carbon bed from very early in the run; the effect of the photolytic reactors and the water was negligible.

Methylethyl ketone (MEK), which has a polarity intermediate to ethanol and ethylbenzene and has some, limited solubility in water, shows behavior, not surprisingly, intermediate to the behavior of ethanol and ethylbenzene. Early in the run, the packed bed scrubbers removed most of the MEK, but after 6 hours no MEK was removed by the water, and almost all (>90%) was removed by the carbon bed. Again, no significant photolytic activity was measured.

Trichloroethylene (TCE) shows still another concentration profile. About 30% of the TCE in the incoming air stream is destroyed in each photolytic reactor; there is an additional 23% reduction in air stream concentration in the first

packed bed scrubber. The remaining TCE is removed by the carbon bed. This profile did not change significantly over time as did the other solvents.

These concentration profiles show that each solvent behaves differently in the hybrid system. Polar solvents with good water solubility are removed predominantly by the packed bed scrubbers, solvents with photolytic activity are destroyed in the photolytic reactors, and non-polar solvents with no photolytic activity are removed by the carbon bed. Thus, when an air stream composed of a mixture of solvents enters the hybrid system, each solvent will be removed and destroyed by a unique combination of technologies specific to its physical and chemical characteristics.

Data collected at two different incoming air velocities (1300 and 2600 cfm) and at varying incoming air stream concentrations (50 to 1100 ppm) showed similar findings.

At relatively low VOC concentrations (100 to 1000 ppm) where thermal oxidizers would require the addition of fuel to maintain destruction, and at relatively high flow rates (up to 120,000 cfm) where pure absorption processes are prohibitively expensive to operate, and where the make-up and concentration of the incoming air stream is variable, hybrid systems have significant advantages over conventional, single technology treatment systems.

ACKNOWLEDGMENTS

We would like to thank the following organizations for their contributions to this project: the Strategic Environmental Research and Development Program (SERDP) for funding this research; the Marine Corps Multi-Commodity Maintenance Centers for their professionalism, and undying confidence and support; and Terr-Aqua Enviro Systems, Inc. for their ongoing contributions to this work.

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Abstract

Environmentally Friendly Cleaning Improvements For Overhaul Operations

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The Sikorsky Aircraft Overhaul and Repair Center (O&R) is committed to providing a safe and healthy work environment for all of its employees by upholding the highest safety and environmental standards. In recent years, a joint team from Manufacturing Engineering, Manufacturing, Design Engineering, and Environmental Health and Safety has implemented a number of initiatives that have resulted in dramatic environmental improvements at this facility. These efforts have led to significant reductions in hazardous waste and SARA reportable air emissions as well as providing a safer, more environmentally friendly working environment.

This report summarizes the O&R process improvements associated with changes in part cleaning methodology. These projects have included: the elimination of perchlorethylene vapor degreasing through the introduction of a power washer and a hot oil / alkaline cleaning line; substitution of a high molecular weight alcohol for Freon in printed wiring board operations; incorporation of an ultrasonic bearing cleaning line using an alkaline cleaner as a replacement for a dip tank system containing hazardous materials; and development of an innovative combination flush/cleaning booth for gearbox housings and assemblies to eliminate the use of 1-1-1 trichlorethane.

Along with the environmental and health benefits gained through the introduction of these projects, each has been shown to provide additional benefits in the areas of cost savings, labor reduction, waste minimization, and increases in process efficiency.

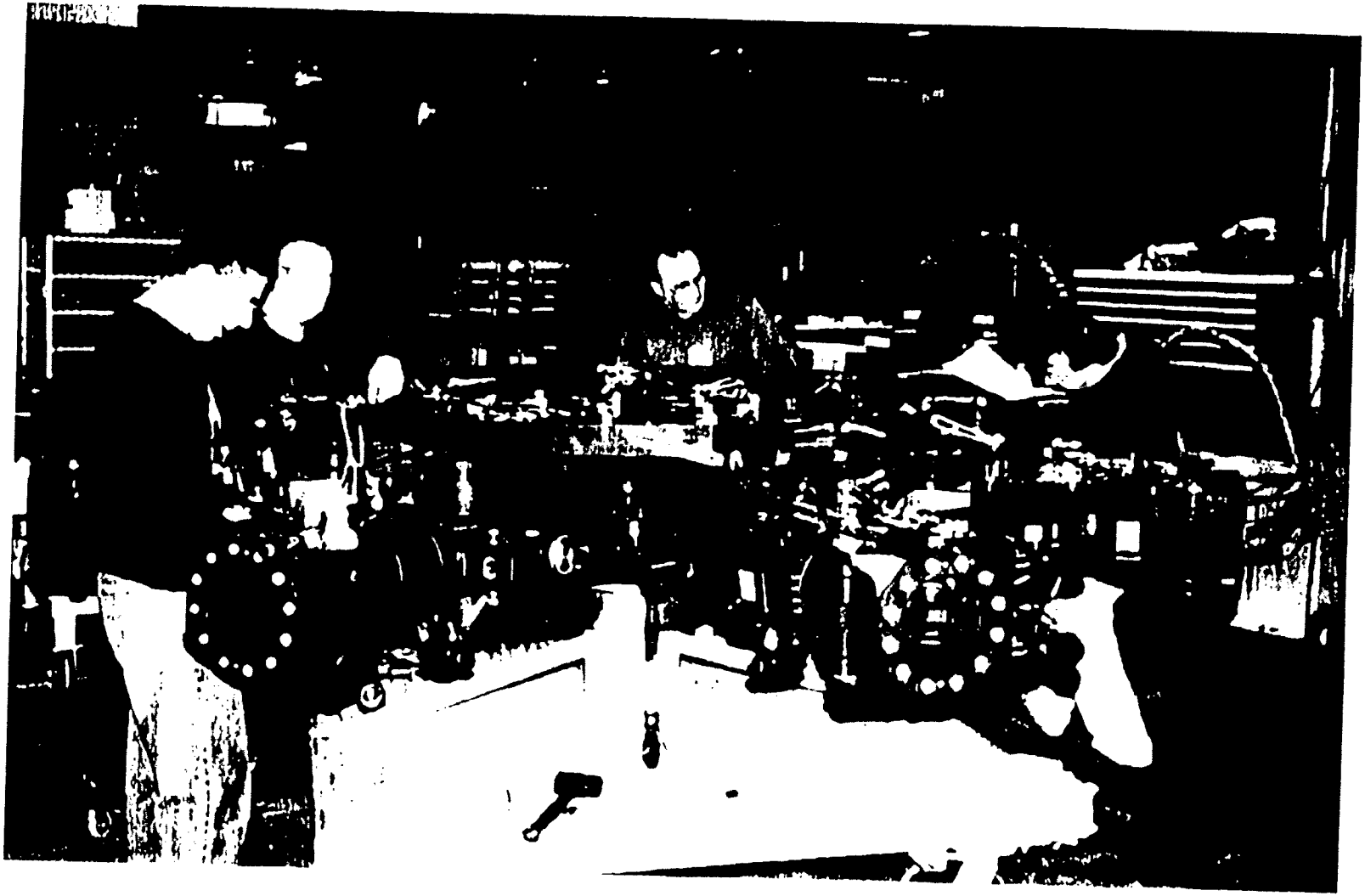
Environmental Friendly Cleaning Improvements for Overhaul Operations

P. H. Johnson and R. M. Melnick
Sikorsky Aircraft

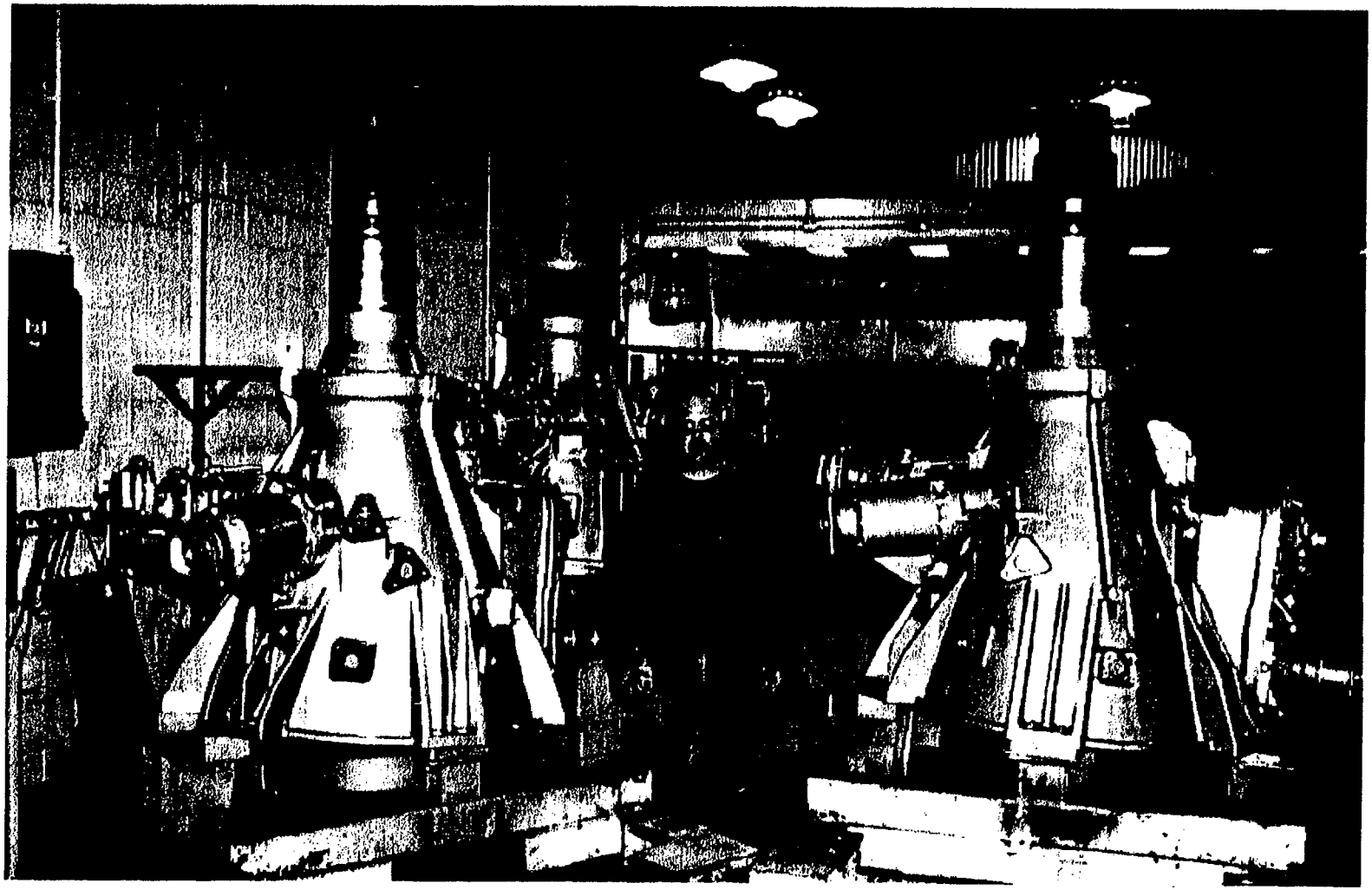
Sikorsky Aircraft Overhaul & Repair Environmental Improvements

<u>Overview of O&R Operations</u>

Sikorsky' overhaul and repair center processes helicopter transmissions, gearboxes, rotor heads, and accessory equipment. Components for O&R are received from Government and commercial customers, domestic and international



CH-53E Main Rotor Head



CH-53D & CH-53E Transmissions

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Operations Resulting in Waste Generation

- Degreasing
- Paint Stripping
- Machining
- Assembly
- Painting

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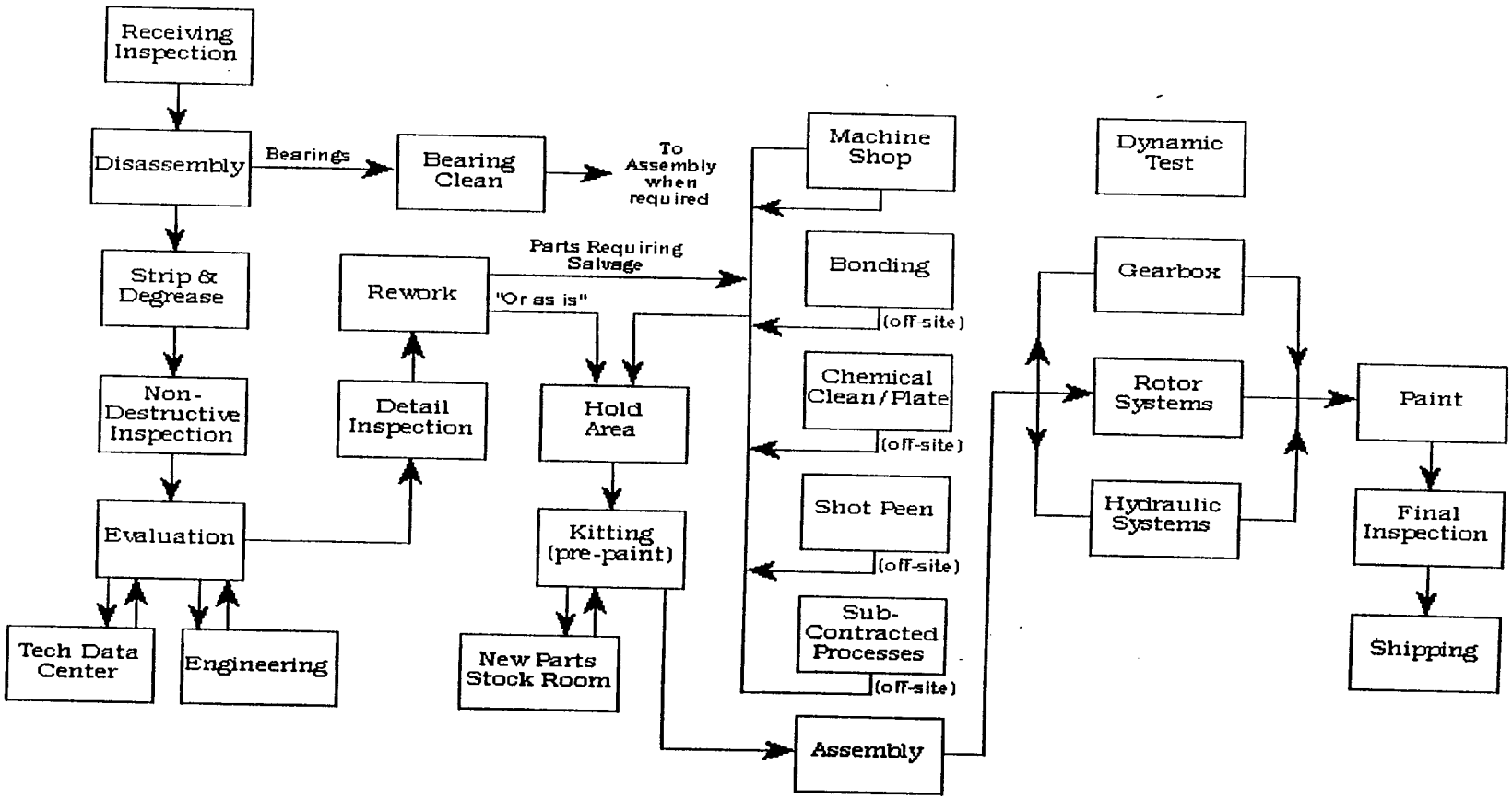
OVERHAUL AND REPAIR "Component Process" Flow



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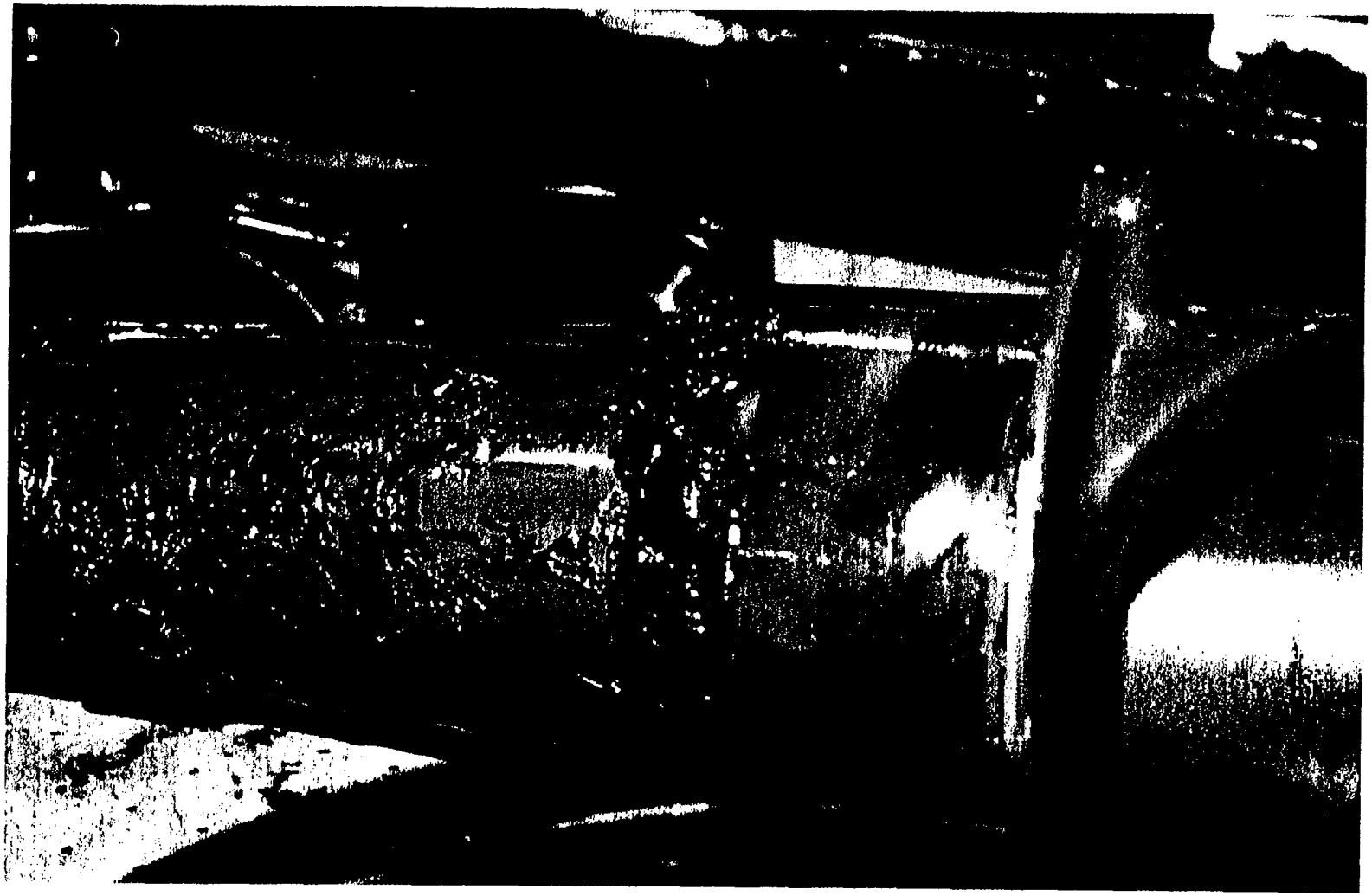
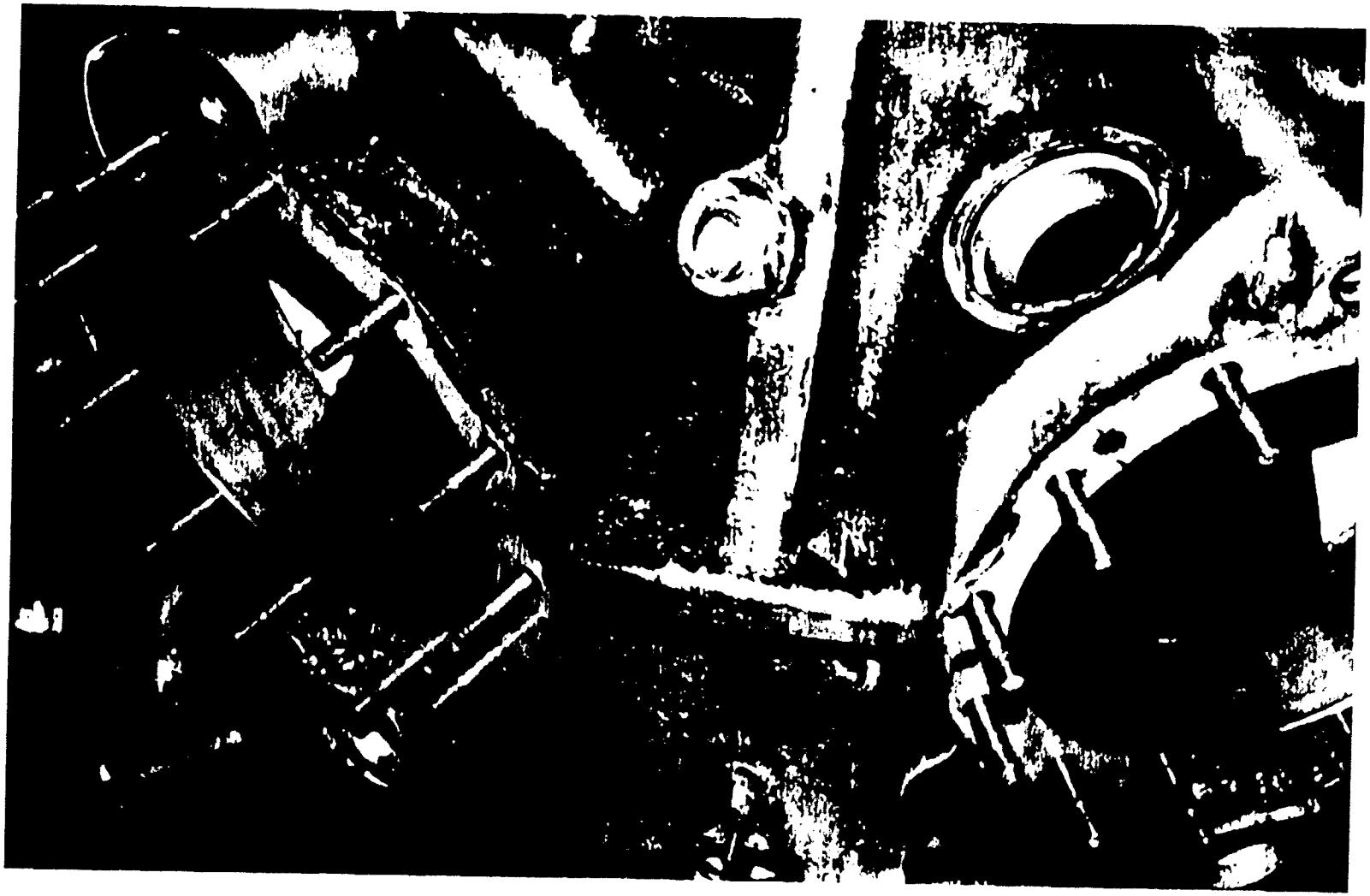
Components inducted into O&R have multiple soils and coatings that need to be removed before further processing can begin.

These soils are typically divided into the following categories:

- Grease, Oils, and Carbon deposits
- Paint/Primer & Protective Coatings



Typical Heavy Grease Contamination



Typical Oil & Grime Contamination

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Past Contamination Removal Methods

Perchloroethane vapor degreasing

Methylene chloride based cleaners and carbon strippers

1,1,1 Trichloroethane spray cleaning

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Project - Power Washer

Prior Situation:

Parts were degreased in two Perchloroethane vapor degreasers

Process Modification:

One large power washer was installed in the first quarter of 1992. Washer features are:

Three cycle operation - Wash/Rinse/Dry - Using water based alkaline detergent

Parts are cleaned and dried in a single step

Automatic system - Cycle time of 25 minutes

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Power Washer

Benefits:

Decreased process flow time

Elimination of VOC generation and waste tracking from vapor degreasers

Increased worker safety from removal of toxic solvents

Increased worker acceptance from elimination of strong odors

O&R Power Washer

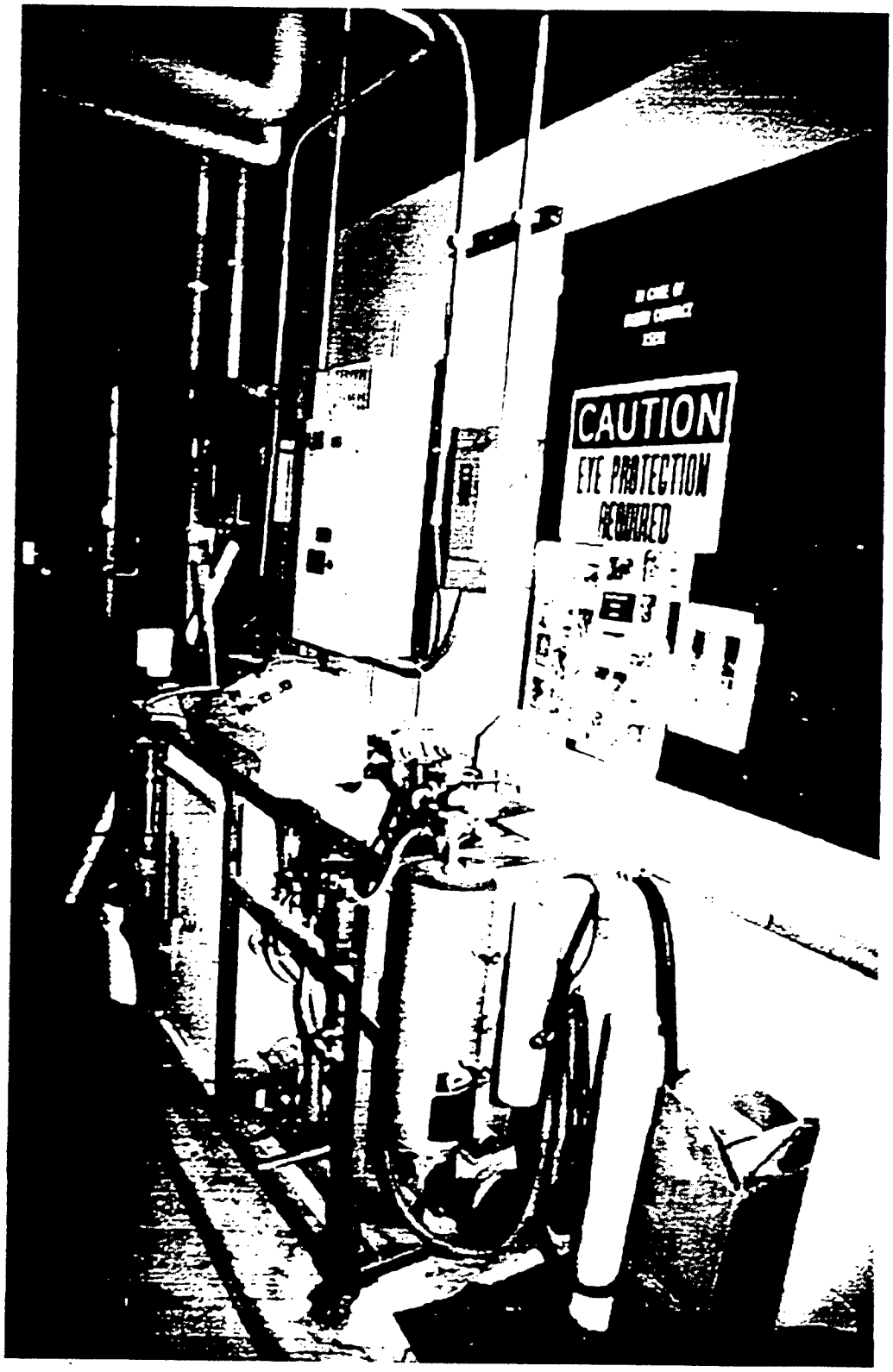
Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Power Washer Ultrafiltration

Due to a high load of heavy grease, an ultrafiltration system was added to the power washer in 1994

Yearly savings are:

- Reduction in the number of system dumps by 63%
- Reduction of 7200 gallons of regulated waste
- 120 Machine hours
- 40 Maintenance hours



Power Washer Ultra-Filtration System

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Heat Transfer Oil Degreaser

Due to continuing high load of parts through the parts washer, an existing paint stripping line was modified to include a degreasing system.

Benefits:

Reduced process flow - Preserved transmission housings are degreased without contamination of the power washer
Backup for the power washer during system dumps and machine maintenance.

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Ultrasonic Bearing Cleaning

During 1994 the solvent based bearing cleaning line was identified as a major source of hazardous waste generation

Prior Situation:

Bearings were cleaned using a 4 solvent system using flammable, high VOC solvents and Methylene Chloride chemistries.

Processing required 150 minutes

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

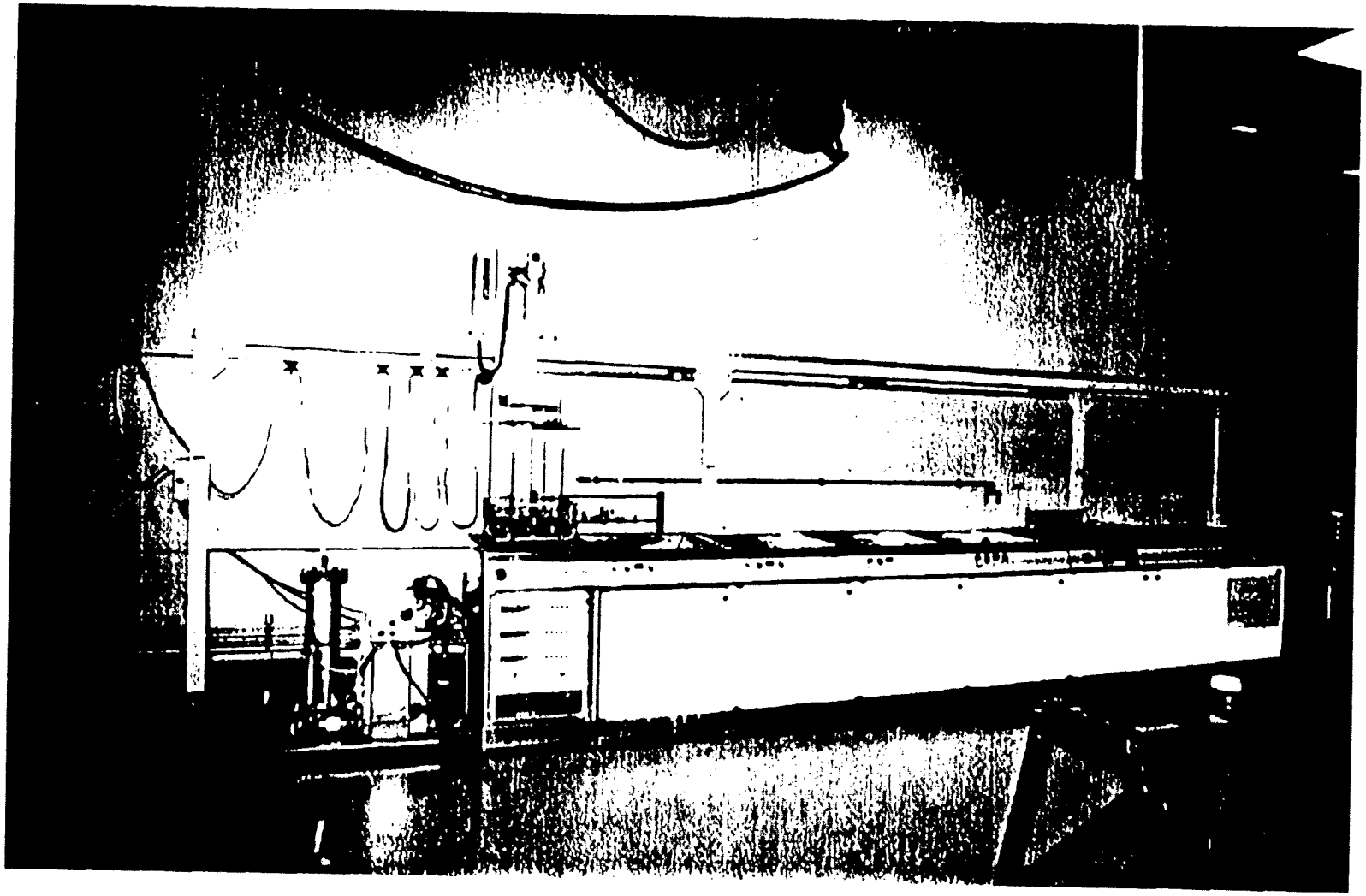
Project - Ultrasonic Bearing Cleaning

Process Modification:

An automatic 5 step, water based, ultrasonic cleaning line was installed in January 1996

Benefits:

- Elimination of all hazardous waste generation from bearing cleaning
- Decreased process flow time - 60 minutes Vs. 150 minutes
- Increased worker acceptance due elimination of odors and improved working environment
- Reduced scrap rate due to a cleaner bearing being presented for inspection



Ultrasonic Bearing Cleaning Line

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Project - Housing Flush/Gearbox Cleaning Booth

In order to eliminate the use of 1,1,1 Trichloroethane for cleaning prior to painting, the housing flush and pre-paint cleaning operations were combined in to on area.

Prior Situation:

Transmission housings were flushed with a light oil
Assembled transmissions were cleaned prior to painting with 1,1,1 Trichloroethane

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Housing Flush/Gearbox Cleaning Booth

Process Modification:

The cleaning and flushing operations were combined in the flushing area

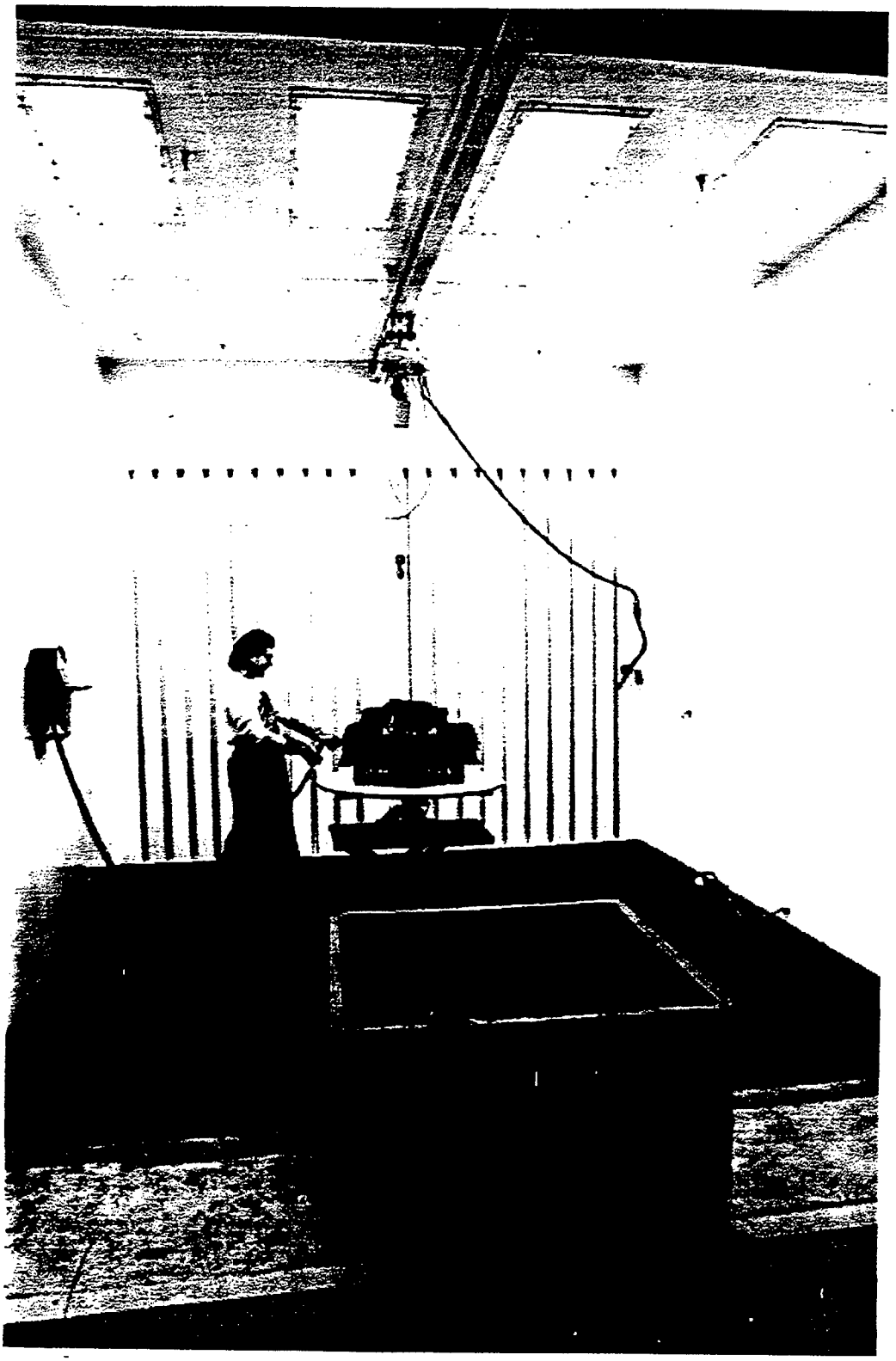
1,1,1 Trichloroethane and the flushing oil were replaced with one solvent

Benefits:

Elimination of 1,1,1 Trichloroethane from Sikorsky

Improved flushing of housings

Reduced paint shop congestion



Flush/Cleaning Booth

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - New Machine Coolants

Prior Situation:

Machining generated 40,000 lb.. of waste coolant per year

Old coolant sump life of 6 to 9 weeks

450 lost machine hours for coolant change outs per year

Process Modification

Replaced to previously used coolant with a synthetic coolant, Syntilo 9930

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - New Machine Coolants

Benefits:

- Machine coolant change outs reduced to 3 per year
- Reduction of lost machining hours for coolant change out of 220 hours
- Reduction of hazardous waste generation of 20,000 lb.

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Waste Treatment Plant

Prior Situation:

Waste water from the paint strip line, strip line emission scrubber, nital etch, and penetrant inspection line was shipped as hazardous waste

Process Modification:

A waste treatment plant was installed in 1994

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Project - Waste Treatment Plant

Benefits:

Waste water is now treated on site and discharged to the sanitary sewer

Reduction in hazardous waste generation of over 3 million pounds

Sikorsky Aircraft Overhaul & Repair Environmental Improvements

Project - Paint Stripper Life Enhancement

Prior Situation:

A 4400 gallon immersion paint tank was dumped every year

Process Modification:

By working with the stripper vendor a system of solution testing and rejuvenation was developed and implemented

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Project - Paint Stripper Life Enhancement

Benefits:

Tank life enhanced from 1 year to 3 years

Reduced the generation of hazardous waste by and average of 2900 gallons per year

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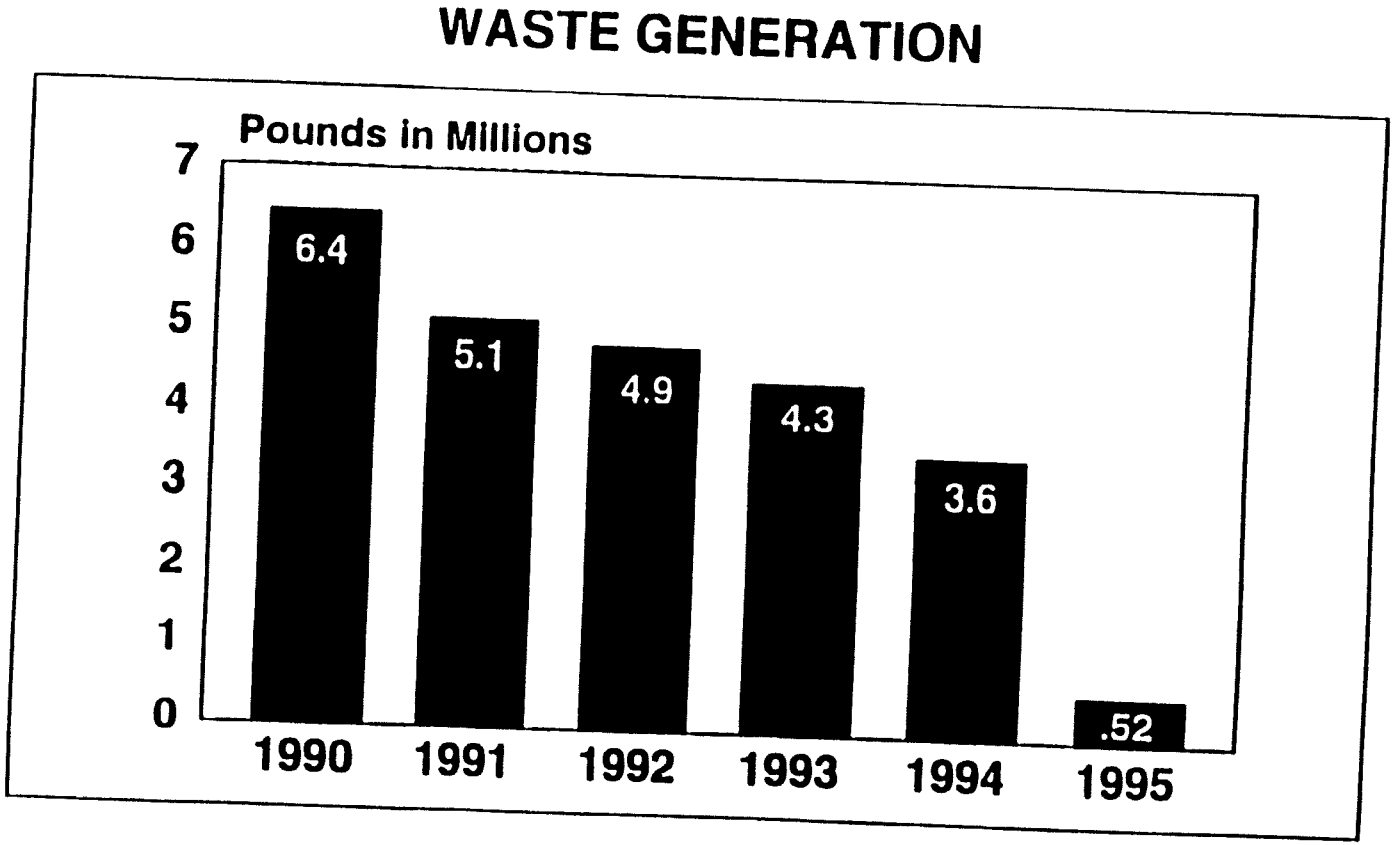
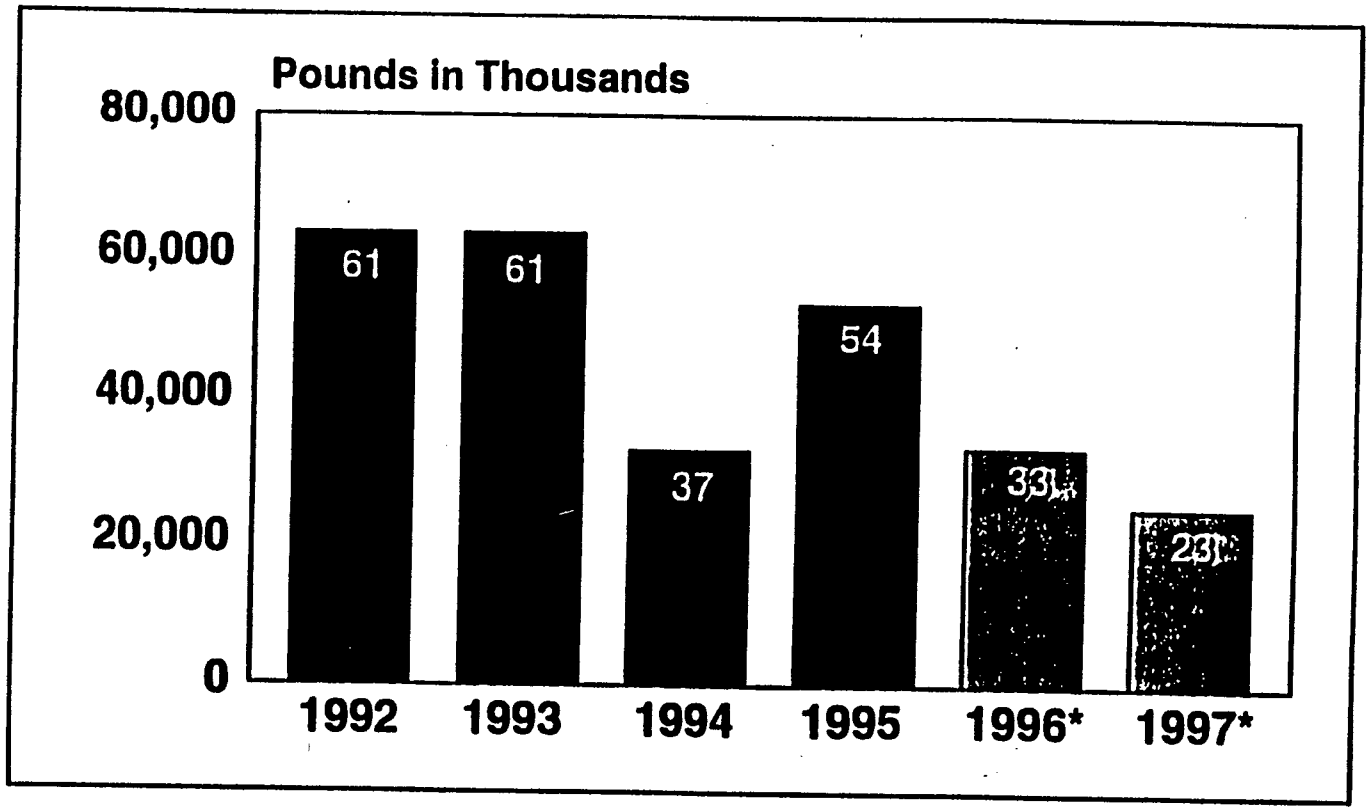


Sikorsky Aircraft Overhaul & Repair Environmental Improvements



*Estimated

ENVIRONMENTALLY COMPLIANT COATINGS TECHNOLOGIES

Environmental Impact and Treatment of Reformulated Chemical Agent Resistant Coatings

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Abstract

The Applied Research Laboratory at The Pennsylvania State University has investigated a hybrid air pollution control system (APCS) to treat an NMP laden air stream. This system has been described in "Air Pollution Control System Research - an Iterative Approach to Developing Affordable Systems" (Watt, 1994) presented at the First Aerospace Environmental Technology Conference. This research was performed concurrently with the reformulation of the CARC coatings to ensure current air treatment systems were capable of removing NMP from exhaust air streams. Bench scale and pilot scale studies focused on the absorption of NMP into an aqueous phase and destruction of the NMP through advanced oxidation processes.

NMP was effectively removed from an air stream using the hybrid APCS. The hybrid system design was optimized for the removal and destruction of NMP from exhaust air streams. Advanced oxidation processes destroyed NMP in the aqueous phase. The products of the oxidation reactions of NMP were determined. The results of these studies show the reformulated CARC is a beneficial step in pollution prevention. The VOC content of the coating was reduced and the replacement solvent NMP was removed using a scale model APCS installed at the ARL facility.

Introduction

The 1990 Clean Air Act provided an incentive to replace highly volatile organic compounds (VOCs) with less volatile solvents. The Marine Corps Multi-Commodity Maintenance Centers (MC)[3] have taken the initiative to reformulate the currently used Chemical Agent Resistant Coatings (CARC) in order to reduce the VOC content. The primary solvents used in the reformulated CARC are water and N-methyl-2-pyrrolidinone (NMP). Because NMP has a very low vapor pressure and high molecular weight (Taylor, 1995), it does not partition rapidly to the gas phase, unlike current industrial solvents. Thus coatings which use water and NMP are beneficial in terms of pollution prevention and are less toxic. However, air treatment systems must be capable of removing NMP from exhaust air streams in addition to solvents currently used in the CARC application process.

A pilot scale air treatment system was installed at the Applied Research Laboratory (ARL). This system is a hybrid system which combines Advanced Oxidation Processes (AOPs), absorption processes and adsorption processes to remove a variety of organic compounds from exhaust air streams (Striebig *et al.*, 1996). This system is shown in Figure 1. Due to the high polarity of NMP and its low vapor pressure, the absorption portion of the air treatment system, and subsequent aqueous reaction were examined to gain an understanding of the removal and destruction mechanisms within the air treatment system for NMP.

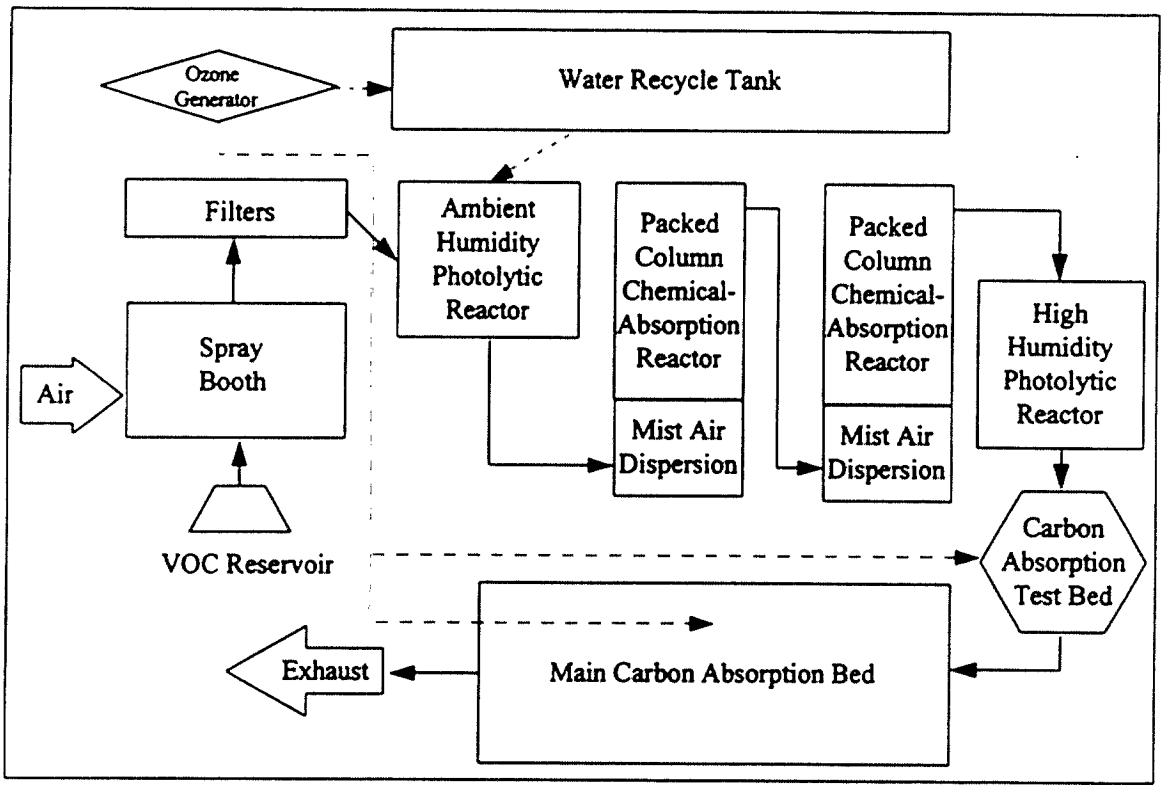

Figure 1: Schematic of the pilot scale air treatment system.

Advanced oxidation reactions of NMP in a semi-batch aqueous reactor

A semi-batch reactor, shown in Figure 2, was used to gain an understanding of the aqueous phase reactions of NMP and the hydroxyl radical. Ozone was added to the reactor in a 1500 PPM ozonated air stream flowing through a diffuser stone at 2.5 l/min. Ozone was generated in the semi-batch reactor experiments by the Oxytech model PXC-20 ozone generator. Ozone concentrations were measured in the inlet and exhaust air streams with a Dasibi model 1008-HC ozone meter. The initial concentration of NMP in the reactor was 10 g/l, the pH was maintained at 9 with potassium phosphate buffers and sodium hydroxide addition. The pH and temperature of the system were monitored with an Orion ATP probe and model 250 Orion pH meter. The water in which the NMP and buffers were dissolved was distilled and deionized prior to the addition of the NMP and buffer salts. The 0-8 % hydrogen peroxide solutions were prepared from 35% stock solution of hydrogen peroxide purchased from Aldrich Chemical Co. The various concentrations of hydrogen peroxide necessary to achieve the desired ratio of ozone and hydrogen peroxide in the aqueous phase were added at 0.07 ml/min. with a constant flow peristaltic pump.

The concentration of NMP in the aqueous matrix was measured with gas chromatography using a flame ionization detector (GC/FID). A 0.53 mm ID x 30 m VOCOL column from Supelco Inc. was used to achieve separation of NMP and the products of reaction. The products of reaction were determined by gas chromatography with a mass selective detector GC/MS, and verified with proton magnetic resonance imaging and injection of GC/FID standards purchased from Aldrich Co. The limit of quantification of the GC/FID analysis was 1 mg/l NMP in the aqueous matrix. All samples were quantified using single point calibrations after linearity in the concentration range of interest had been validated.

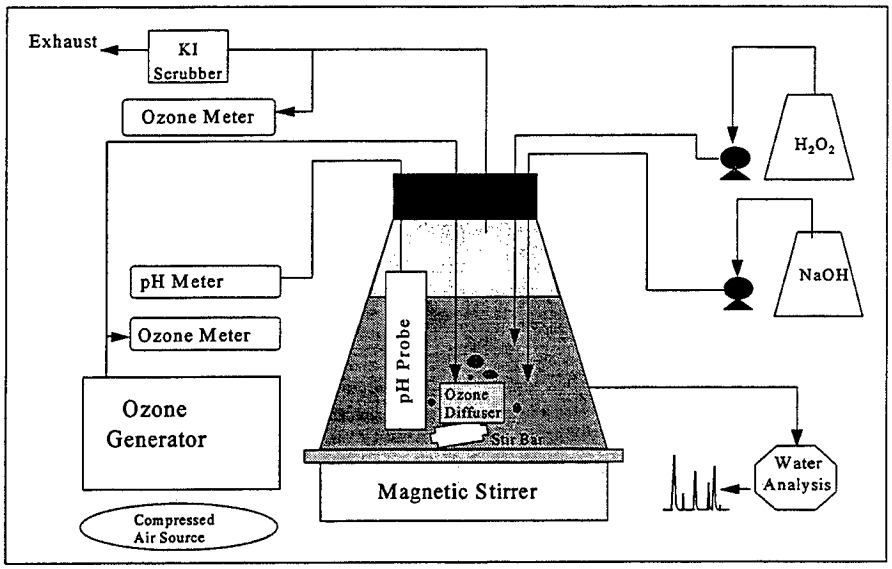

Figure 2: Diagram of the semi-batch advanced oxidation reactor.

Products of the Hydroxyl Radical Reaction with NMP

The chemical mechanism by which NMP was oxidized by the hydroxyl radical was determined in a preliminary experiment carried out for 120 hours. A mass balance was performed upon the semi-batch reactor and liquid samples were injected onto the GC/MS to determine the byproducts. The mass balance upon the reactor is shown in Figure 3.

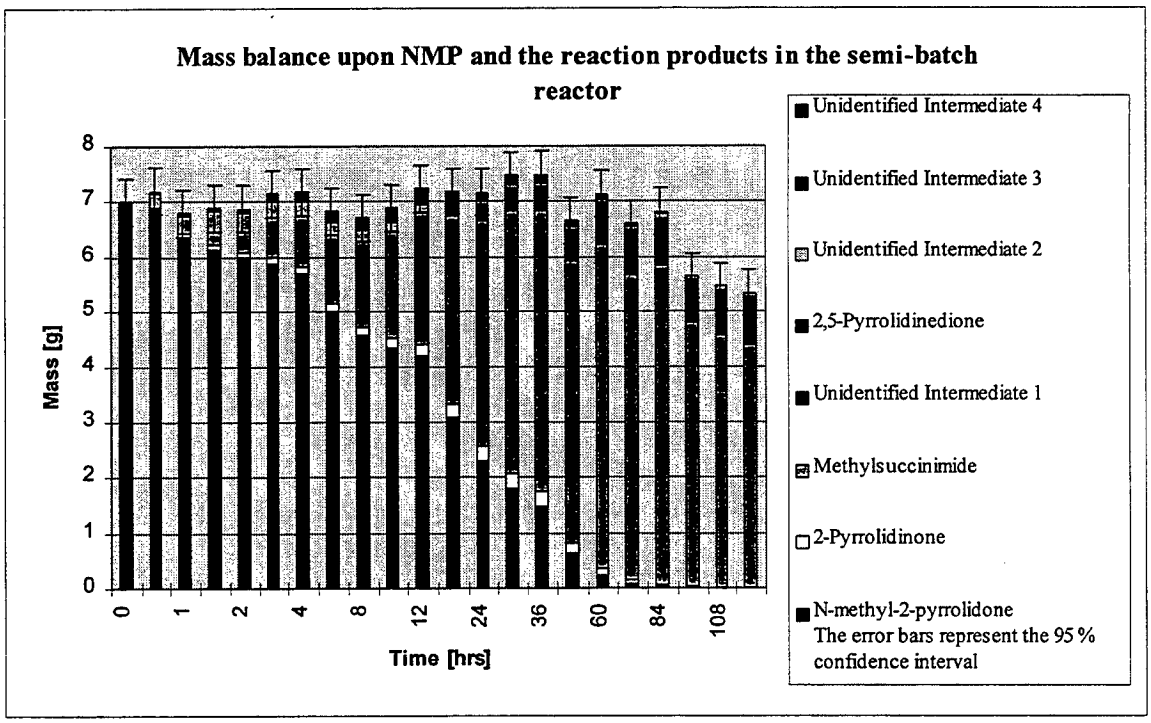

Figure 3: Mass balance upon NMP and the reaction products in the advanced oxidation semi-batch reactor.

Three stable products of the reaction with NMP and the hydroxyl radical were identified, methylsuccinimide, 2-pyrrolidinone, and 2,5-pyrrolidinedione. By examining the structure of each product and the mass balance results which indicates the relative time of formation of each compound, the following chemical mechanism shown in Figure 4 was proposed for the reaction of NMP with the hydroxyl radical in a pH 9 solution.

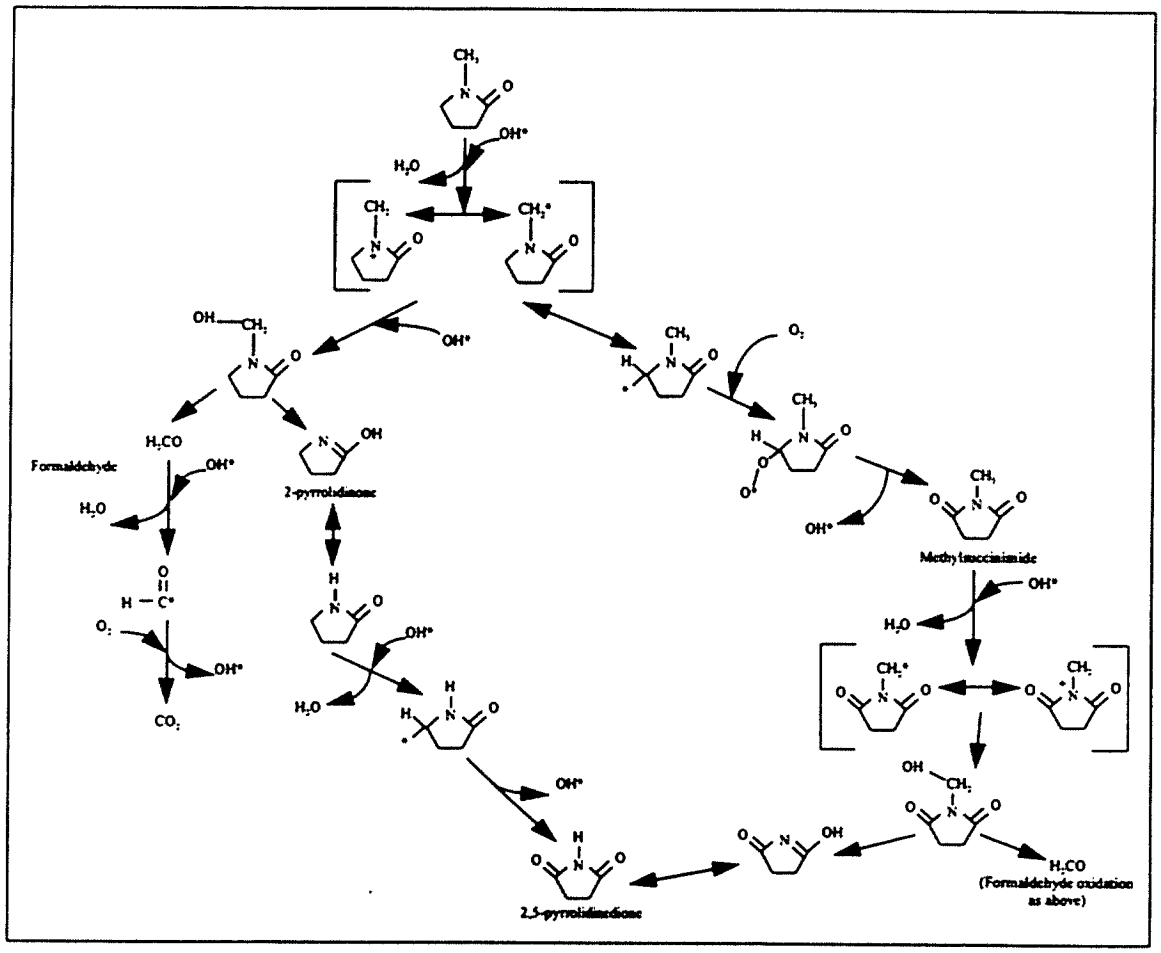

Figure 4: Proposed reaction mechanism for NMP and the hydroxyl radical.

The proposed mechanism follows a pathway similar to other organic compounds which react with the hydroxyl radical. First, a hydroxyl radical abstracts a hydrogen from the methyl group on NMP. A radical isomer is formed which allows parallel reaction pathways for the oxidation of NMP. The second step either involves the cleavage of the methyl group from the NMP radical to form 2-pyrrolidinone and formaldehyde or, more frequently, a second hydrogen abstraction from the NMP radical with the addition of a doubly bonded oxygen to form methylsuccinimide. The same hydrogen abstraction process or methyl group cleavage again occurs with 2-pyrrolidinone and methylsuccinimide respectively to form 2,5-pyrrolidinedione.

Kinetic Model of the O_3/H_2O_2 System in Regions II and III, At and Beyond the Stoichiometric Point

Simplified chemical kinetics of advanced oxidation processes have been modeled by Glaze and Kang (1989). Their model was based upon the hydroxyl radical reactions with organic compounds initiated by ozone, hydrogen peroxide, and ultraviolet radiation. The set of equations used in the simplified kinetics model are shown in Table 1. Glaze and Kang defined three kinetic regimes in their model, Region I where ozone was in excess, Region II where ozone and hydrogen peroxide have a stoichiometric ratio

equal to 2 moles of ozone per mole of hydrogen peroxide necessary for complete reaction, and Region III where hydrogen peroxide is in excess.

Table 1: Chemical reactions used in the kinetics model for oxidation of organic compounds in aqueous media (Glaze *et al.* 1987).

Reaction	Reaction Rate	Reference
Initiation reactions:		
(1) $H_2O_2 \leftrightarrow HO_2^- + H^+$	pK = 11.8	Behar *et al.* (1970)
(2) $HO_2^- + O_3 \rightarrow O_3^- + HO_2$	$2.8 \times 10^6\ M^{-1}\ s^{-1}$	Staehelin and Hoigné (1982)
(3) $OH^- + O_3 \rightarrow O_2^- + HO_2$	$70\ M^{-1}\ s^{-1}$	Staehelin and Hoigné (1982)
(4) $HO_2 \leftrightarrow H^+ + O_2$	pK = 4.8	Staehelin and Hoigné (1982)
(5) $O_3 + h\upsilon \rightarrow H_2O_2$	f (UV source & system)	Glaze *et al.* (1987)
(6) $H_2O_2 + h\upsilon \rightarrow 2\ OH$	f (UV source & system)	Glaze *et al.* (1992)
Propagation:		
(7) $O_2^- + O_3 \rightarrow O_3^- + O_2$	$1.6 \times 10^9\ M^{-1}\ s^{-1}$	Buhler *et al.* (1984)
(8) $O_3^- + H^+ \rightarrow HO_3$	$5.2 \times 10^{10}\ M^{-1}\ s^{-1}$	Buhler *et al.* (1984)
(9) $HO_3 \rightarrow OH + O_2$	$1.1 \times 10^5\ M^{-1}\ s^{-1}$	Buhler *et al.* (1984)
Net Equation for OH Radical Formation:		
(10) OH^- initiation: $3O_3 + OH^- \rightarrow 2OH + 4O_2$		
(11) HO_2^- initiation: $2O_3 + H_2O_2 \rightarrow 2OH + 3O_2$		
Radical Scavenger Reactions:		
(12) $OH + PCE \rightarrow$ products	$2.3 \times 10^9\ M^{-1}\ s^{-1}$	Koester *et al.* (1971)
(13) $OH + HO_2^- \rightarrow OH^- + HO_2$	$7.5 \times 10^9\ M^{-1}\ s^{-1}$	Christensen *et al.* (1982)
(14) $OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.7 \times 10^7\ M^{-1}\ s^{-1}$	Christensen *et al.* (1982)
(15) $OH + S_i \rightarrow$ products		
(16) $OH + HCO_3^- \rightarrow H_2O + CO_3^-$	$1.5 \times 10^7\ M^{-1}\ s^{-1}$	Weeks and Rabani (1966)
(17) $OH + CO_3^{2-} \rightarrow OH^- + CO_3^-$	$4.2 \times 10^8\ M^{-1}\ s^{-1}$	Weeks and Rabani (1966)
(18) $OH + O_3 \rightarrow HO_2 + O_2$	$2.0 \times 10^9\ M^{-1}\ s^{-1}$	Buhler *et al.* (1984)
(19) $CO_3^- + H_2O_2 \rightarrow HO_2 + HCO_3^-$	$8.0 \times 10^5\ M^{-1}\ s^{-1}$	Behar *et al.* (1970)
(20) $CO_3^- + I_j \rightarrow CO_3^{2-} + I_j^-$		

The liquid phase chemical reactions occur very rapidly when the peroxide/ozone ratio is near the stoichiometric point. For this reason, the reaction rate is expected to be limited by the mass transfer of ozone into the liquid phase. In this region, the ozone concentration is assumed to be very low (i.e., [O3]<< P/H), and the ozone concentration is assumed to be at steady state (i.e., d[O3]/dt = 0). Glaze and Kang have solved for the steady state hydroxyl radical concentration in regions II and III:

$$[OH]_{ss} = \frac{k_l a\left(P/H\right)}{k_{M,OH}[M] + k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}] + \left(k_{10}\left(10^{pH-pK}\right) + k_{11}\right)[H_2O_2]} \tag{21}$$

where $[OH]_{ss}$, is the steady state concentration of hydroxyl radicals in the semi-batch reactor, $k_l a$ is the mass transfer coefficient, P is the partial pressure of ozone in the gas phase, H is the Henry's Law constant for ozone (0.0839 atm m^3 mol^{-1} at 23°C)(Kosak-Channing and Heltz, 1983), $k_{M,OH}$ is the second order rate constant for the reaction of NMP and the hydroxyl radical,pK is the equilibrium constant for reaction 1, and k_{13}, k_{14}, k_{10}, and k_{11} are the respective rate constants from Table 1.

The expression for the pseudo-first order rate constant, neglecting direct reaction with ozone and sparging becomes:

$$k_0 = \frac{[k_{M,OH}]k_l a]\left(P/H\right)}{k_{M,OH}[M] + k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}] + \left(k_{10}\left(10^{pH-pK}\right) + k_{11}\right)[H_2O_2]} \tag{22}$$

The ozone dose rate was measured by a mass balance around the semi-batch reactor, thus equations 21 and 22 were modified by substituting the ozone dose rate, D_{oz}, measured under the experimental conditions in the numerator for the terms $[k_l a](P/H)$. Then the steady-state hydroxyl radical concentration and the pseudo-first-order reaction rate are:

$$[OH]_{ss} = \frac{D_{oz}}{k_{M,OH}[M] + k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}] + \left(k_{10}\left(10^{pH-pK}\right) + k_{11}\right)[H_2O_2]} \tag{23}$$

and

$$k_0 = \frac{[k_{M,OH}]D_{oz}}{k_{M,OH}[M] + k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}] + \left(k_{10}\left(10^{pH-pK}\right) + k_{11}\right)[H_2O_2]} \tag{24}$$

Equations 23 and 24 predict that the rate of substrate oxidation will be proportional to the concentration of ozone in the gas phase and the efficiency of mass transfer ($k_l a$) and inversely proportional to the concentration of the scavengers. Equations 23 and 24 also suggests that too large a dose of peroxide may have an inhibitive effect on the substrate oxidation rate. Furthermore, if the peroxide dose is low so that the residual hydrogen peroxide concentration is low compared to the carbonate-bicarbonate concentration, then the term $(k_{10}(10^{pH-pK})+k_{11})[H_2O_2]$ may be neglected.

Kinetic Model of the O3/H2O2 System in Region I, when Doz >2F.

In region I, hydrogen peroxide is consumed as rapidly as it enters the reactor, and the ozone concentration in the reactor builds over time. In this region, the hydrogen peroxide concentration is assumed to be at steady state (i.e., $d[H_2O_2]/dt = 0$), and the reaction rate of hydrogen peroxide is assumed to be equal to its feed rate.

Glaze and Kang defined an expression for the steady state concentration of OH radicals and the pseudo-first order rate constant for oxidation of substrate M in Region I as:

$$[OH]_{ss} = \frac{2F}{\left(k_{M,OH}[M] + (1 + S_{PER})\left(k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}]\right)\right)} \tag{25}$$

and

$$k_0 = \frac{2k_{M,OH}F}{\left(k_{M,OH}[M] + (1 + S_{PER})\left(k_{13}[HCO_3^-] + k_{14}[CO_3^{2-}]\right)\right)} \tag{26}$$

where

$$S_{PER} = \frac{k_{16}\left[CO_3^-\right]\left[H_2O_2\right]}{k_{16}\left[CO_3^-\right]\left[H_2O_2\right] + \sum k_j\left[CO_3^-\right]\left[I_j\right]} \quad (27).$$

When the peroxide dose is close to zero, S_{PER} is equal to zero, since the peroxide concentration is negligible. However, S_{PER} may become significant when the peroxide dose increases.

The Glaze and Kang model correlated very well with experimental results used to determine the optimum ratio of the moles of hydrogen peroxide per mole of ozone in the aqueous matrix. The results of the computer modeling and experimental results are shown in Figure 5.

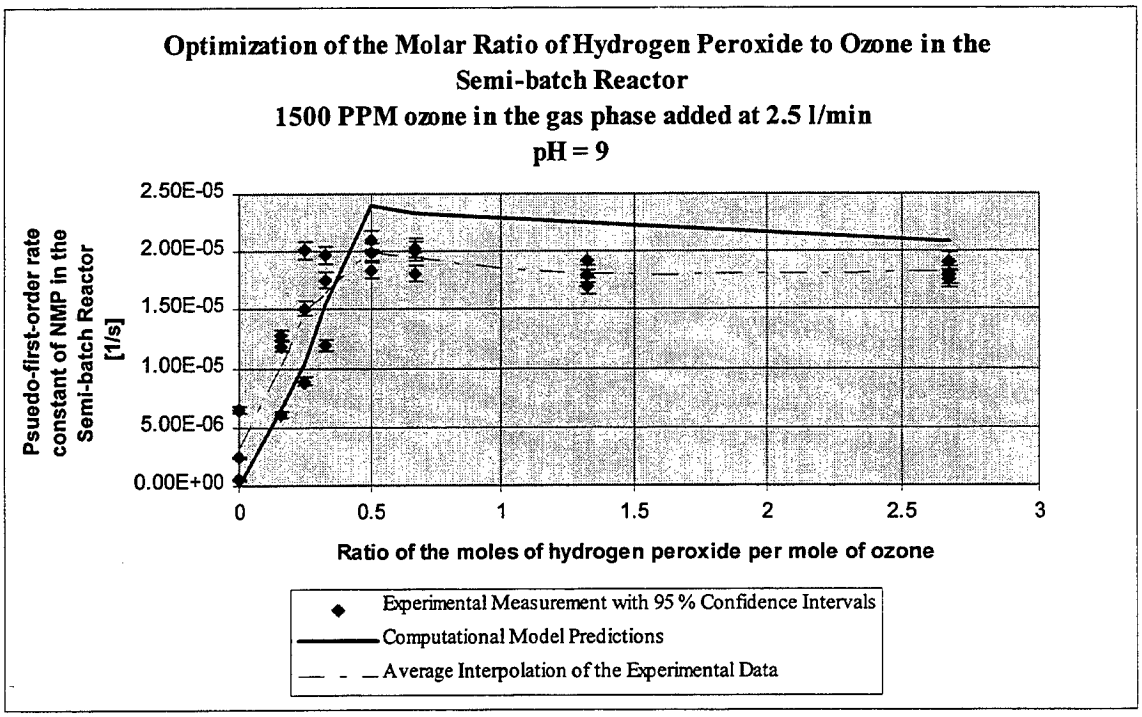

Figure 5: Optimization of the molar ratio of hydrogen peroxide to ozone in the semi-batch reactor.

From the model predictions, and the experimental results the optimum ratio of 0.5 moles of hydrogen peroxide per mole of ozone was obtained. Good correlation between the Glaze and Kang simplified kinetics model and the experimental results also allowed us to predict the order of magnitude of the second order reaction rate constant of NMP and the hydroxyl radical. The second order rate constant which gave the best fit to the data shown in Figure 5 was 10^9, which is consistent with a wide variety of organic compound's reaction rates with the hydroxyl radical(Barker and Jones, 1988).

Pilot Scale Test Results

The pilot scale system was run to determine if NMP would be removed by absorbtion from an exhaust air stream and if NMP in the liquid phase could be oxidized in the pilot scale system. The absorption process was modeled with Simulation Sciences Inc. PROII Distillation Model. The PRO/II simulation model from Simulation Sciences Inc. models absorption in a packed bed or distillation column. Heat and material balances are rigorously solved to meet column specifications input by the user. The feed stream to the column may contain multiple components. A variety of thermodynamic methods are available

for use in solving the heat and material balances. PRO/II uses the DipperII database for determining thermodynamic data of each component or the user may specify data for each component. The oxidation reactions were modeled with the Glaze and Kang kinetics model described above. These models were combined as shown in Figure 6.

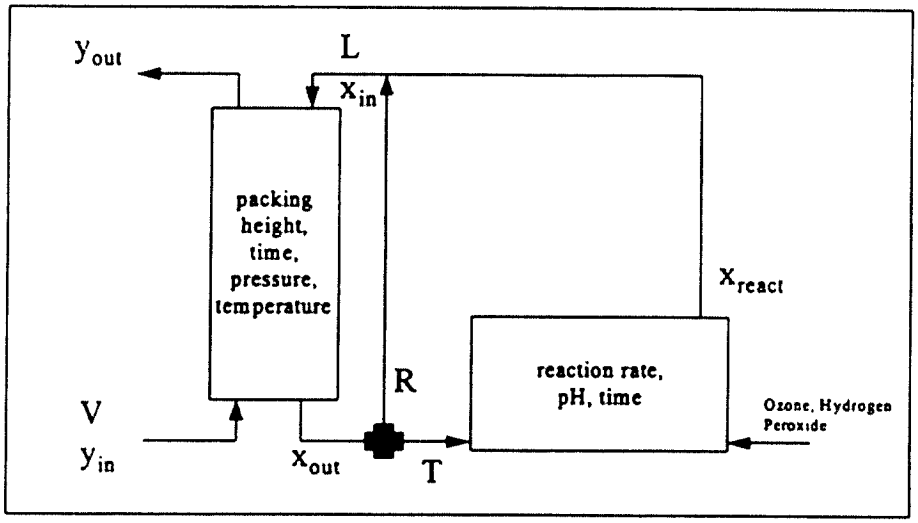

Figure 6: Computer Model of absorption and advanced oxidation processes in the pilot scale air pollution control system.

The air flow rate, V, in the pilot scale treatment system was 2500 SCFM. The water flow rate, L, through the eight foot high countercurrent packed bed column was 100 gpm, and the retention time in the advanced oxidation water treatment tank was 10 minutes. The pH was buffered with sodium phosphate buffer to maintain the pH at 8. The reflux ratio, R, of the pilot scale system was 50%. A temperature of 23°C, pressure of approximately 1 atm, and a relative humidity of 50% were the ambient conditions at the time of the experiments.

Ozone was produced with low pressure photolytic ozone generators. An air stream containing 150 PPM of ozone was diffused into the water treatment tank of the pilot scale system. Hydrogen peroxide was added at the optimum stoichiometric ratio of 0.5 moles of hydrogen peroxide per mole of ozone absorbed into the liquid., as determined from the semi-batch reactor.

The concentration of NMP in the gas phase entering and exiting the packed column was measured with NGA 2000 Rosemont® Analytical, Flame ionization detectors (FIDs). The concentration of NMP and reaction products in the scrubbing liquid were measured by GC/FID as described above in the semi-batch reactor experiments.

The packed bed scrubber is a part of the pilot scale air treatment system at ARL. This pilot scale system is a modified scale version of a commercially available air pollution control system.

NMP was removed from the gas phase in the packed bed absorption column as shown in Figure 7. Over the four hour run time in which 0 to 44 PPM of NMP was sprayed into the pilot scale system there was no detectable level of NMP in the gas stream exiting the packed column reactor. These results are in agreement with those predicted by the PROII computer simulation with the simplified kinetics model. Because NMP has such a low vapor pressure and is a very polar compound the effects of hydrogen peroxide addition to the advanced oxidation liquid phase reactor did not measurably affect the efficiency of the gas phase absorption process over the four hour time period.

The combined absorption and simplified chemical kinetics model predicted the gas and liquid phase concentrations of NMP and reaction products over the four hours of the experiment. The computer predictions showed good agreement with the experimental results shown in Figures 7 and 8.

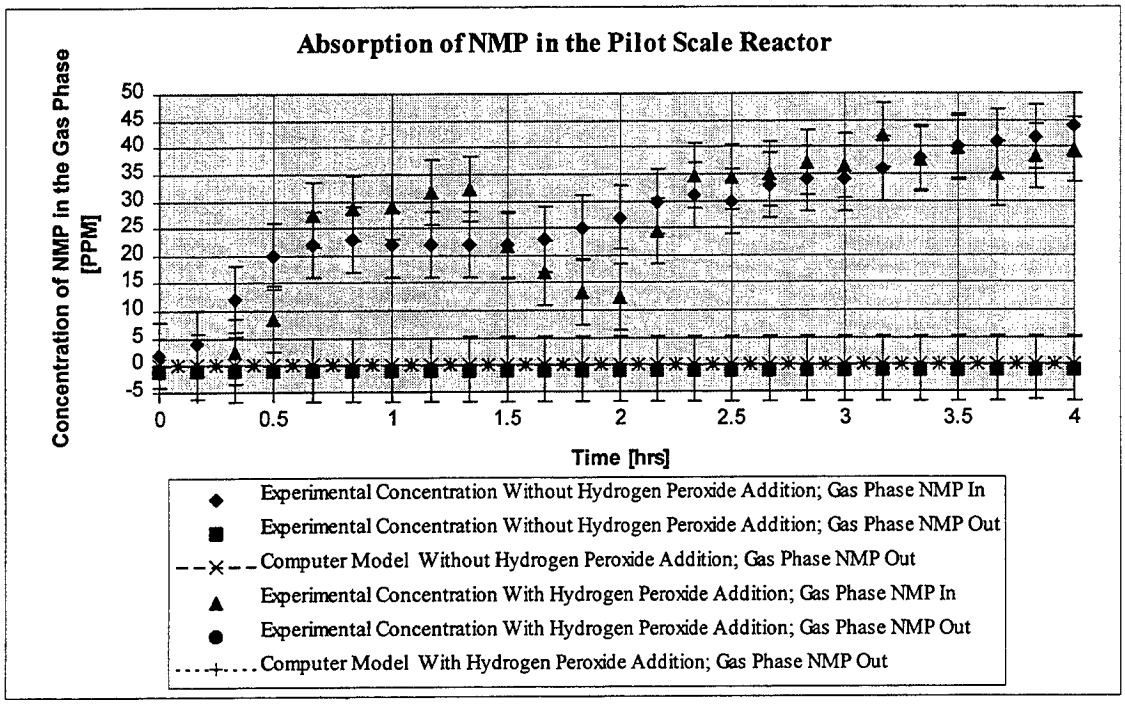

Figure 7: Absorption of NMP in the pilot scale air pollution control system.

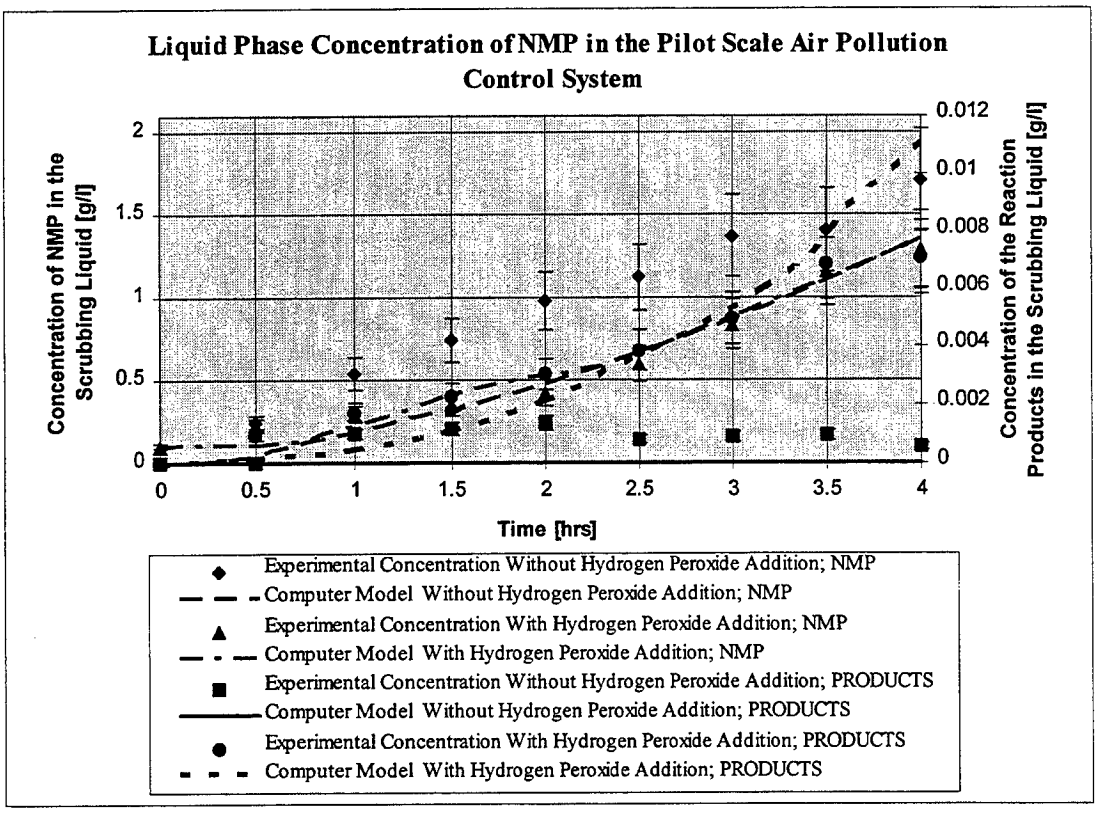

Figure 8: Liquid phase concentration of NMP and the reaction products in the scrubbing liquid in the pilot scale system.

The liquid phase data shows the concentration of NMP increases over time in the scrubbing liquid. No measurable increase in the reaction products was observed over the four hour experiment when the water was treated with ozone only. However, when hydrogen peroxide was added to the liquid, the reaction rate increased close to that predicted by the simplified kinetics model. NMP did not appear to be oxidized in the water treatment tank with ozone, but with the addition of hydrogen peroxide along with ozone, NMP was oxidized.

Conclusions

NMP is being used as a replacement solvent for more volatile compound in surface coating, as a cleaning agent, and as a stripping agent. Existing pollution control systems should be evaluated to treat NMP emissions in the gas phase, since NMP is still considered by the USEPA to be a VOC.

NMP can be oxidized in the liquid phase by the hydroxyl radical to form methylsuccinimide, 2-pyrrolidinone, and 2,5-pyrrolidinedione.

The addition of ozone and hydrogen peroxide increased the rate of oxidation in a semi-batch reactor and a pilot scale pollution control system. The optimum molar ratio of hydrogen peroxide to ozone in the liquid phase was 0.5. This optimum ratio was predicted with the simplified chemical kinetics model developed by Glaze and Kang and agrees with the overall stoichiometry of ozone/peroxide reactions which produce the hydroxyl radical (Staehelin and Hoigné, 1982).

Up to 44 PPM of NMP was removed to below detection limits (2 PPM) in the counter current packed bed scrubber in the pilot scale APCS over a four hour time period. Air and liquid phase concentrations in the packed column were predicted by combining the simplified chemical kinetics model and commercially available distillation column design programs.

The simplified chemical kinetics model may be used in conjunction with commercially available chemical engineering distillation models to gain insight into the cost and design of advanced oxidation processes and absorption systems to treat NMP in an exhaust air stream.

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An Interagency Study of Depainting Techniques

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Abstract

Many popular and widely used paint stripping products now contain methylene chloride as their active ingredient. However, the Environmental Protection Agency (EPA) will critically curb the use of methylene chloride under an aerospace national emission standard for hazardous air pollutants (NESHAP) within the next 2-1/2 years. An effort is underway to identify and evaluate alternative depainting technologies emphasizing those believed to be both effective and environmentally benign.

On behalf of the EPA and in cooperation with the U. S. Air Force (USAF), the National Aeronautics and Space Administration (NASA) is conducting a technical assessment of nine alternative technologies (i.e.: chemical stripping, two CO_2 blasting processes, FLASHJET™ coating removal, laser stripping, plastic media blasting, sodium bicarbonate wet stripping, high-pressure water stripping, and wheat starch blasting). These depainting processes represent five removal method categories, namely abrasive, impact, cryogenic, thermal, and/or molecular bonding dissociation.

This paper discusses the test plan and parameters for this interagency study. Several thicknesses of clad and non-clad aluminum substrates were used to prepare test specimens, which have been cut, cleaned, painted, and environmentally aged. Each depainting process has been assigned a specimen lot, which is now undergoing an initial strip cycle. Metallurgical impacts will be determined after these specimens complete five cycles of preparation and stripping.

Test Plan Description

As the result of an extensive literature search, NASA's Marshall Space Flight Center personnel, with the direction from the EPA and the USAF, selected nine processes to evaluate in the interagency study. These nine processes, listed previously in the abstract, use five distinct stripping technologies: Abrasive (A), Cryogenic (C), Impact (I), Molecular Bonding Dissociation (MBD), and Thermal (T). The following Table 1 associates each selected process with the appropriate stripping technologies. Some processes use more than one technology for effective stripping.

Table 1: Stripping Technologies Included in the Study.

Stripping Process	Stripping Technology
Chemical Stripping	MBD
COLDJET (CO_2 blasting)	C, I
TOMCO_2 (CO_2 blasting)	C, I
Flashjet	T, C, I
Laser Stripping	T
Plastic Media Blasting	A
Sodium Bicarbonate Water Stripping	I
Water Blasting	I
Wheatstarch Stripping	A

With the selection of the processes made, an appropriate test plan needed to be prepared. The group of Marshall personnel, with guidance from several industry and federal agency counterparts,

decided to follow the plan described in the then-current draft of the International Standards Organization (ISO)/ Standard for Automotive Engineers (SAE) standard MA 4872, draft #4, as closely as possible. This document calls for five iterations of specimen preparation and stripping before comparing metallurgical results to a baseline. The seven steps involved in each of the five iterations are as follows:

1. CLEANING. The first step is the cleaning of the specimens which is performed in compliance with NAS MP 200, "Cleaning Procedure for Low Strength Steel and Steel Alloy, High Strength Steel and Steel Alloy, and Aluminum and Aluminum Alloy." This procedure begins with a methyl ethyl ketone hand clean to remove oil and ink from the surface followed by a 10 minute vapor degreasing operation in perchloroethylene. The specimens are then completely immersed in an alkaline bath for approximately 25 minutes and immersed in a hot deionized water rinse for about five minutes. Next, the specimens are immersed for 11 minutes in a deoxidizing bath followed by a final cold deionized water rinse for five minutes. The specimens are all tested for water break free conditions before advancing to the next step.

2. SURFACE TREAT. After the cleaning of the specimens, they are protected with a chromate conversion coating per NAS MP 204, "Procedure for Chemical Conversion Coating for Aluminum and Aluminum Alloys." The specimens are immersed in an Iridite 14-2 bath for five minutes followed by a cold deionized water rinse for another five minutes. After air drying using a missile grade air supply, the specimens are individually wrapped in wax-free paper to prevent surface contamination.

3. COLLECT DATA. At this time, measurements are made on each specimen. The initial measurements serve as baseline data and the subsequent measurements taken throughout the study will be compared back to the original readings to determine if any significant amount of substrate metal was removed during the depainting process. Substrate thicknesses are measured with a NOVA 800 Plus gage with a broad-band pulse receiver and a Model D11 transducer at a center frequency of 15 MHz. Nine thickness measurements are taken per specimen. Surface roughness is also measured using a TMA Microscan surface roughness monitor that measures the scattering of a 670-nm laser aimed at a 25° angle of incidence. This measurement is made in root mean square (RMS) microinches and again, nine measurements are taken per specimen. The ISO/SAE MA 4872, draft #4, requires a surface roughness measurement less than 125 RMS.

4. APPLY PAINT SYSTEM. The coating application is performed in compliance with the two documents used to specify the primer and topcoat, MIL-P-23377F, "Primer Coatings: Epoxy, Chemical, and Solvent Resistant" and MIL-C-83286B, "Coatings Urethane, Aliphatic Isocyanate, for Aerospace Applications" respectively. The procedure for applying these materials requires that the epoxy primer (Type 1, Class 2) be applied to a dry-film thickness of 0.6 to 0.9 mils and then be allowed to air dry for at least five hours. The polyurethane topcoat is applied to a dry-film thickness of 1.6 to 2.3 mils and cured for 24 hours at 122 ±5°F. The total dry-film thickness should range between 2.3 and 3.2 mils.

5. COLLECT DATA. The coating thicknesses are measured using a Fisher isoscope Model MP2 eddy current probe. These measurements are also measured at nine locations on the specimen and are used as quality control in the preparation of the specimens during each iteration. After the measurements have been made and all readings are within the guidelines of the ISO/SAE MA 4872, draft #4, document, the specimens are individually wrapped to prevent scratches and surface contamination and are shipped across the Center to the aging chambers.

6. AGING. The aging scenario of the specimens requires a 12 hour precondition of the specimens at 120°F and 95% relative humidity followed by a one hour hold at -65°F. After

that the specimens must be cycled 400 times from -65°F to 160°F. Then the specimens are returned to ambient temperature and the entire process is repeated. This process has proven to take 97 days in the chambers NASA has available for use.

7. STRIPPING. Finally, the specimens are ready to be stripped. The specimens have been marked with identification numbers so each potential alternative stripping process will see the same specimens with each iteration of the study. The specimens are distributed and each process engineer uses its optimum parameters for stripping. The parameters are documented and the stripping rates are determined. Any anomalies are also documented. After the stripping, the specimen surface is studied for any chemical variations with an electron spectroscopy for chemical analysis (ESCA) and returned for processing in the next iteration.

Material Selection

The materials selected for use in the study were aluminum 2024-T3 clad and non-clad substrate, a MIL-P-23377, Type 1, Class 2, primer, and a MIL-C-83286 polyurethane topcoat. These materials are referenced in the ISO/SAE MA 4872, draft #4, under section 2.0 APPLICABLE DOCUMENTS. SAE AMS 4037 details the requirements of Al 2024 T3, while MIL-P-23377 and MIL-C-83286 are referenced as typical primers and topcoats. The study was limited to this one substrate and coating system for manageability of the study parameters and comparability of the data to existing data on a similar substrate. Although the primer and topcoat being used are both targeted by EPA as high VOC materials, they have been partnered as a preferred paint system for many years and a strong database of information exists in the technical field on the performance of that paint system. For this reason, NASA, EPA, and the involved industries, collectively called the Technical Advisory Committee (TAC), opted to test the alternative paint stripping technologies against a paint system which would allow the comparison of stripping rates on like paint systems.

The aging cycle was also selected in compliance with the ISO/SAE MA 4872 document, draft #4, which was available at the time of these decisions. At this time, the TAC strongly suggested our study follow closely the parameters established in that proposed document. That 4th draft of the ISO/SAE MA 4872 stated in section 5.1, sentence a, that test panels must be prepared in accordance with Appendix C. Appendix C describes an intense aging scenario as described in the following table:

Table 2: Aging Steps per ISO/SAE MA4872.

STEP	PROCEDURE
1	Precondition for 12 hours at 120°F and 95% relative humidity.
2	Hold at -65°F for 1 hour.
3	Thermally cycle the chamber from -65°F to 160°F 400 times.
4	Return chamber to ambient temperature.
5	Repeat steps 1-4.

The aging scenario in the ISO/SAE MA 4872, draft #4, also requires that the cycling from -65°F to 160°F and back down to -65°F occur within 30 minutes. NASA was unable to meet this ramp in less than 3 hours with a full chamber, so the study was approved to age the specimens at the rate NASA could achieve and to still run five iterations of painting, aging, and stripping. As stated earlier, this aging scenario is quite lengthy and greatly impacts the timeline of the study. Let it here be noted that more current drafts of the ISO/SAE MA 4872 state that the aging of the specimens in this manner is optional.

Another observation from the use of this aging cycle is that the paint system is quite tenacious. Removal of the topcoat and primer is quite difficult for all processes being used. Even the chemical strippers which contain methylene chloride (for baselining purposes) require up to four hours to remove the paint system when they have traditionally been able to remove paints in no more that 45 minutes.

Preliminary Results from First Stripping Sequence

At this time, NASA has completed one iteration of the five stripping sequences. Preliminary data exists on all nine processes being reviewed. A brief summary of results from each process follows. However, this information in inconclusive, and complete details of the results to date remain with the study data for compilation and comparison to baseline results.

CHEMICAL STRIPPING. The alkaline strippers were applied using two methods, brush-on and spray-on, neither one of which seemed to work better than the other. The five most effective alkaline strippers were Turco 6813, Turco 6840, McGean Rohco Cee-Bee 2002, Autre Nu-Strip, and Dynacraft Back to Nature VIII. However, even these strippers showed minimal effect over a 24 hour period. Raytheon's Selma facility graciously stripped some test specimens with these and other strippers in their facility to demonstrate some modified process parameters which work in the field. This modified approach is described in Table 3. The most effective strippers at the Raytheon facility are being retested on specimens in the laboratory at MSFC.

Table 3: Modified Chemical Stripping Procedure.

Step	Process
1	Insure a temperature between 80°F and 90°F, relative humidity at 32%.
2	Spray a fine mist of stripper on surface.
3	Reapply a slightly heavier mist 30 minutes later.
4	When debonding occurs (2-4 hours), agitate surface with brass bristle brushes and wipe clean.
5	Repeat steps 2 and three.
6	When all coating is removed (8-9 hours), clean and demask specimens.

The acid strippers were applied in the same fashion as the alkaline strippers and five of them effectively removed the coating in 3-8 hours. These five strippers were Calgon EZE 540, Eldorado PR-2002, McGean-Rohco Cee-Bee E 1004B, McGean-Rohco Cee-Bee A-202, and Turco 6776.

COLDJET (CO_2 BLASTING). This testing was performed manually using a COLDJET Model 65-200 system with two independent blast systems. Testing was conducted using 0.12 inch pellets. During the first practice run, a 16 mil specimen was blasted at a pressure of 300 psi with a 5 inch wide nozzle. In order to remove any of the paint, the standoff distance had to be steadily decreased and as a result, the thin substrate was quite pelted and deformed. A subsequent stripping of a 64 mil specimen also damaged the substrate significantly. As this process was originally designed to clean surface contaminants rather than to strip paint systems, the results are not surprising. The system has been determined ineffective as a stand alone paint removal process and will be removed from the interagency depainting study.

TOMCO$_2$ (CO_2 BLASTING). The second CO_2 blasting system used was a TOMCO$_2$ DI-250 system. This system did not include a pelletizer so 0.12 inch pellets have been purchased from S&S Carbonic Industries. This testing was automated in the MSFC's Productivity Enhancement Complex (PEC) using a Fanuc S-420F robot and a 10 foot turntable. Testing of this process began and ended during the initial efforts to fine-tune the test parameters using 64 mil specimens. The coating system used in this study is much too tenacious for the TOMCO$_2$'s maximum allowable blast pressure (150 psi) and flow rate (350 lbs/hr). Two test runs removed no coating whatsoever. A third run did remove most of the topcoat from the top half of the specimen, but the aluminum test fixture cooled as stripping progressed, allowing a 0.25 inch layer of ice to build up ahead of the nozzle. The process was halted so the ice could be removed by hosing down the fixture. However, frost and ice quickly reformed as the testing resumed. The processing parameters of the TOMCO$_2$ system are not such that they can accommodate stripping this paint system. Therefore this process is also being removed from the study. Again, this CO_2 system is

designed for particulate cleaning, not paint stripping and is quite effective when used within its design parameters.

FLASHJET™. The specimens which were stripped with the FLASHJET™ process were shipped off-site for paint removal by McDonnell Douglas. When the specimens were returned to MSFC, visual inspection revealed a uniform amount of primer remaining on the entire surface of the 51 mil specimens and less uniform remnants of primer on the 16 mil specimens. The substrates were undamaged and surface roughness measurements were well within the required range per ISO/SAE MA 4872, draft #4. Before these specimens are recoated, MSFC will remove any remaining primer from these panels by applying Cee-Bee A-202 for about 20 minutes and then lightly abrading them with Scotch Brite pads to remove any remaining spots.

The study requires that each process completely remove an artificially aged coating system in order to return the specimens to bare substrate. This allows for each specimen, from whichever process to be exposed to the same number of processing steps in each iteration of the study. McDonnell Douglas elected to not remove the final 0.5 mils of primer to avoid damaging the substrate. However, this demonstrates that FLASHJET™ is capable of selectively stripping layers of coatings (a capability shared by the laser, waterjet, and wheat starch techniques).

LASER STRIPPING. The specimens for the laser stripping process were also shipped off-site. These specimens were stripped by Silicon Alps in Santa Clara, CA using a CO_2 gas laser system. A horizontal band between 4 and 5 inches was stripped across each panel. This process delivered excellent results. The stripped areas were very clean, with few traces of paint. The coating which remained on the unstripped sections of the specimens was removed with the Cee-Bee A-202 methylene chloride product and Scotch Brite pads as discussed earlier.

PLASTIC MEDIA BLASTING. Plastic media blasting (PMB) is a manual process with some health related hazards requiring operators to use noise reduction and airborne particle protection equipment. Selected test parameters are based on the results of other PMB efforts reported by government and industry studies. A 0.5 inch nozzle was used to deploy Type V plastic media. Some 16/20 mesh media was combined with 20/30 mesh media to improve strip rates and increase the aggressiveness of this process. Media effectiveness was noticeably reduced after about 10 stripping cycles. The 16 mil specimens were stripped at 30 psi: the 51 mil specimens were stripped at 35 psi: and the 64 mil specimens were stripped at 40 psi. The strip rate was slow compared to more aggressive mechanical stripping processes and became even slower at the low operating pressures required for thin substrates. However, with the lower pressures, no substrate damage occurred, and the process removed 100% of the primer and topcoat.

SODIUM BICARBONATE WATER STRIPPING. This process was operated manually using a Bicarbonate of Soda System (BOSS) from Caroline Equipment. The pressure was 15,000 psi with a 2 lbs/min flow rate of media. The standoff distance was 1 inch. The specimens tended to bow somewhat after stripping and removal from the support structure. The surface roughness measurements on the 51 mil and the 64 mil specimens were well within the range specified in the ISO/SAE MA 4872, draft #4, but the measurements could not be made on the 16 mil specimens because the substrate arched in a semi-circle when unsupported. Removal of the topcoat was complete and a small amount of primer remained on the surface of some specimens.

WATER BLASTING. MSFC has extensive experience in the use of high pressure water blasting to strip materials, including paint. For this application, a two-pass completion was targeted. This double pass technique moved high energy water streams over the control specimens more quickly, greatly reducing the possibility of damaging the substrate by dwelling too long on one spot. The pressures used were between 18,000 and 32,000 psi for the 16 mil thick specimens, just at 32,000 psi for the 51 mil specimens, and between 22,000 and 32,000 psi for the 64 mil specimens. The standoff distance on all of these runs was 2 inches with a flow rate between 8 and 10.75 gallons per minute. The high pressure

streams impacted the 51 mil and 64 mil specimens without distortion, but some 16 mil specimens sustained some dimpling and molding to the backing panel. The 16 mil specimens did withstand 22,000 psi pressures without any damage. The process effectively removed all topcoat and primer before moving to the next stage of processing.

WHEATSTARCH STRIPPING. The specimens to be stripped with the wheat starch blasting process were shipped off-site to CAE Electronics in Montreal, Quebec, Canada. All were stripped and returned to MSFC on schedule. Envirostrip media was used for several cycles and was continuously replenished with new 12/30 media at a rate of 10 to 15% per cycle. The 16 mil specimens had to be stripped at a lower pressure and higher flow rate (20 psi, 18 lbs/hr) to obtain good stripping rates without damaging the specimens. The pressure and flow rate used for the other specimens was 40 psi and 12 lbs/hr. Visual inspection at MSFC revealed that this method removed 100% of the topcoat with only trace amounts of primer remaining, except for an area around the perimeter where the specimens were clamped to the test fixture.

Status of Testing

At this time, the specimens are all in the preparation stage of the second cycle. All of the interim measurements have been made and the painting is near completion. The specimens should be in the aging chambers by the end of the summer months. As stated earlier, Two processes, TOMCO$_2$ and COLJET, have been dropped from the study as they did not perform well for this application. Let it be noted that these CO_2 blasting processes were not intended for use as paint stripping systems and this application is beyond thier design criteria. Also, several processes did demonstrate some effect on the substrate and this is being monitored through the study. The completion of the five iterations of stripping and then the final metallurgical analysis is projected for the end of calander year 1998. The findings along the way are preliminary and in no way conclusive.

Acknowledgment

I would like to thank all the personnel at MSFC who are working on this project. This integrated study requires the expertise of many individuals across the Center, and it requires a significant cooperative effort. I could not report any of these findings without the profound effort of these dedicated individuals.

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Testing of Solvents for Removal of Urethanes/Epoxies

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ABSTRACT

For many years, methylene chloride has been the solvent of choice for softening or dissolving polyurethane and epoxy bonds and/or coatings. However, methylene chloride has been implicated as a suspect carcinogen and is now regulated under the Resource Conservation and Recovery Act (RCRA), as a hazardous air pollutant under the Clean Air Act (CAA), and is in the rulemaking process by the Occupational Safety and Health Administration (OSHA) to have the permissible exposure limit lowered from 500 to 25 ppm for an 8 hour time weighted average. Because of these concerns, many people have begun investigating alternatives for methylene chloride in this application. For paint removal, many people have turned to dry methods or various types of stripping using carbon dioxide pellets, baking soda, corn husks, etc. However, in some applications due to geometry constraints these methods cannot be used. Personnel at the Oak Ridge Y-12 Plant have been investigating many solvents or solvent blends as substitutes for methylene chloride. Several different pure solvents of various chemical types have been tested along with blends formulated using Hansen Solubility Parameter Theory which states that solvents with similar parameters will have similar dissolution properties. Initially, the solvents were screened by conducting weight gain tests on pieces of cured urethane and/or epoxies. Solvents or solvent blends which appeared promising were tested more thoroughly. Four solvent blends have been tested on thin bondlines of polyurethane with some success. Solvents have also been tested on panels coated with both urethanes and epoxies.

Introduction

Polyurethanes and epoxies are used throughout industry for bonding, protective coatings and composite applications. Many of these systems were designed to extend the life and wear of surfaces or to aid surfaces in withstanding exposures to solvents or weather. Since they are designed to withstand such attack, removal can be difficult. Many "dry" techniques have proven useful for removing coatings such as carbon dioxide pellet blasting, baking soda blasting, plastic media blasting, etc. However, due to geometry constraints, these methods are not conducive to debonding or for paint removal on complex geometries.

Methylene chloride has been the solvent of choice for years for removing polyurethanes and/or epoxies. However, methylene chloride is considered an animal carcinogen by the National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC) although IARC has determined that the data is inadequate for an evaluation of carcinogenicity in humans. The American Conference of Governmental Industrial Hygienists (ACGIH) considers methylene chloride an A2 which means it is a suspect human carcinogen. Due to these health concerns, methylene chloride has been regulated quite heavily. It is considered a hazardous air pollutant (HAP) under the Clean Air Act (CAA) and strict emission standards have been adopted for its use. It is considered a Resource Conservation and Recovery Act (RCRA) waste and attempts are being made by the Occupational Safety and Health Administration (OSHA) to lower the permissible exposure limit from 500 ppm to 25 ppm for an 8 hour time weighted average. Because of these concerns, substitutes for methylene chloride are being evaluated.

Several solvents are being touted as replacements for methylene chloride in removing polyurethanes/epoxies including N-methylpyrrolidone (NMP), dibasic esters (DBEs), ethyl 3-ethoxypropionate (EEP), butyrolactone, ethylene glycol ethers, amines or blends of these compounds. Testing was conducted using solvents such as these and other solvents which had been found to be effective in the past on polymeric materials. Blends of solvents were formulated and tested based upon solvent interactions with the material and/or Hansen Solubility Parameter Theory. Hansen Solubility Parameter Theory[1] states that solvents which have similar parameters (dispersion cohesion parameter, hydrogen bonding cohesion parameter and polar cohesion parameter) behave similarly with regard to solubility. Thus, attempts were made to make solvent blends which had parameters similar to methylene chloride.

Urethanes

Initial testing of the solvents was conducted using a weight gain test on small pieces of the polymeric material of interest. Testing was conducted on a polyurethane based on Halthane 88 and Asilamine 170. Halthane 88 is a reaction product of polytetramethylene ether glycol 2000 (PTMEG 2000) and bis(4-isocyanotocyclohexyl)methane ($H_{12}MDI$). Asilamine 170 is a low toxicity diamine curing agent. Small pieces weighing between 2.5 to 3.0 g of the Halthane 88/Asilamine (88/3) were weighed and then submerged in the solvent. The samples were removed periodically, wiped dry and reweighed. Table One summarizes the effect of many of the solvents tested on the polyurethane.

Table One -
Results of Weight Gain Experiment for Halthane 88/Asilamine 170

SOLVENT	% WEIGHT GAIN AFTER 4 HR
Methylene Chloride	281.79
S-1A	124.21
S-1B	93.33
S-2A	92.33
S-2B	91.61
S-3A	83.60
S-2C	82.67
S-1C	81.43
Anisole	76.46
S-2D	71.86
S-4A	71.8
S-2E	70.28
S-1D	60.07
S-5A	58.53
S-6A	55.87
S-6B	51.0
S-4B	44.94
S-3B	44.53
S-1E	43.07

Table One (continued)

SOLVENT	% WEIGHT GAIN AFTER 4 HR
S-7A	42.98
S-6C	41.84
S-6C	41.35
S-1F	40.39
S-2F	37.94
Acetone	36.20
Benzyl Alcohol	34.55
Phenetole	32.88
S-8A	32.37
Octanone	30.94
S-2G	28.98
S-2H	38.18
S-9A	26.96
S-3C	25.38
Hexanol	24.9
S-5B	23.24
S-9C	21.38
Pentoxone	19.27
S-3D	17.38
EEP	15.37
S-10A	14.71
Ethylhexyl acetate	8.9
DBE	7.57
Diisopropylbenzene	7.04
Butyrolactone	5.28
S-10B	4.87
NMP	4.49
Dimethylsulfoxide	3.31

The actual compositions are not disclosed due to proprietary concerns; however, a patent is pending on several of the blends which are available for licensing. To aid in following the results, blends based on the same major component are identified with the same numeral.

As shown in Table One, the blends vary tremendously in their effectiveness based upon the formulation. For instance, the S-1 blends varied in effectiveness from a weight gain of 40.39% to 124.21% in a 4 hour time frame. Several blends formulated using the Hansen Solubility Parameter Theory, such as blend S-8A, were not as effective as those formulated due to noted behavior of the individual solvents on the material, such as blend S-1A. The majority of the blends were much more effective than solvents currently being touted for use such as NMP, DBE and butyrolactone.

Based upon these results, blends S-1A, S-1B and S-2A were selected for further evaluation. The specific area of interest at the Y-12 Plant was to defeat a thin bondline of Halthane 88/XU-205 (a methylene dianiline based curing agent). Stainless steel lap shear specimens were prepared and bonded using a 5-mil bondline of Halthane 88/XU-205. After the specimens were allowed to cure, they were submerged in solvent blends S-1A, S-1B and S-2A at 50°C. A higher temperature than room temperature was selected to accelerate the effectiveness of the solvent blends. However, 50°C was the maximum operating temperature allowed. At different time intervals, 3 samples each were removed and tested to determine bond strength. The results of these tests are shown in Figure 1.

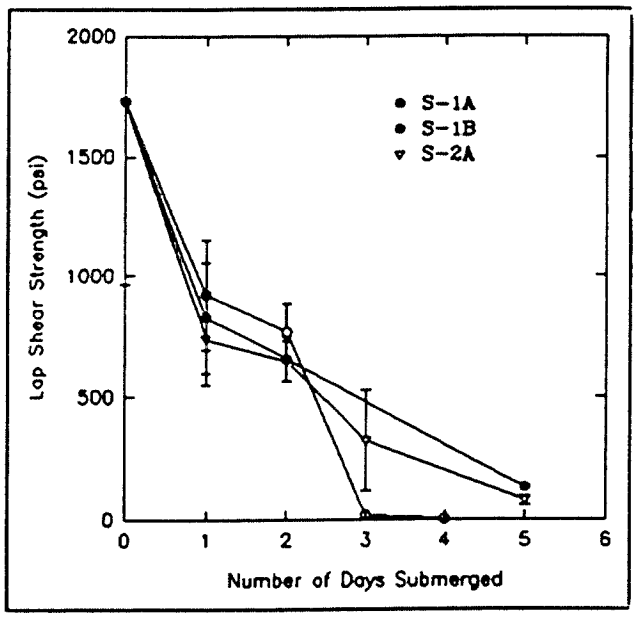

Figure 1 - Effects of Solvent Blends at 50°C on Lap Shear Strength of Stainless Steel Lap Shears Bonded with a 5-mil Bondline of Halthane 88/ XU-205

The solvent blends were effective at defeating the thin bondline. The lap shear specimens submerged in blend S-1A fell apart in the solution after 4 days. The other blends were not quite as effective although the strength of the bonds were only a few psi after 5 days submersion. Testing has also been conducted on blend S-1A by pouring the solvent (~15 ml) into thin gaps surrounding a patch of adhesive between two parts (~4.5 in^2 area). After exposure to the solvent blend for 4 days at 50°C, the parts pulled apart easily.

A paste was made of solvent blends S-1A and S-2A using fumed silica as a thixotropic agent. The pastes were tested on coatings of Halthane 88/Asilamine 170 on metal substrates. Within 30 min, the coatings had swelled sufficiently so that they could be wiped off easily.

Epoxies

Weight gain studies were also conducted on samples of an epoxy system consisting of D.E.R. 332 (diglycidyl ether of bisphenol A resin manufactured by Dow Chemical Co.)/tetraethylenepentamine (TEPA). The results of these studies are shown in Tables Two and Three. Three commercial solvent blends found effective in removing epoxy paints by other agencies were included in the tests. The tested blends were Brand T, consisting of benzyl alcohol, propylene glycol, hydroxyacetic acid, and sodium xylenesulfonate, and Brand B-1000 and Brand B-HT, consisting of 2-butoxyethanol and monoethanolamine, and diethylene glycol n-butyl ether and monoethanolamine, respectively.

Table Two -
Results of Weight Gain Study Conducted on DER 332/TEPA at Room Temperature

SOLVENT	% WEIGHT GAIN AFTER 4 HRS	% WEIGHT GAIN AFTER 1 DAY
Methylene chloride	20.81	Fell apart
Dimethylsulfoxide	1.63	4.08
S-2B	1.25	3.07
S-10C	1.24	2.80
S-2A	0.99	2.40
S-1B	0.96	1.87
S-3A	0.88	0.79
NMP	0.84	1.46
S-10B	0.83	2.06
S-10A	0.78	2.08
Brand T	0.52	NA
Octanone	0.45	0.44
Sulfolane	0.43	0.45
Brand B-1000	0.41	0.6
S-10E	0.39	0.74
Butyrolactone	0.33	0.57
Propylene Carbonate	0.32	0.18
Brand B-HT	0.23	0.61
Diisopropylbenzene	0.17	0.07
DBE	0.04	0.03

Table Three -
Results of Weight Gain Study Conducted on DER 332/TEPA at 50°C

SOLVENT	% WEIGHT GAIN AFTER 4 HRS	% WEIGHT GAIN AFTER 1 DAY
Butyrolactone	3.65	8.36
Brand B-HT	3.09	6.62
S-10B	2.14	4.87
NMP	1.96	4.23
S-10A	1.95	4.74
S-10E	1.74	3.71
DBE	1.26	3.21
Brand T	1.10	NA
Brand B-1000	0.82	1.57
Sulfolane	0.79	1.61
Propylene carbonate	0.60	1.40
Octanone	0.28	0.77
Diisopropylbenzene	0.14	0.14

None of the solvents tested approached the effectiveness of methylene chloride. The addition of temperature did enhance the effectiveness of the solvents tested with the exception of octanone and diisopropylbenzene. However, these two solvents were not found to be very effective in either case. Temperature greatly improved the effectiveness of butyrolactone and the Brand B-1000.

Several of these solvents have also been tested on parts obtained from the United States Army to determine their effectiveness on paint removal. There are three main coatings used by the Army: chemical agent resistant coating (CARC), which consists of a waterborne epoxy primer and a polyurethane topcoat (MIL-P53030/MIL-C53039), a vinyl wash primer with an epoxy polyamide topcoat (DOD-P-15321/MIL-P-24441) and an alkyd primer with an alkyd topcoat (TT-P-1757/TT-E-489). Unfortunately, the history or type of coatings which were present on the parts obtained from the Army was unknown. The parts varied in surface preparation, coating thickness, layers of coating, and type of coating, thus the test results were inconsistent. Panels have been obtained which were specially prepared and coated for testing. However, testing has not been conducted on these panels.

Conclusions

Although no solvents have been identified which are as effective as methylene chloride for softening or swelling polyurethanes and epoxies, several solvent blends have been formulated which work well on polyurethane. These blends have been found to be more effective than several solvents which are currently being touted for softening/swelling of polyurethanes, including DBE and NMP. A synergistic effect has been found with some solvent blends which causes the blends to be more effective in softening/swelling the polyurethane than the individual solvents. Two of the solvent blends have been found to be effective in defeating thin bondlines of polyurethane. A paste composed of two of the blends mixed with fumed silica has also been found to be effective in removing urethane coatings from metal substrates.

With regard to epoxies, very little effect was noted with any of the solvents tested. Increasing the temperature did

appear to enhance the performance of several of the solvents but effects were still only slight. Testing of the solvents for coating removal was inconclusive due to variances in the parts being used for testing.

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Alternative Coating Removal Methods for Radome Materials

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ABSTRACT

Warner Robins Air Logistics Center (WR-ALC), like many of its counterparts throughout the DoD, continues to develop viable and effective alternative coating removal methods to replace the methods currently in use. The current methods used by WR-ALC for removal of the protective coatings from radomes are some form of chemical stripping. These chemical stripping processes are based on chemicals that are not considered environmentally safe, such as methylene chloride and methyl ethyl ketone. This paper discusses the initial feasibility testing of several methods that could have the potential to be used as an environmentally acceptable alternative method for use on the radomes that are inspected and repaired by WR-ALC. The successful attainment of the goals of this program includes compliance with WR-ALC production requirements, as well as satisfying weapons systems program directorate constraints regarding possible radome performance degradation produced by an alternative coatings removal process. This paper will present the prospective alternative methods/processes being evaluated, the feasibility test protocol, the WR-ALC acceptance criteria being applied to determine process feasibility, and the interim test results from the on-going feasibility assessments.

INTRODUCTION

The goal of this program entails identifying, and recommending an environmentally safe replacement process for removal of the protective coating systems applied to the radomes comprising the work load for the WR-ALC radome inspection and repair facility. For such a process to be viable for WR-ALC use, it must be mutually acceptable to the individual weapons systems directorates (F-15, C-130 and C-141), and to the production staff responsible for the inspection and repair of the radomes. The scope of the program also dictates that an alternative process be identified from a pool of existing coatings removal technologies. No provision has been made for the development of new technology for this application.

Weapons systems program directorate concerns are focused on the performance characteristics of the 'finished' product, i.e., no degradation of radome performance that could be attributed to the coating removal process used in the inspection/repair cycle. On the other hand, the primary requirement cited by WR-ALC production staff is that an acceptable alternative process must not impede throughput. An alternative process could adversely affect throughput in several ways. A process must remove the protective coating systems in a period of time that does not increase throughput time unsatisfactorily, and at the same time does not produce a level of substrate damage that would require additional time/manpower for repair. Furthermore, since normal inspection and repair procedures places the final radome testing at the end of the repair cycle, the potential for wasting a great deal of time and money exists if a removal process produced a form of radome damage not easily detected by visual inspection methods.

To satisfy Air Force and WR-ALC goals, the program has been structured to conduct initial evaluations of existent technologies to ascertain any feasibility for potential use as an alternative process for WR-ALC. This initial phase, feasibility testing, will serve as a screening device to truncate the process evaluation efforts down to only those processes that can satisfy WR-ALC acceptance criteria. The acceptance criteria to be applied for this purpose have been developed through cooperative efforts involving the respective WR-ALC representatives for the ALC technical/scientific functions, the individual weapons systems program directorates, and the production staff responsible for radome inspection and repair. For the purposes of the feasibility evaluations, no rankings have been assigned to the acceptance individual acceptance criterion.

The results of the feasibility evaluations will be included in considerations used to develop any recommendations for a single process for additional work. At this juncture feasibility results may be given some ranking in the process of comparing life cycle costs and tradeoffs to down select a single process for further work. This subsequent work will include process optimization, which will then be followed with more stringent testing. It is expected that WR-ALC will require more conservative, full scale radome testing to ensure that the prospective replacement process will satisfy WR-ALC requirements at the production level. The final recommendation for a possible replacement process, or for continuation of use of the current process, will be made at the conclusion of this final phase of testing.

The feasibility evaluation phase of the program is currently ongoing. This presentation will furnish the test results available at this time. Feasibility test data acquisition and compilation are expected to be completed during late 1996.

ALTERNATIVE RADOME COATING REMOVAL PROCESSES FOR EVALUATION

The feasibility evaluations encompasses light energy or ablative, pressurized water blasting (no additive), and dry abrasive media blasting processes. This selection spans a good base of existing technologies. The intent of this program is to establish the viability, or a lack of viability, of these different types of processes at their current stage, and as regards this particular application.

The ablative methods under evaluation include pulsed CO_2 laser stripping, and pulsed high intensity UV light, used in conjunction with CO_2 pellet cleaning. Each of these processes use some form of an automated, or semi-automated system for application of the process, which provides precise process parameter control. The primary advantage of this form of coating removal is a predictable, repeatable stripping process, which inherently offers the capability to selectively strip coatings systems on the basis of applied energy. The applied energy may be controlled by such process parameters as pulse frequency, pulse duration, controlled traverse rate, etc.

The water blasting techniques being evaluated include various nozzle designs, in conjunction with various water blast pressures and flow rates. The foundation for this portion of the program is the water blasting process currently used for the majority of aircraft and off-aircraft parts stripped by WR-ALC. The system in use has a nominal blast pressure of 15,000 psi, a flow of 3.2 g.p.m., an abrasive additive, and in most applications, a proprietary 7 degree fan nozzle. However, the use of this process for the applications of interest to this program dictates that no abrasive additive be used in the blast stream. Other fan nozzle geometries and rotating water jets (multiple) are also being evaluated in this task. A radome coatings removal process based on this technology would offer the advantages of being, in essence, an adjunct to a process currently used by WR-ALC for several similar applications.

Various dry media blasting processes, based on either synthetic or biodegradable polymers, are gaining an increasing acceptance within the aerospace community for miscellaneous coatings removal applications. Several of these media are reputed to produce minimal substrate damage, and productive coating removal rates when used on metallic materials. If this attribute can be demonstrated to hold true for this study, this would be very advantageous, since the substrate materials used for testing in this program are quite susceptible to damage from all forms of coatings removal. The media selected for evaluations under this program are the following:

1) Type VI Media - A Thermoset Poly Carbonate
2) Sodium Bicarbonate
3) Wheat Starch Based Biodegradable Polymer
4) Biodegradable Starch/Acrylic Graft Polymer

TEST MATERIALS

The selection of test materials for this feasibility study was intended to represent the typical radome materials reconditioned by WR-ALC. To achieve this goal, it was determined that test samples sectioned from radomes that have seen in the field service, and therefore naturally occurring environmental conditioning, would best serve this purpose. Past experience has shown that the reaction of most coating systems to various removal processes invariably differ in a significant manner for laboratory prepared, conditioned test materials when compared to similar coating systems/materials that have been conditioned through field service exposure.

The selection of materials to provide a reasonable representation of the range of materials required by WR-ALC for the feasibility study included F-15 radome materials (2 types) and C-141 materials. Two types of radome construction are in use by the Air Force for the F-15 system. These are known as the standard construction and the Improved Construction Radome (ICR). Both are basically an epoxy/fiberglass filament wound shell, but the ICR radome adds a ± 45 degree nylon ply covering to the shell to provide structural reinforcement. The coating systems for the two types of F-15 radomes also differ significantly. The ICR coating system incorporates a thick (0.011-0.013 inch) elastomeric antistatic component, which covers the exterior surface of the radome. This coating component replaces the rain erosion rubber boot that covers the tip of the standard F-15 radome, as well as the polyurethane exterior coating found on the standard F-15 radome.

Due to limitations in acquiring complete radomes for sectioning into test panels, and the similarity in materials and structure, it was decided that either a C-130 or a C-141 radome could serve the purposes of the feasibility test work. Both types of radomes are constructed of an epoxy/fiber laminate bonded to a phenolic honeycomb core. There are some differences in construction that were not considered significant, while the issues regarding material/radome degradation possibly associated with various coating removal methods are identical. The rain erosion coating system applied to these radomes are very similar, with the exception that the C-141 radomes have a polyurethane topcoat over the polyurethane anti-static coat.

A C-141 radome and both types of F-15 radomes were provided by WR-ALC for sectioning into feasibility test panels. Measurements to determine typical coating system thicknesses and characteristics were made by cross sectioning samples at various locations for each radome. It was found by this procedure that C-141 radome had an extra application of topcoat, thought to have been added sometime by a field operation. It was believed that this would produce conservative, but realistic testing on the basis of the C-141 materials. Observations made during feasibility testing were consistent with the above findings. Typical dry film thickness measurements by coating system component for each radome are as follows:

<u>F-15 ICR</u>
Primer Coat - 0.00059 inch
Polyurethane Rain Erosion Coat - 0.00591 inch
Fluoroelastomer Tie Coat - 0.00079 inch
Fluoroelastomer Anti-Static Topcoat - 0.00197 inch

<u>F-15 Standard Construction</u>
Polyurethane Tracer Coat - 0.00078 inch
Polyurethane Topcoat - 0.00177 inch

C-141
Wash Primer - 0.00079 inch
Polyurethane Coat - 0.00079 inch
Polyurethane Rain Erosion Coat - 0.00630 inch
Polyurethane Anti-Static Coat - 0.00394 inch
Epoxy Tie Coat - 0.00039 inch
Polyurethane Topcoat - 0.00197 inch.

FEASIBILITY TEST PROTOCOL

The intent of feasibility testing is an assessment of the ability of several prospective removal methods to effectively remove the coating systems from radome materials reconditioned by WR-ALC. Effective coatings removal is defined as removal of a given coating system to a designated level of removal consistent with current WR-ALC preparation methods. In general, this is a point at which at least a discernable trace of the primer system remains intact. The coating removal rate (strip rate) is determined on the basis of achieving this goal. Coatings removal rates are measured as area stripped (ft^2) versus the elapsed time (minutes) required to effectively strip that area.

Several types of substrate inspections may be used, as appropriate, to a given removal process in establishing material conditions. These information provided by these inspections have been used to determine possible detrimental changes to the substrate materials following, or during application of prospective removal processes, and as would be applicable to assess process feasibility. A more thorough evaluation focusing on a single prospective process will be conducted in a subsequent phase of this program to fully assess possible substrate damage per WR-ALC criteria.

The principal assessment that will be used to determine process feasibility will be the evaluation of possible process related effects upon the dielectric properties of suitable radome test samples following application of a given coating removal process. The other inspection methods/procedures cited in this protocol may be considered to be ancillary to the performance characterization based on dielectric properties, but the nature of these inspection methods are such that their results can provide immediate feedback during testing in the field.

The inspection methods/procedures that may be used in conducting the feasibility testing include the following:

1) Radome performance characterization have been established for baseline materials, and will be re-evaluated as necessary after coatings removal to assess any potential to degrade radome performance. The dielectric parameter to be measured will be phase shift at experimentally determined frequencies. A minimum of 5 locations are measured per dielectric test specimen to provide sound characterization for each process tested. The basic technical approach for these measurements uses a shorted waveguide technique commonly used in the industry for radio frequency measurements.

2) Surface roughness measurements are conducted per the *Draft Air Force Guidance Specification for Coatings/Paint Removal Techniques*. Surface profile measurements are made on the test materials after application of prospective removal processes as an indication of possible substrate damage or resin erosion. Measurements are made at a minimum of five locations to attain good characterization of the resultant surface profile.

3) As appropriate, water intrusion into the honeycomb core of radome structures is determined using procedures specified by T.O. 1-1-24. A moisture meter that is qualified to T.O. 1-1-24 is used for these measurements. Moisture detection measurements are

made over the entire surface of a given test piece (6-inch x 6-inch minimum) to ascertain any water entrapment or intrusion. These measurements are made before and after coating removal.

4) Visual and microscopic inspections to characterize test material surfaces have been made throughout feasibility testing.

FEASIBILITY ACCEPTANCE CRITERIA

The criteria that will be applied to determine acceptance or rejection of a given process, or set of process parameters, are as follows:

1) An effective coating strip rate of 0.75 ft^2/minute will be considered the minimum acceptable removal rate

2) Water entrapment or intrusion will be evaluated per current WR-ALC standards, which specify that a maximum reading of 5, as determined by a qualified moisture meter, is allowable.

3) The criterion that will be applied to assess acceptable surface roughness is that the average roughness, R_a, must be greater than 20 μinches and less than 200 μinches.

4) The radome dielectric transmission characteristics (phase shift) have been established with bench top testing using test samples representing each radome material included in the feasibility testing. These samples have been/will be measured with the as-received coating system intact. The transmission measurements are over a range of 8 to 12 GHz. As appropriate, the original samples will be measured after the coating system has been removed, and after a duplicate coating system is re-applied. Any change in phase shift will be documented and presented to the appropriate WR-ALC technical representative for review.

The minimum acceptable effective removal rate cited by this protocol translates into approximately 2 hours of continuous stripping for a C-141 radome. This estimate *does not* include any considerations for staging, process setup/preparation, radome handling/fixturing, etcetera. The surface roughness acceptance range is bounded by a minimum R_a value consistent with measurements from F-15 radomes immediately prior to coatings application, and the maximum R_a value cited is slightly less than maximum R_a values measured on F-15 radomes chemically stripped by WR-ALC. The maximum R_a measurements were made following chemical stripping, and before any touch up sanding or sealer materials were applied.

INTERIM FEASIBILITY TEST RESULTS

The feasibility test phase of this program is on-going, therefore much of the test data (unless noted otherwise) is in the process of being acquired and/or compiled. Most of the feasibility testing has relied on technical support given (please see Acknowledgments) by various proprietary interests affiliated with several of the processes under assessment. All final feasibility data, plus much of the preliminary data, have been developed in cooperation with Battelle, and all data used to assess feasibility have been or will be documented by Battelle. The available feasibility data are given in Table 1, and a brief discussion of these data follows. No dielectric test data are available for any of the prospective processes. The final dielectric measurements and data analysis will be conducted in association with only those processes that have demonstrated compliance with the preceding acceptance criteria.

The data developed from the UV light ablative method testing presented in Table 1 gives the range of strip rates and R_a from lowest to highest. The strip rate results produced by this process are lower for the C-141 and F-15 ICR materials, but this is not unusual when the thickness and material characteristics of the coatings systems for the

materials are considered. The order of the R_a data is reversed, as the surface on the standard F-15 materials had the lowest average roughness measurements following coatings removal with this process. There were no chemically stripped F-15 ICR materials available for baseline surface roughness measurements at the time the feasibility data were developed. Therefore, it is not possible to compare the surface profile for this substrate material after stripping with this process (or any of the other processes) with the profile produced by the chemical stripping process used by WR-ALC for this material. The appearance of the stripped surface is such that it is believed that no substrate damage occurred. It is also believed that some portion of the surface profile was attributable to the original surface condition, and was not entirely produced by this process.

All of the feasibility test results to date place this process within the limits established by the acceptance criteria developed in this program. As was noted in Table 1, the optimal strip rate was achieved with a relatively flat surface, which maximizes the UV exposure footprint (approximately 11 inches wide). If the contour changes rapidly, the effective footprint falls off rapidly dependent on the flash head orientation. The strip rates cited for the C-141 and F-15 ICR tests are on the basis of 6 cycles to attain sufficient coatings removal. Complete stripping was achieved on the standard F-15 sample with one cycle. Selectively stripping of individual components of a coating system can be achieved by controlling the UV flash frequency, the input power to the UV flash power supply, and traverse rate. In the case of the C-141 and F-15 ICR materials, the toughness of these coating systems meant that selective stripping was the only mode possible since the unit was operating at maximum power and flash frequency.

Table 1. Feasibility Test Data

PROCESS	STRIP RATES, ft^2/min	SURFACE CONDITION	R_a, μinches	COMMENTS
Ablative Methods				
High Intensity UV*	0.77 to 4.58	Good to Acceptable	75.6 to 197.9	Strip Rates are Contour Dependent
Pulsed CO_2	N/A	N/A	N/A	No data available
Water Blast Methods				
Fan @ 15 ksi	0.63 to 1.0	Fair to Unacceptable	N/A	Narrow Window of Parameters
Rotary 8 to 14 ksi	0.42	Fair to Unacceptable	N/A	Narrow Window of Parameters
Dry Media Methods				
Type VI Media*	0.12 to 0.61	Fair	322.1 to 428.5	Operator Dependent
Sodium Bicarbonate	N/A	N/A	N/A	No data available
Wheat Starch Media	N/A	N/A	N/A	No data available
Co-polymer	0.28 to 0.49	Fair	202.7 to 326.7	ICR Data N/A, Operator Dependent

* - Final Data Set

The strip rate results associated with the water blast methods evaluated follow similar trends to the ablative strip rate data. The coating systems on the F-15 ICR and C-141 materials appear to be more resistive to removal by the water blast methods, and this is consistent with the character of these coating systems. The strip rates reported in the preliminary data are close to acceptable, but the potential for substrate damage resulting from these removal rates is marginal. It is thought that the water blast processes do not offer a wide enough margin of acceptable process parameters. The band of possibly acceptable process parameters allows for no deviation form prescribed process parameters, nor variations in the condition of the substrate being stripped.

As may be seen in Table 1, approximately 50 percent of the dry media testing remains to be completed. The data that are available appears to indicate that, overall, the dry media produce lower strip rates. It should be noted that the testing conducted with the methods documented in this paper were applied in a manual mode, which may not be the most efficient means of applying these processes. Any direct comparisons of strip rate data with a semi or fully automated process should be somewhat tempered since it is not known if application of these processes by other means would produce an improvement. The dry media processes that remain to be tested are expected to be tested with some means of mechanical process control and manipulation, therefore it is hoped that this test work may provide further insight into this issue.

The nozzles used in the evaluations of the processes being discussed here were ½ inch diameter double venturi. It is thought that a nozzle designed specifically for a given media could produce a significant process improvement. This is another issue that may be resolved with the remaining evaluations, since it is anticipated that both processes will be utilizing such a nozzle design.

The strip rate data trends observed with the dry media processes are similar to those seen with the ablative and water blast processes. The R_a values associated with the dry media may tend to be exacerbated by the mode of stripping typical to the dry media processes evaluated. The tougher coating systems required longer dwell, or blast exposure, which in turn can create an increased potential for substrate damage since the operator(s) tend to remove all of the coating in a single cycle. Another way of stating this, is that manual application of these processes relied on more operator skill and acumen than may be required for a process that can be adapted to a semi or fully automated application.

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The Effects of Long Term Cure on Offgassed Products of Coatings

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Abstract

The Environmental Chemistry and Compatability Team at The Marshall Space Flight Center conducts toxic offgassing analysis on materials and flight hardware for use in habitable environments aboard the Space Shuttle and the International Space Station. As part of Research and Development, the Toxic Offgassing Laboratory conducted a long term cure study on four polyurethane coatings which are slated for potential use on Space Station (see list below). This study demonstrates the effects of cure time and temperature on the total tox value (sum T) and the maximum usage weight for each coating. All analysis was conducted according to test procedures outlined specifically for Space Station environments. Therefore, the ratings and weight limits generated for these materials are most applicable to space environments. However, this test does give some indication of time frames for solvent removal and is therefore of interest to the environmental community as a whole.

Coating	Composition
Chemglaze Z352	Polyurethane
Conathane CE-1155	Polyurethane
512 X 310/910 X 533 Primer w/821 X 817 Topcoat	Polyurethane
03-W-182 White Semi-Gloss	Polyurethane w/Aliphatic Isocyanate

Introduction

Before use in a habitable environment, all materials must be tested per NHB 8060.1C test 7 for potential offgassed products. This involves a bake period in which the sample material is sealed into a chamber (in this case a 4 liter volume chamber) and held at 120° F for 72 hours. After completion of the 72 hours, the chambers are allowed to cool to ambient temperature and gas samples are then pulled through a septum in the chamber and analyzed by Gas Chromatography and Mass Spectrometry. Individual organic compounds are identified and quantified. Each component amount is then applied a Space Maximum Allowable Concentration (SMAC) value which is assigned by toxicologists at Johnson Space Center (JSC) using Threshold Limit Values (TLV). A SMAC value is the maximum concentration of that compound which is allowed in the habitable areas of the spacecraft for a specified flight duration. A subsequent

calculation using the SMAC value and the offgassed quantity of the compound determines the T (Toxic Hazard Index) value for that component (Table 1). All component T values are then summed for that particular material giving an overall sumT for the material, the total T value for 100 pounds of material. This T value determines the Maximum Limit Weight (MLW) that can be used for that material. Materials are then rated according to the MLW (Table 2).

Toxicity Calculation

TX1 = Offgassed amount of each gas in μg/g of material
TX2 = Offgassed amount in mg/m
SMAC = Space maximum allowable concentration in mg/m (JSC limit)
TC = T value of each component gas
SumT = Total T value for 100 pounds of material. Add all TC values.
ML WT = Maximum limit weight in pounds of material

TX2 = TX1 x .3845 *

TC = TX2/SMAC

Sum T = sum of TC values for all components

ML WT = 0.5/T100 x 100 lbs

*.3845 is a conversion factor related to the volume of Space Station. It's derivation involves units which allow the conversion of TX1 to units of mg/m .

Table 1

RATING	ML WT
K	100 lbs and greater
H	50 lbs - 99.999 lbs
A	10 lbs - 49.999 lbs
V	5 lbs - 9.999 lbs
X	0 lbs - 4.999 lbs

Table 2

In preparation for the test, each coating was applied to an aluminum substrate in thicknesses designated for use by the manufacturer. Duplicate coated panels sized 4"x 7" were prepared until a sample weight of approximately 20.0 grams was obtained. This is in accordance with NHB 8060.1C test 7 section 4.7.5. The coatings were then tested according to the aforementioned procedure with ambient open air cure times of 1-2 months in between test periods. Every test for each individual coating has an associated cure that reflects all previously accumulated test times and temperature as well as the ambient cure times. This specific cure data, though not provided in this report, is part of a permanent database of materials test information, The Materials and Processes Technical Information System (MAPTIS). Test dates supplied represent the beginning of the 72 hr bake period at the end of which begins an ambient cure. Table 3 provides the results of the individual tests for each coating.

		Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Chemglaze Z352	Date	1/27/95	3/6/95	4/17/95	5/23/95	7/25/95	9/20/95	11/3/95	1/16/96
	T100	29.7523	22.4048	15.0236	6.4829	2.5232	2.9255	3.1825	1.131
	MLW (lbs)	1.6805	2.2317	3.3281	7.71254	19.8155	17.0906	15.7109	44.2085
	Max Sq ft	130.156	172.840	257.756	597.326	1534.6841	1323.649	1216.789	3423.879
	Rating	X	X	X	V	A	A	A	A
Conathane CE-1155	Date	3/6/95	4/17/95	5/23/95	7/25/95	9/20/95	11/3/95	1/16/96	
	T100	99.1939	71.5532	64.4435	29.8226	19.1019	17.2637	11.8996	
	MLW (lbs)	.5041	.6988	.7758	1.6765	2.6175	2.8962	4.2018	
	Max Sq ft	25.8175	35.7907	39.7393	85.8724	134.067	148.4405	215.2368	
	Rating	X	X	X	X	X	X	X	
512x310/910x533 Primer 821x817 Topcoat	Date	6/20/94	4/18/95	5/23/95	7/25/95	9/20/95	11/3/95	1/16/96	
	T100	18.5214	7.9234	9.5969	2.6057	2.2691	3.1977	2.6134	
	MLW (lbs)	2.6996	6.3104	5.2100	19.1891	22.0344	15.6359	19.1322	
	Max Sq ft	108.808	245.343	209.990	773.4201	888.1024	630.2092	771.1267	
	Rating	X	V	V	A	A	A	A	
03-W-182 White Semi-Gloss	Date	7/21/95	9/20/95	11/3/95	1/16/96				
	T100	49.7800	37.2989	16.8414	11.6342				
	MLW (lbs)	.1202	1.3405	2.9688	4.2976				
	Max Sq ft	1.3673	15.2382	33.7484	48.8534				
	Rating	X	X	X	X				

Table 3

Discussion

Most resins used as media for paints are either solids or highly viscous materials which must be diluted with a liquid to lower viscosity to allow application to a substrate. In practical paints, this liquid is usually a mixture of solvents. Different solvent mixtures may be used to control evaporation, flash point, cost, or to reduce health risks (Marrion).

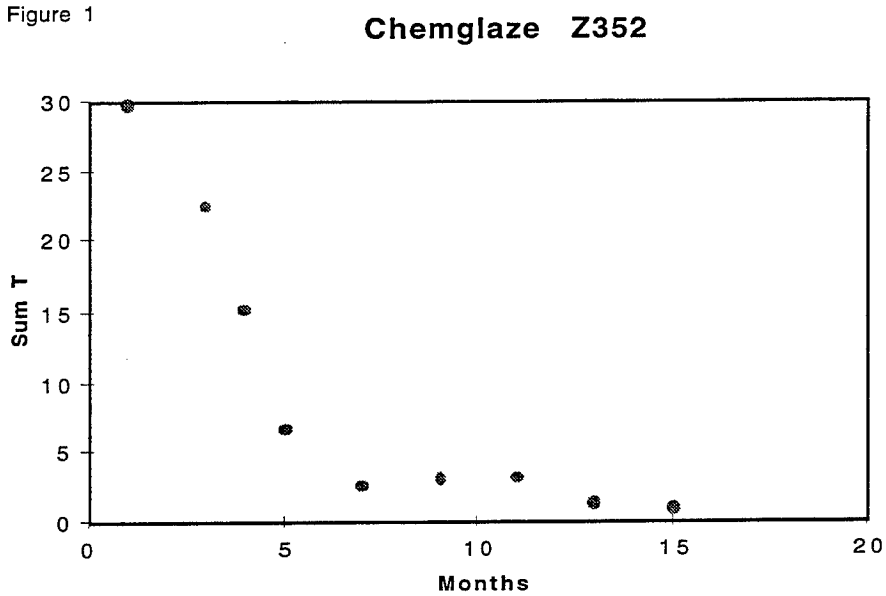
In this study, the offgassed components detected were consistent with typical solvents used for paint resins (Marrion). They are low molecular weight aliphatic, aromatic or oxygenated organic compounds. Aromatic solvents were found in abundance in all coatings. These included xylene mixtures, toluene, and substituted benzenes such as cumene and trimethyl benzenes. Some common oxygenated solvents were: Alcohols - methanol, ethanol, isopropyl alcohol and isobutanol. Ketones - acetone, methylethyl ketone, isobutyl ketone. Esters - butyl acetate, propyl acetate, and methoxyethyl acetate.

Film formation is an important step in any coating process. That is, the conversion of the coating from a liquid state to a solid after application. Film formation in crosslinking polymers involves chemical reactions between functional groups on polymeric species accompanied by the evaporation of solvent. This evaporation is initally dependent upon the vapor pressures of the solvents, how quickly the solvent is removed from the immediate environment, and the ratio of surface area to volume of coating (Marrion). Evaporation rates of individual solvents at room temperature are available. These solvents are often rated using butyl acetate as a reference. Coatings, however, employ the use of a mixture of solvents. The evaporation rates of these mixtures cannot be predicted from the rates of the individual solvents since attractive forces between molecules and attraction for the forming polymer itself will vary from mixture to mixture and can delay evaporation(Turner). As crosslinking progresses and a polymer film is formed, solvent will be retained within the film and any subsequent solvent loss will become a diffusion-controlled, slow process. As much as 20% of the solvent may still be retained when this latter stage is in progress (Lambourne). If the final glass transition temperature is above the film formation or 'touch dry' temperature, the rate of diffusion can be significantly lower as is the case with glassy coatings. These coatings can retain large amounts of solvent for long periods of time(Marrion).

In this study, initial testing of the coatings showed a consistent decline in offgassed products from evaporation of solvent (Table 3). By tests 6 and 7 there was some fluctuation of the Sum T in three of the coatings. These fluctuations in solvent evaporation could be expected due to film formation and polymerization which tend to impede solvent diffusion. In addition, this offgassing at elevated temperature takes place in a sealed environment, hence there is no solvent removal from the immediate environment. Also, once the chamber is cooled to ambient temperature, as required by NHB 8060.1C, some offgassed constituents may condense to the walls of the chamber or onto the coating surface. In the event of the later, an increase in offgassed amounts could be expected in subsequent testing.

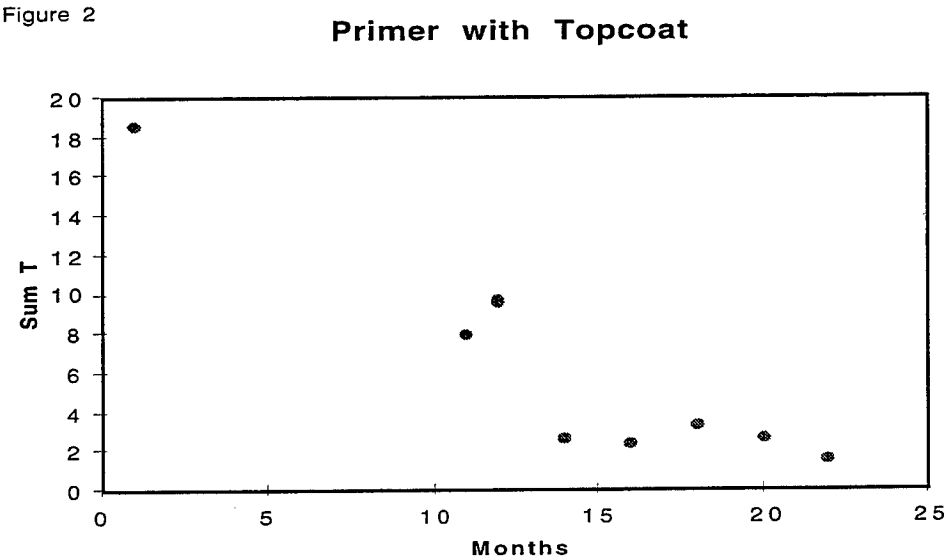
Figure 1 demonstrates changes in the Sum T of Chemglaze Z352 during a series of nine tests over a period of 15 months. Each point represents a test run which constitutes 72 hours at 120° F. The time in between represents an ambient cure. The initial decrease in the Sum T is due to the loss of xylenes and Methyl Isobutyl Ketone. The bulk of these solvents were removed by test 5 after 6 months of alternating ambient cures and exposure to test temperatures. It received an A rating with test 5. Slight increases in Sum T seen in tests 6 and 7 could be due to solvent retention within the polymer which finally surfaced in these tests.

Figure 1



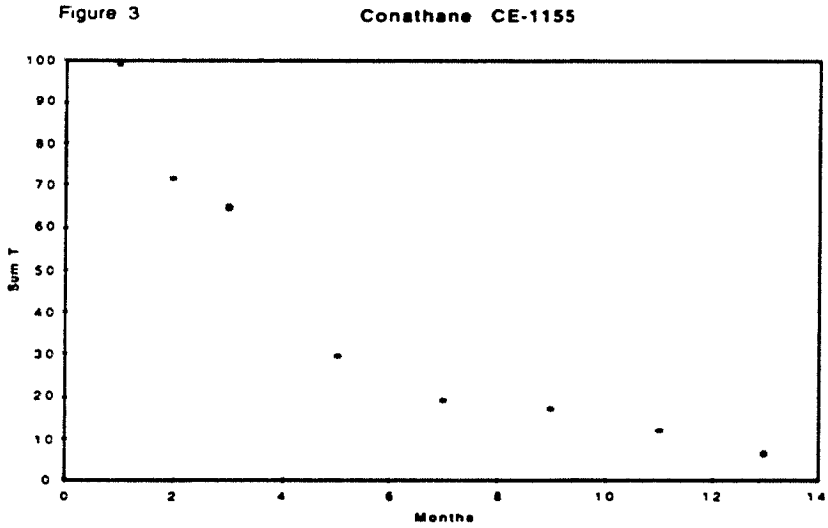
The primer with polyurethane topcoat (Figure 2) received an extended ambient cure of 10 months before it was retested. The initial decrease in Sum T in test 2 was followed by an increase in test 3. Again, this could be due to retained solvent within the polymer which was mobilized by the higher temperatures of test 2 and finally surfaced in test 3. Following test 3, the Sum T dropped sharply and leveled out for the most part with only slight fluctuations in subsequent tests. It received an A rating with test 4.

Figure 2



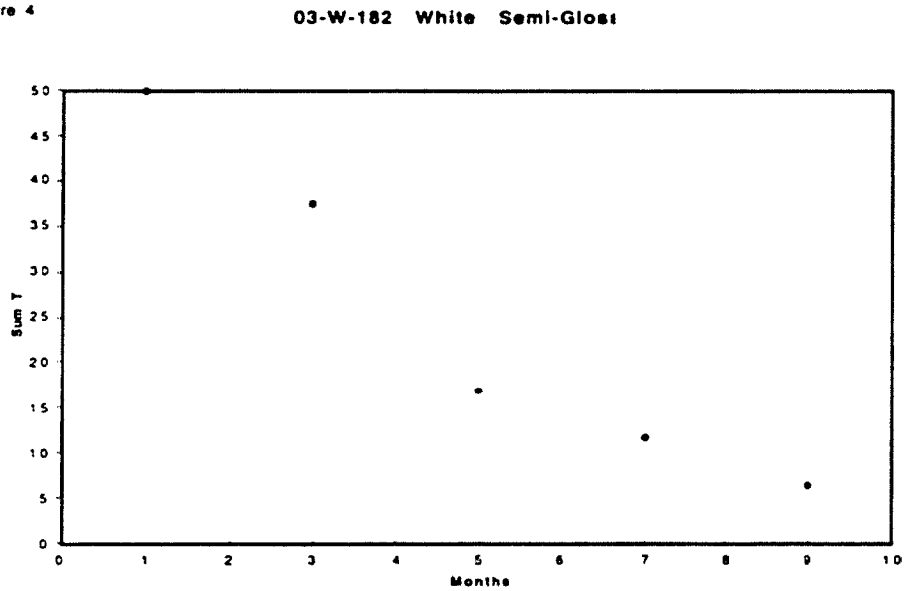
Conathane CE-1155 (Figure 3) started with a much higher SumT and maintained a poor rating because of a constituent which is particularly resistent to cure. Along with xylenes, 2-Methoxyethyl acetate was found in abundance in this coating. It has a low vapor pressure of 2.0 mm Hg at ambient temperature. This compound also has a low SMAC value of 4.8 indicating a higher toxicity. Although it showed consistent improvement, this coating maintained an X rating after almost a year, which included 7 test runs.

Figure 3



03-W-182 White Semi-gloss (Figure 4) has had limited testing at this point. Tests 1 through 5 have demonstrated a consistent decline in offgassed products, with the loss of solvents such as Methy Ethyl Ketone and Methyl Isobutyl Ketone. As is the case with Conathane CE-1155, this coating also contains a solvent, 4-methyl-3-pentenal, which has a low SMAC value of 4. Although loss of ketone solvents has been sufficient to lower the Sum T value to obtain a V rating, substantial loss of 4-methyl-3-pentenal will be necessary to significantly improve the rating. As mentioned earlier, glassy coatings such as this may have a lower rate of diffusion and therefore retain solvents for long periods of time.

Figure 4



It is important to mention here the use of default SMAC values. While most compounds have been assigned permanent SMAC values by JSC toxicologists, other less familiar components have not been sufficiently researched and therefore have a worst case scenario SMAC value which is 0.1. While this measure is neccessary to insure the safety of the crew, it sometimes allows a small quantity of solvent to greatly affect the maximum usage weight of a material. As Table 4 below demonstrates, any amount over 0.14 ug/g will give a Sum T over 0.5 when a default SMAC is used. This will automatically drop the usage weight of a material below 100 lbs.

The Affect of Default SMAC Values

0.14 ug/g x .3845 = 0.05 mg/m
0.05/0.1 = 0.5 T value
0.5/0.5 x 100 lbs = 100 lbs MLW

With a 0.1 default SMAC value, amounts over 0.14 ug/g will give a Sum T over 0.5 and a rating below K

Table 4

Conclusions

While exposure to elevated temperature certainly accelerates the curing process, particularly lengthy cure times are needed for sufficient removal of solvents to meet the stringent requirements of NHB 8060.1C. Depending on how much of the coating is to be used, however, lower maximum usage weights may be acceptable for some coatings and the assignment of a K rating unnecessary. Actual cure times needed for an acceptable rating will vary with every coating depending upon the components identified. Materials containing solvents with low rates of evaporation coupled with low or default SMAC values may require exceptionally long cures as is the case with Conathane CE-1155. Coatings of this nature will require repeated cures, retests and perhaps an extended, elevated temperature cure. Since solvent loss eventually becomes a slow, diffusion-controlled process, prediction of the actual cure time needed is difficult. Offgassing as conducted in this study does not demonstrate a consistent decline in offgassed products as seen by the fluctuating Sum T values. While much of this may be attributed to the nature of the curing polymers themselves, it also may be due in part to the test procedures employed by NHB 8060.1C. The sealed chambers required for this test are necessary to allow the sampling of the offgassed constituents. This closed environment can hinder the further loss of solvent. This approach to curing is an unusual circumstance since typical curing procedures leave the curing article open in a vented oven. Furthermore, the stabilization of the chamber at ambient temperature prior to analysis can lead to condensation within the chamber as well as on the sample itself. This could also cause fluctuations in offgassed amounts.

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CST ™ SPRAY PROCESS FOR ENVIRONMENTALLY FRIENDLY COATINGS

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ABSTRACT

Conventional spray application processes have poor transfer efficiencies, resulting in extraordinary loss in materials, solvents, and time. With increasing restrictive Environmental Protection Agency (EPA) regulations and Occupational Safety and Health Administration(OSHA) requirements, these processes which significantly impact the amount of materials and solvents that are released into the environment are becoming unacceptable. High solids spray processes are also limited by material viscosity, and may require many passes over the surface to achieve desired thickness which results in high application costs and a negative impact on the environment.

Until recently, requirements for a 100% solid sprayable, environmentally friendly, lightweight thermal protection system that can be applied in a thick (>0.125 inch) single-pass operation exceeded the capability of existing systems. Such coatings have been typically applied by hand lay-up techniques, especially for thermal and/or fire protection systems.

The current formulation of these coatings presents many potential issues including, environmental hazards, excessive waste, high cost, and application constraints. A system that can apply coatings without using hazardous materials would alleviate many of these issues.

Potential applications include the aerospace thermal protective specialty coatings and chemical and petroleum industries fire-protection coatings that resist impact, chemicals, and weather. These markets can be penetrated by offering customized coatings applied by automated processes that are environmentally friendly.

INTRODUCTION

Currently EPA is implementing regulations and performing studies to meet standards set by the Congress in the Clean Air Act Amendments (CAAA) of 1990. EPA is proposing new Control Techniques guidelines (CTG's), developing regulations to limit emissions of toxic air pollutants through two programs, National Emission Standards for Hazardous Air Pollutants (NESHAP's) and Hazardous Air Pollutants (HAP's).

Certain low-usage coatings were not addressed in the NESHAP. These include adhesives, sealants, and thirty types of specialty coatings that represent less than 6 percent of the total HAP emissions from the industry. Also, the EPA data analyses indicate that the maximum achievable control technology (MACT) floor for these coatings would be no control. The EPA is now requesting public comment on the need for a separate CTG providing guidance for the control of these types of coatings.

The overall objectives of the convergent spray project are to develop and demonstrate a convergent spraying process capable of applying successfully a variety of high-solid coatings. Specific objectives are:

- To develop a solventless, zero-content volatile organic compound (VOC) Convergent Spray Technology (CST) to meet proposed EPA regulations

- To improve the transfer efficiencies of high-solids coating formulations, and

- To increase the application thickness per pass while maintaining the surface properties and coating characteristics.

- To minimize waste through unique processing.

This project focuses on developing a state-of-the-art high-solids formulation and its associated application processes for thermal protection materials, insulative and structural restoration coatings. Work to date has centered on improving process characteristics while reducing costs and associated potential hazards.

SYSTEM DESIGN FOR ENVIRONMENTAL REGULATIONS

In order to address environmental issues such as reducing VOC's and, waste minimization a CST (spray on demand) process system was designed to meet the challenges of the 1990's for specialty coating applications. Batch processing and associated wastes with pots and material transfer lines should be significantly eliminated along with the associated costs of material wasted due to equipment failures. After each spray application is completed the end

effector's resin mix system is purged with some 200-300 ml of environmentally acceptable cleaner. Resin and solid filler transfer lines are not purged because there is no mixed materials in the lines. This reduces process waste to a minimum, whether coatings are applied to large or small parts of any configuration.

The ergonomic design of the system also allows for efficient use and experimentation. Simple change out of resin materials, fillers and with changes in material flows can lead to new coating development and optimized performance.

The spray on demand design also allows for more complex application techniques to be used that reduce manual or hand close-out of more complex hardware configurations.

BASIC CST ™ ROBOTIC SYSTEM

The CST spray process causes mixed resins to be sprayed and entrained with solid filler materials external to the spray end effector to form a coherent coating material. See Figure 1

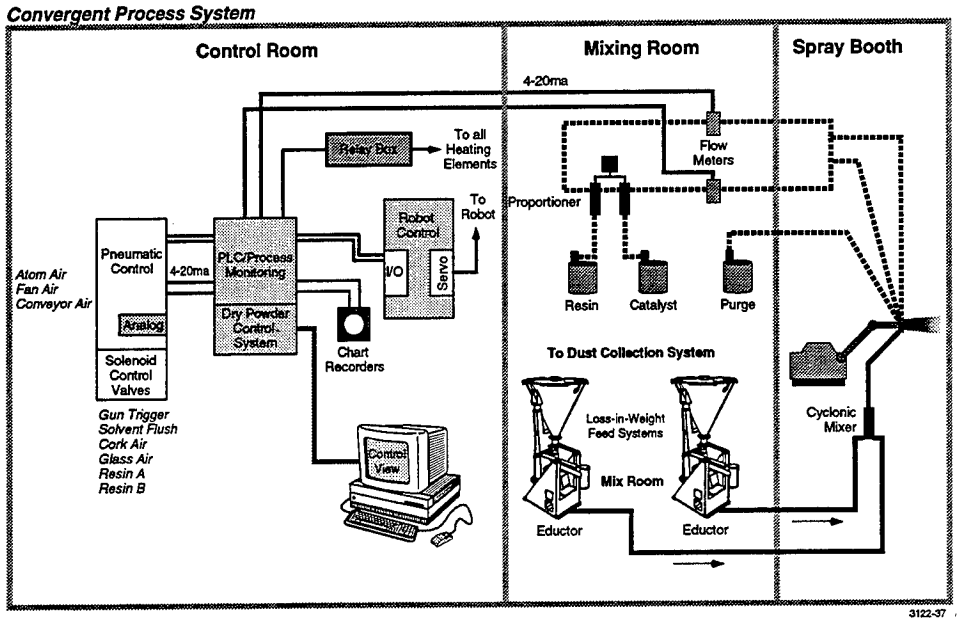

Figure 1. Schematic of CST ™ spray system. (3122-37)

Two fluid transfer systems supply the end effector with the resin polymer components while separately maintaining proportional flow.

Two vibratory loss-in-weight units pneumatically feed a constant and continuous stream of glass spheres and cork granules to a cyclonic mixer which then feeds the end effector. Although they are solid, the eccospheres and cork flow much like a fluid.

The CST spray end effector design consists of a spray head that mixes and atomizes the epoxy components and a larger surrounding shroud, that carries the glass/cork mixture. The resin/cork/glass sphere mixture is deposited on the substrate. The resulting high viscosity coating can be applied to vertical surfaces without slumping.

CST APPLICATIONS

Thermal Protection for SRB

A well known two-part room temperature or heat-cure epoxy, was selected because it is a familiar adhesive used in the NASA Space Shuttle solid rocket booster (SRB) thermal protection system. It has excellent mechanical property characteristics. Granular cork and glass microspheres were selected as the dry system materials.

Tests of coatings comprised of epoxy clear resin, granular cork, and glass eccospheres showed the best mix is 75 to 80 percent resin and 20 to 25 percent cork and glass eccospheres. Densities ranged from 30 to 35 lbs/ft^3 and flatwise tensile strength measured from 150-400 pounds per square inch. Adding catalyst was shown be an efficient way to speed the cure of the epoxy resin with no adverse effects.

In 1993, a production prototype system was installed in Marshall Space Flight Center's Productivity Enhancement Laboratory (building 4707) for detailed assessment and evaluation of the USBI IR&D developed thermal protection coating(TPS), USI.

Equipment was procured and facilities modified to accommodate the prototype system . Programmable logic controller and host communications programs were developed to control the system. A spray test program was executed to produce test panels and demonstrate the end effector. As a result, USBI'S CST spray process and TPS coating formulation were selected (January 94) for qualification as NASA's next generation thermal protection coating for the Solid Rocket Booster (SRB).

In 1993, USBI Materials and Processes (using internal IR&D funding) designed, fabricated and tested a more efficient convergent spray end effector. Improvements in the wet resin spray system were also developed. This new design was successfully tested in USBI's labs. The coatings also performed well in aerodynamic heating tests which characterize the coatings ability to withstand aeroshear launch environments.

We also demonstrated that the coating will adhere to complex geometries such as stringers, risers, and bolt heads protruding from a structure.

Other lower recession formulations are being developed including a higher temperature epoxy formulation which will potentially enhance insulation characteristics.

Finally, the EPA toxic characteristic leaching procedure indicates heavy metal concentrations are well below acceptable limits, thus allowing cured material in a city landfill as non-regulated waste.

OTHER POTENTIAL CST COATINGS

Silicone Thermal Protection Coatings

Recycled rubber coatings

Filled Foams Coatings

High Solids, Skid Resistant coatings

Decorative architectural coatings

Zinc- Rich, Corrosion Prevention Coatings

With the advent of increased processability and a wide selection of polymer resin systems such as epoxies, urethanes, acrylics, and polyesters, potentially new high solids coatings for use as structural, architectural and protective applications can now be pursued. The capability of CST spray process to use inexpensive filler can reduce cost of coating materials.

Unsaturated polyester resins convergently combined with traditional aggregate materials can be used as a low cost polymer concrete for resurfacing of highways and or support structures. Polyesters offer longer endurance, skid resistance and short cure times. New ultraviolet cure polyester resin systems eliminate complicated catalyst addition metering and improve processing for highway application.

CST CONTROL SYSTEMS DEVELOPMENT

Development of the convergent spray system for Thermal Protection involved a wet side (resin) and a dry side (granular cork). The feed and control integrity of each side of the materials delivery system is crucial to ensure an accurate spray and mixing of the applied coating.

The Spray On-Demand design of CST spray process puts more emphasis on process control in materials coatings design. It also provides the understanding and knowledge in what's occurring in different areas of the process. It allows the user to take a step back, look at the big picture and divide the process into modules. The control system can be designed from the top down and implemented and tested from the bottom up ensuring the operational requirements of total quality management are satisfied.(TQM)

Object-oriented control systems and program logic control software (PLC) systems are being used on CST spray systems. These control systems integrate data acquisition, supervisory control and management information functions and create a single graphic window into the whole process. In addition, these systems perform alarming, trending and event detection.

A portable cart system is being developed to address less critical more commercially applicable coatings such as for floors, roofs, etc. This manually-operated system will avoid the major cost associated with software control and PLC design.

SUMMARY

The new CST spray process that eliminates volatile, environmentally hazardous solvents has been demonstrated and selected as a the next Thermal Protection Coatings process to be used on both the Solid Rocket Boosters (SRB's) on NASA's Space Shuttle and the Air Force Titan launch vehicles.

ENVIRONMENTAL INFORMATION TECHNOLOGY

Air Force Aeronautical Systems Center Hazardous Materials Alternatives Guide: A Creative Way to Better Exchange Information

Presented at the Second Conference on Aerospace Environmental Technology
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Abstract

This paper describes the results of work at Aeronautical Systems Center to develop more effective and easier to use ways to exchange technical and project information dealing with hazardous materials alternatives. The paper will discuss the background of the ASC technical effort and describe the features and content of the ASC Guide as it now resides on the Internet. It will also convey thoughts on future use and development of the resource.

Introduction

The Aeronautical Systems Center Acquisition Environmental Management Office (ASC/EM) prepared the original version of a Hazardous Materials Alternatives Guide in 1993 as a handbook for use within the ASC community. (The expression "ASC community" is used in this paper is in the same sense that USEPA uses when it talks about "the regulated community".) The ASC community consists of all the technical and managerial people engaged in aeronautical weapon system development and acquisition. The community also includes owners and operators of all facilities that support these systems during their life cycle. These facilities may be government or contractor owned and government or contractor operated. The ASC community also includes research and development support organizations like Wright Laboratory. An example of the support activities of Wright Laboratory is the development of the ASC Hazardous Materials Alternatives Guide.

The Air Force Aeronautical Systems Center (ASC) is one of the Air Force Materiel Command (AFMC) acquisition centers. Other AFMC centers are the Space and Missile Center and the Electronic Systems Center. ASC is responsible for developing and acquiring aeronautical systems for the Air Force. Major programs include the F-16, F-22 and B-2 weapon systems. Program management at ASC and the other AFMC centers is performed by System Program Offices or SPOs. After weapon systems are deployed, the AFMC Air Logistics Centers take over logistics management and depot level maintenance of the mature systems. Although this paper takes the perspective of Aeronautical Systems Center programs, the relationship between the ASC program and those of other Centers is very close. Like ASC, their collective missions are sustained by support in the environmental science and technology areas from activities such as

Wright Laboratory, Human Services Center (HSC) and the Air Force Center for Environmental Excellence (AFCEE).

Within ASC, the Acquisition Environmental Management Directorate (ASC/EM), provides environmental policy and technical support to the management, engineering, and other elements of the SPOs. The framework for this support is the ASC Acquisition Pollution Prevention Program. As mentioned earlier Wright Laboratory, provides research support in the areas of materials science and engineering to this program and to the engineering elements of the SPOs. This support is sustained by a coalition of in house and collocated scientists and engineers and support contractors.

The next important background topic is the decision making environment that the ASC Hazardous Materials Alternatives Guide ("the Guide") is intended to serve.

The first element of concern regarding hazardous materials use and generation is the process site, "the shop floor". This is where the real pressure to perform is manifested. This is also the traditional focus of compliance and enforcement activities. Of course, it should be understood that the owner or operator of a process site does not always have the power to decide to change material or process specifications related to the site. Most of the time, product managers and customers must make these decisions. In the aerospace acquisition world, changing product technical specifications to ease a hurt on the shop floor can be a very complex proposition.

On Air Force acquisition programs, major process change decisions cannot usually be made unless product changes are approved. The SPOs and other product owners for these programs are exposed to policy mandates to minimize use and generation of hazardous materials during the life cycle of the products they are responsible for. They must consider these mandates in all their activities, especially those concerning release or approval of the product specifications and proposals to changes to processes at the various process sites. This process can be more complicated than it first appears because system products may be manufactured, operated and maintained at facilities located in different compliance jurisdictions. When this occurs, product and site owners must find more than one acceptable material or process alternative to the same hazardous material use. Finally, it is important to understand that the integrity of military systems capabilities depends very strongly upon careful documentation of product and process changes and their linkage to system operation maintenance and remanufacturing via technical orders (T.O.s) and other process and product specifications.

The next important background item deals with engineering changes in Air Force system acquisition. There are two main types. Engineering changes that require customer approval are "Class I" changes. Traditionally, Class I changes affect form, fit, function, interchangeability, reliability, health, safety, or cost. Changes that affect the product in these ways require product qualification by one of the methods listed in Figure 1 below. Changes that do not significantly impact product performance criteria are referred to as Class II changes. Class II changes are normally made without customer approval. Examples of this type of change would be minor changes to process routing instructions or manufacturing methods. As emphasized earlier, changes to manufacturing methods that impact product technical orders (T.O.s) for maintenance or operation also require a change to the T.O. documentation.

Qualification of Class I changes can be a laborious and expensive process. Of the methods listed, by far the least costly method of qualification is by analysis. This method depends on test procedures and test data from prior applications to assess, by similarity, the impact of a proposed change on current or life cycle product performance. A decision is made on the basis of no impact, improved performance, or degraded performance that can be tolerated. In the context of the Guide relevance to this process, it is important to recognize that successful prior applications of a material or process change may have been tested, validated and approved by project and process owners for different systems or commodities. Qualification by analysis cannot occur if the seekers of change are unaware of the successful prior application. The primary motivation of the ASC Guide is to offer a creative way to foster exchange of information within the ASC community so that time, effort and dollars can be conserved in the systems acquisition process.

Product/System Engineering Changes

- Class I engineering changes (Impacts qualification status)
  - Inspection
  - Demonstration
  - Test
  - Analysis
    - Qualification by "similarity", uses precedent decisions
    - Avoids tests
- Class II engineering changes
  - Empowers process owners to make product decisions
- Technical Order Changes (Class I vs Class II)

Changes must be assessed for product impacts

Figure 1 - Product /System Engineering Changes

Process and product change decisions, regardless of whether the driver of change is environmental safety or system performance, are made in a rather complex decision environment. The chart in Figure 2 pictures the linkages between process change decisions at the plant level (lower left) with the product change decisions by the customer or product owner (upper right). In the ASC environmental management realm, these change decisions are stimulated by technology forcing features of environmental law and policy and by Air Force and DOD policies and regulations. It is beyond the scope of this paper to detail these features, but the reader is encouraged to become familiar with them. This might be a good topic for another paper.

Remember that process owners must deal with many products and customers. Product owners must deal with many manufacturing, operating, and maintenance sites. If changes are to be made for any reason, environmental or otherwise, long established change management procedures must be honored to preserve product quality and integrity.

Note the "Contractor Persons" icon in the center of the chart. The people who focus on

processes and seek change must channel their needs and/or proposed actions to the process owner/plant management for a decision to investigate alternatives or approve a process change, such as to substitute a less hazardous material. The first consideration is whether the process change is a Class II change not needing customer approval. Next, the plant manager must look for impact of a change on other products and customers and on overall plant operations assess whether it affects other customer's products. If the change is not authorized as a Class II, customer approval is sought for a Class I change. Wright Laboratory personnel and ASC/EM provide support to the SPO engineer as required in assessing the changes. The role of the ASC Hazardous Materials Alternatives Guide is to serve as an information resource on alternatives and substitutes that are available or being sought within the ASC community. The framework for this role is the Integrated Weapon System Integrated Management (ISWM) concept. As stated earlier, the payoff for the effort is to support cheaper, faster and better efforts to qualify material and process changes to minimize HazMat use and generation.

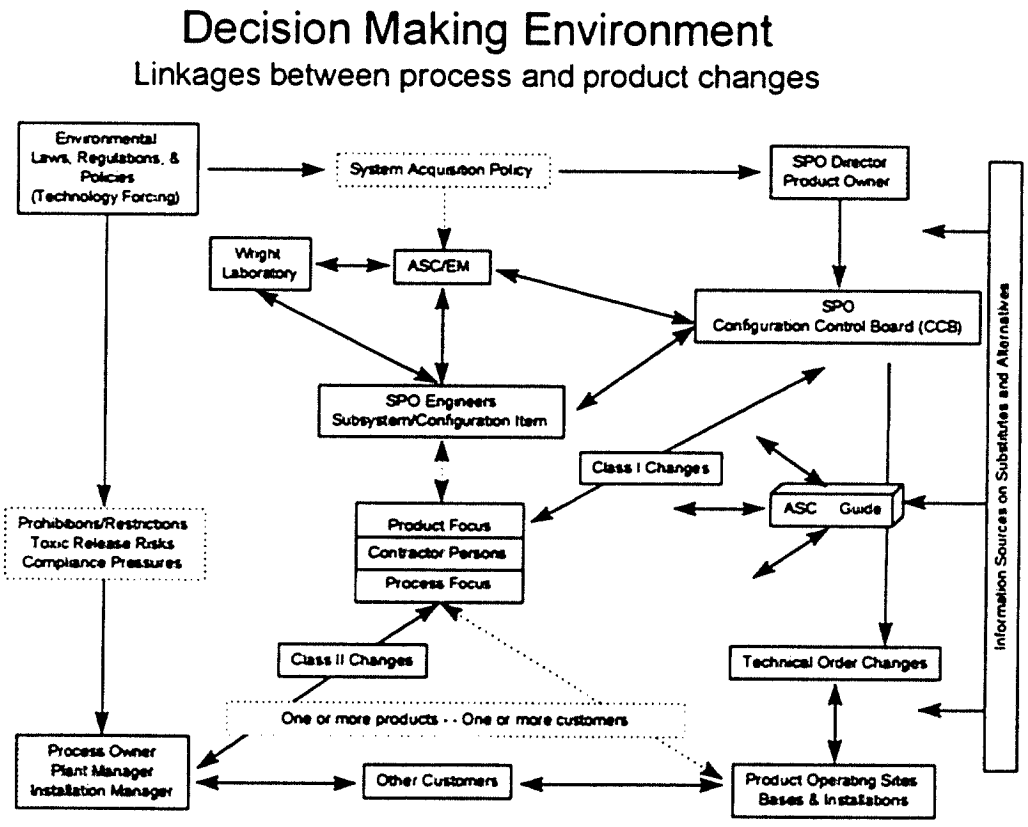


Figure 2 - Decision Framework

Effective communication among process site owners and product owners with similar problems and missions is vital to preserving product integrity in the face of system change. Cooperation is the key to intelligent decisions to use substitute materials or alternative manufacturing processes. This cooperation has been a cornerstone of individual ASC system programs. It is part of the SPO director's job to sustain this cooperation. On the other hand, the constraints on budgets and personnel levels and the demands of program execution often work against proactive efforts to pass on information to others about successful qualification of HazMat

alternatives. No one has disputed the value of exchange of pollution prevention information among the ASC program offices and with other Commands or military departments, but the exchange will not occur without a faster, cheaper, better way. The ASC Guide tries to achieve this objective.

Returning to the theme of cooperation, ASC is actively supporting a major cooperative effort in pollution prevention known by the acronym JG-APP (for Joint Group on Acquisition Pollution Prevention). This initiative is a pilot program instituted by the Joint Logistics Commanders to deal specifically with the multiple DOD customer situation often encountered by defense contractors. A detailed discussion is beyond the scope of this paper, but you should understand that a major thrust of JG-APP is to facilitate the development of joint test protocols to qualify substitute materials or alternative processes for multiple products at key manufacturing facilities. This process will reduce redundant testing and maximize the use of qualification by analysis, as defined above. The payoff: material and process changes can be qualified faster and at lower cost.

As suggested earlier, ASC Pollution Prevention programs operate in a decision environment where process and product changes interact in myriad ways within a far-flung complex of government and contractor owned industrial and logistics installations.

The ASC Hazardous Materials Alternatives Guide was developed to support the product decision processes that are the specific responsibility of Aeronautical Systems Center. The primary stimulus was to foster and facilitate sharing of information within ASC concerning its collective efforts to identify and qualify candidate replacements for hazardous materials and processes used in ASC systems. One fact of life had to keep in mind: SPO directors, supported by engineering staff, are responsible for the performance of the product. These executives have the ultimate responsibility for approving any change to the product specifications for their product. For this reason, it was unrealistic to expect any specific document to dictate substitute materials or alternative processes to be used "across the board" without the process of change qualification. The primary objective of the Guide development was to users link to project managers or technical people who are investigating or who have qualified HazMat alternatives.

A secondary objective of the Guide was to provide a tutorial, tailored to the ASC community audience to environmental implications of processes and commodities important to aeronautical systems development and acquisition.

The original version of the Guide was published in paper format and was also accessible electronically on the Wright-Patterson Air Force Base Bulletin Board. The original guide also provided a reference tables listing material substitutes that were known to the ASC/EM home office at the time of publication. There was also a bibliography of ASC/EM document holdings on pollution prevention subjects. The "Guide" addresses a priority list, of processes and commodities important to ASC. This list is presented in Figure 3.

Aeronautical Systems
Critical Processes and Commodities

- Process technologies
  - Cleaning,
  - Coating,
  - Coating removal,
  - Composites,
  - Electronics and
  - Precision cleaning,
  - Metal plating,
  - Metal treatment, bonding (surface preparation and adhesives)
- Commodities
  - Aerosols and propellants,
  - Batteries,
  - Fire suppression,
  - Fuels, lubricants, hydraulic fluids,
  - Inks,
  - Instruments and testing,
  - Refrigerants,
  - Sterilants, and
  - Deicing materials

Figure 3 - Critical Processes and Commodities

Several factors motivated the task to update the original Guide. More substances came within the domain, many potential available substitutes and alternatives emerged, information technology advanced rapidly and understanding of technical issues matured to the point where a need and opportunity became evident for better support the ASC decision processes for reducing environmental risk in the system acquisition process.

The next step was to issue a task order to one of the Wright Laboratory support contractors, Universal Technology Corporation, to assist in developing improved Guide features and content. Priority for the technical content was assigned to cleaning, coating and coating removal.

Early in the development effort, it was apparent that the Internet provides a suitable platform for the desired network access to the Guide. When ASC/EM decided to create a World Wide Web home page, it was a logical next step to make the Guide resident on the ASC/EM site.

The current version of the Guide has introduced several new or modified features. These features have greatly enhanced the bibliography feature of the original guide. This was done by creating a major section called simply "Document/Project Files". This section contains summaries of documents owned or created by the ASC Environmental Management staff relevant to its pollution prevention activities. This section also contains summaries of HazMat alternatives projects that ASC manages or is a partner or stakeholder. The design of this feature gives the user the ability to browse technical document holdings and project data within the same Web file. The ability to cross reference this information promises to be very valuable.

The purpose of this feature is to facilitate sharing of HazMat alternatives information within the ASC community and with other members of what USEPA likes to call "the regulated community".

Consider some examples of how this feature can be used. One use is to share results of literature searches conducted by or for ASC/EM. These search efforts often involve considerable effort and cost. If a comprehensive literature review of a number of databases or exchanges has been done in search for an alternative material or technology area, it may be desirable to archive the results and refer to the document in the Guide. This will enable other users to find and retrieve the results rather that start at "Zero." Another use of the document section is to archive reviews of meetings and conferences that ASC hosts or attends. These events are often rich in technical information and dialog, but attendance may be restricted to one or two people out of a large group of interest persons. The Guide Document section provides a way to browse reviews of papers at meetings and conferences. A related feature is the Meetings and Conferences file. When a set of reviews is first created, the file is entered in both the Meetings and Conferences section and the Document section. This helps highlight new or even upcoming events. After two or three months, the Meetings and Conferences section is purged of "old" events. Also, trip reports often contain excellent information about HazMat alternatives developments at a particular process site that is worth sharing. Finally, technical reports, engineering assessments and qualification decisions can be recorded for reference and use in supporting qualification by similarity decisions.

The other part of the Documents/Projects section contains summaries of HazMat alternatives projects that ASC sponsors or considers itself a partner or stakeholder. The intent of the summaries is to provide links for the project managers and performers to share project information of mutual interest within ASC and with relevant external organizations. The Web site has the capability to store comprehensive files regarding every aspect of a project - time, schedule, test and qualification data. This is not essential, however. Project information can reside at its source or sources for the life of a project. What ASC is trying to do with the Guide is to help primary users access all possible information from within their own "information space". Although this has not been done yet, the Guide features make it possible for individual project summaries to function as Web sites in their own right, giving the user an opportunity to interact with the project team via a Web link.

A key to successfully finding and qualifying HazMat alternatives is finding meaningful technical information and relating that information to the decisions to be made. As mentioned earlier, a major source of this type of information is the process sites - the action point where material, process and product come together. This is where decisions are made, such as decisions to use alternative materials or processes to reduce environmental risk. Remember also that each change decision can be a precedent for other decisions. Information supporting these change decisions can be invaluable to other process site owners and product managers facing similar circumstances. Links to this information are provided for each project in the ASC Guide. A deliberate effort is made to give richness to these links to make sure that Web search engines give them high priority. Links are created to materials and ingredients involved, products affected, substances being considered and substances rejected from consideration. This last concept is very important. Knowing the reason why substances were rejected could significantly reduce the search cost for HazMat alternatives on the part of other programs and products. On the other hand, if an item has been qualified, the source of the qualification data should be available and the data itself should be accessible.

For ease of reference, the Guide groups the project summaries into convenient categories called "dockets" to relate them to the critical product/technology groupings that have been established. The docket approach permits a technology view and perspective that may be useful for program management.

The hypertext links in the Guide have been made "rich" to improve the likelihood that the links will cause Web search engines to put the Guide near the top of the lists of "hits". Also, the Guide content is searchable using Internet browser capabilities and the "find" function on word processors.

Figure 4 shows the results of a sample search on the project summaries involving methyl ethyl ketone, or MEK. The search found thirteen actions aimed at reducing or eliminating use of MEK. The user can access any or all actions to find out what problems are being addressed or successes have been achieved, and , perhaps most important, who is working the problem for ASC. Note that substitutes for MEK were approved for two cases. One would certainly want to see what precedent decisions were made to determine their applicability to the user's problem.

Test Case Example Of Guide Use

Substance:

MEK = Methyl Ethyl Ketone = 2 - Butanone

Guide includes projects dealing with reduction/elimination of MEK use for:

- Aircraft leading edges
- Aircraft surfaces prior to paint/repaint (T.O. 1-1-8)
- Cleaning of F-16 components at Air Force Plant 4
- Compliant paint and primer, including camouflage topcoats
- Foam insulation coating
- Metal parts cleaning
- Missile coating systems
- Radome stripping
- Removal of heavy grease and carbon prior to paint or adhesive application
- Removal of Koroflex primer
- Replacement paint thinner
- DS-104 as an MEK substitute
- B-6274-1,-2,-3 and -4 as an MEK substitute

Figure 4 - Example of Guide Use

The Guide is not a philosopher's stone or a push button problem solving tool. The Guide enables the ASC community to share technical data and project information with its members, partners and allies seeking alternatives to HazMat use and generation. The Guide organizes information in an orderly fashion to support meaningful access to information that ASC/EM owns or has created relevant to the quest for HazMat alternatives. Perhaps more important the Guide provides a way for users to interact via the Internet with ASC managers and technical people who are leading the way to cleaner aerospace materials and processes.

Next Steps in Guide Development

Next steps will involve addition of content in the Guide relating to additional precedent decisions on substitutes and alternatives that are pending or that have been approved through either Class I or Class II Engineering Changes and/or changes to Technical Orders. In this effort care is taken to capture information about disapproved materials as well as qualified materials. When "shopping" for alternatives it is important to know what material or process does not qualify for a particular application. Information on Class I change decisions is distributed throughout the SPOs at ASC as are Technical Order changes requiring Class I type actions. Information on the results of Class II change actions, however, will be more difficult to collect since these decision are made almost entirely at the plant or process site level. In either case, the capability to share this type of information within ASC via the Guide will be useful.

Planned future effort will involve assessing use of the Guide features and content to support the JG-APP process. Again, the capability to share precedent decisions on engineering changes and to record approved test protocols for specific project groupings is attractive. As indicated previously, the objective is promote an across the board increase in the number of qualification decisions supported by analysis vs. the more costly process of qualification by testing.

With installation of the Guide on the ASC/EM Web Site, the capability exists to network and interact with users. This activity is expected to create a foundation for improving the features and content of the Guide. The idea is not to create another database. The idea is to develop a way for the ASC community to share its discoveries, achievements and challenges with its peers without undue burdens on the individual program missions.

As an electronic file, the Guide helps users improve decision support by leveraging the electronic linkages to existing and developing on-line information resources residing on the Internet. The links can be retained by users via their browser software. Links to "Hot" sites can be added to the Guide home page. As various sources are tapped and valuable search results are obtained, the results can and should be appended to the Guide so others may benefit from them. Finally, the access to people responsible for precedent engineering and technical order changes will build an experience base akin to expert system processes. In other words, the Guide will improve through use. The key to the entire concept, however, is sharing. Few would dispute the idea that networking among those concerned with pollution prevention in an organization is good. The answer is that the sharing process should not be burdensome or time consuming. The Guide vision is to make sharing a milestone, not a millstone for the ASC environmental management community.

How Can Users Help

ASC has created a resource that will facilitate sharing of pollution prevention information within the ASC community and with the aerospace industry community at large. Those who use the ASC Guide can help by using it and by interacting with the content presented. Many information resources wither and die because the client community withdraws information but never makes deposits. As ASC organizations collectively seek to develop and implement cleaner production alternatives, time and money can be saved by haring technical information. The exciting implications of the electronic communications technologies now available is that one can

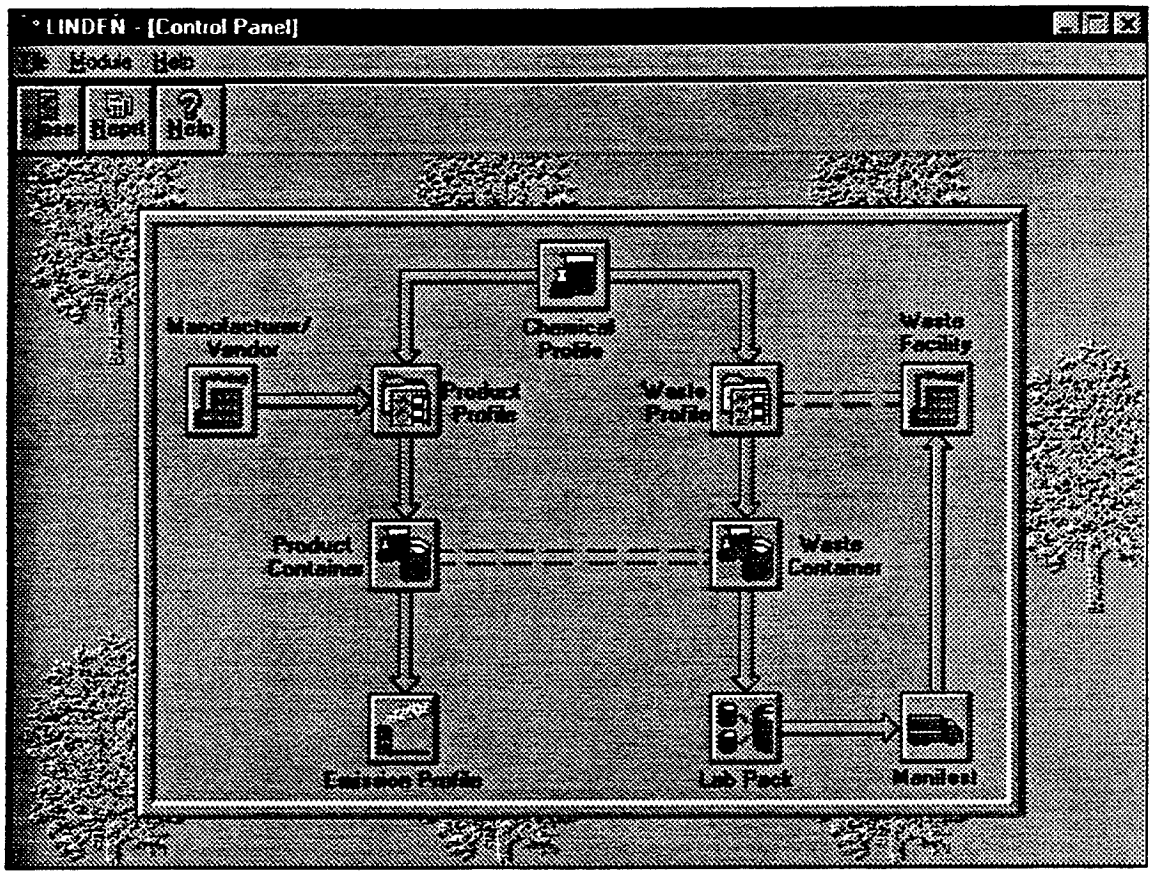
create links to information without compiling vast repositories and libraries at specific locations. This is not to advocate eliminating electronic or paper libraries altogether. Data searches and literature reviews performed by ASC and Wright Laboratory have extensively used formal repositories of technical information as sources for leads on what to do and what not to do. ASC plans to continue to replenish and refresh those technical sources with the fruits of its labors. Everyone in the aerospace industry should cooperate with and contribute to the formal networks and repositories available, such as the Defense Technology Information Center (DTIC), National Technical Information Service (NTIS), DENIX and the USEPA Environene, to name a few. To use an environmental analogy, the ground water may drop to dangerously low levels unless it is recharged.

A specific way users can help is to document and share decisions from Class II engineering changes. Many opportunities to benefit from process improvements at the plant floor level are lost because the successes are not shared as widely as they could be. There is a continuing challenge to capture and share the results of Class I changes as well. The effort will continue to identify ASC information holdings about HazMat alternatives that should be shared.

Meetings, and conferences are often rich sources of lessons learned including what worked and what did not work. That information is often of value only to those who physically attended. Results need to be captured and shared with a broader audience, especially those at the lower tiers of the industrial base. Further results of technical assessments involving literature reviews, conferences, and site visits also yield rich information of what was considered prior to the final decision. Sharing this information identifies dry holes.

In conclusion, it should be understood that the search for cleaner production alternatives is a long term process often attended by near term deadlines. Because pollution prevention is a national policy goal, all members of the aerospace industrial community are, or should be, partners in this process. Everyone can help by continuing their individual and cooperative efforts and sharing those results with others in the aerospace regulated community. Leave tracks so that others may share in your successes and your learning experiences. Consider adding links to the ASC/EM Web sit on your own Web sites. If you support ASC acquisition programs, share technical data on engineering changes or technical assessments. Share reports of meetings or conferences. Finally, provide feedback when using the ASC Guide. It is important to know if the Guide is worth the effort and expense involved so that the future course can be accurately charted.

Implementation of Delta Air Lines' Environmental Management Information System (EMIS)



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Delta Air Lines

Introduction

In our changing business environment, Chemical Management becomes the infrastructure and the corner stone of environmental compliance assurance for the future of the aerospace industry. With well planned, well defined system requirements, extensive data quality assurance and strong coordination, great benefits can be achieved through implementation of a Hazardous Chemical Management Program in the aerospace industry. With strict regulatory assurance and cost effective Material Safety Data Sheets (MSDS) access, enhanced employee safety and operation cost benefits can be obtained. Delta Air Lines Inc.'s experience in moving to this goal is outlined in this paper. Please remember that the steps that Delta Air Lines took to obtain these goals were unique to Delta Air Lines; however, the basic methods that were used to meet these objectives can be used by any company in the aerospace industry.

Background

Delta Air Lines' Technical Operations Center (TOC) located in Atlanta, GA is responsible for the primary maintenance and overhaul of Delta's fleet of 542 aircraft. Maintenance operations at the TOC include aircraft painting and depainting, plating, solvent degreasing, composite bonding, dry cleaning, jet engine testing, waste water treatment and analytical laboratory testing. The TOC is a major source as defined by the Clean Air Act (CAA) regulations for emissions of Volatile Organic Compounds (VOCs), Hazardous Air Pollutants (HAPs), Oxides of Nitrogen (NOx) and a large quantity generator of hazardous wastes. The TOC employs approximately 6,000 mechanics and staff personnel. Approximately 800 different chemical materials, at an estimated annual cost of $12 million (excluding local purchases at outstations) are consumed in support of TOC maintenance function. These materials included a wide range of chemicals including paints, sealers, solvents, lubricants, acids, adhesives and epoxies.

History of Chemical Management at Delta

The large quantities of hazardous materials used at the TOC present numerous challenges for compliance with environmental and occupational regulations. Traditionally, chemical management at Delta was focused on compliance with Federal Aviation Administration (FAA) regulations and Delta's process standards, and was handled by the Materials and Process Engineering Group. There was no prior product approval process other than that for FAA regulations. Much of the data used in preparing environmental reports was gathered through informal surveys of employees and legacy purchasing systems.

Delta's previous system for handling hazardous materials was characterized by a lack of controls over the entry of hazardous materials into the facility. Numerous modes of entry existed for bringing chemical products into the workplace, including vendor samples, field purchase orders, stock materials, test materials, petty cash purchases, etc. Often, there was no oversight to ensure that these materials came with Material Safety Data Sheets, or that they were in compliance with Delta's process standards, and that environmental and occupational safety regulations were being followed.

The purchasing methods and inventory controls used at the time were focused on minimizing material costs through bulk purchases. Rather than rely on just-in-time delivery methods, emphasis was placed on ensuring that product inventories were consistently inflated to prevent work stoppages. This practice resulted in increased safety and environmental liabilities, high storage and warehousing costs, and unnecessary hazardous waste disposal costs from expired products.

Furthermore, because of these multiple purchasing mechanisms, there was no centralized system for capturing data on chemical entry and usage at the facility. Data for environmental reports had to be gathered from numerous sources, both electronic and on paper. Frequently, reports had to be based on informal surveys of departments and employees – asking employees to estimate annual usage of consumption of VOC-containing materials, for example. The following table indicates the number of man hours required to complete the VOC consumption report required under CAA for the manual method (one time per year); the manual method (12 times per year); and after the implementation of the Environmental Management Information System:

Process:	**VOC Material Usage Data Collection**			
	Environmental Compliance	Data Entry	End User Shops	Total Man Hours
	Skilled Labor Hrs	Unskilled Labor Hrs	Skilled Labor Hrs	
Manual Process 1993 (once per year)	240	240	360	840
Manual Process Option 1 (per month as required by permit conditions)	2880	240	4320	7440
After EMIS Implementation Option 2 (per month as required by permit conditions)	192	2880	0	3072

The environmental compliance staff and the end user shop personnel that typically were required for the manual data collection process consisted of employees that were mechanic skill, and environmental professionals with higher wages per man hour. With implementation of the EMIS, the man hours required for compliance data reporting shifted from the higher dollar per hour employees to the lower dollar per hour data entry skills. The automation of data collection helped reduce the man-hours required for reporting by 50%, and the shift of labor to the lower dollar per hour personnel created significantly reduced reporting costs.

Goals and Objectives

In an effort to increase access to critical information, improve efficiency of data gathering and handling, and to enhance compliance with environmental and occupational safety regulations, Delta implemented a new Hazardous Chemical Management System.

Needs identified for a complete Hazardous Chemical Management Program included:

- **Improved Accuracy and Consistency of Regulatory Reporting**

  Previous reporting tasks were calculated manually with significant fluctuations in reporting totals from year to year. These fluctuations could not be verified for accuracy due to the lack of manageable data and the perceived inaccuracy of the data. Air emissions reports prior to implementation of the EMIS have an estimated accuracy of about +/- 90% and ranged from 100 tons per year to 750 tons per year. Current emissions reports are estimated to have an accuracy of +/- 15% and range from 435 to 500 tons per year. The addition of an EMIS automated system allows for real time updating of emission factors for all materials used, not just 10 to 20% of materials that represent the highest usage items.

- **Full Compliance with CAA NESHAP's, especially Aerospace NESHAP (compliant hand-wipe cleaners, depainting agents, and specialty coatings) and Control Technology Guidelines (CTG)**

Compliance with the Aerospace NESHAP presents many unique challenges to the industry -- there are many provisions of the rule that regulate materials based on their application. For example, use of solvents containing Hazardous Air Pollutants like 1,1,1-trichloroethylene are permitted for some applications, such as cleaning of charged electrical parts, but are prohibited for most hand-wipe applications. Likewise, there is a broad VOC limit of 3.5 pounds per gallon for topcoats in the NESHAP/CTG, but there are numerous exemptions for infrequently used specialty coatings which require a higher solvent content. In order to assure compliance with these regulations, it is necessary to restrict access to non-compliant materials to those personnel who are authorized to use them for exempt applications, and it is necessary to maintain records of such usage.

- **Hazardous Waste Minimization (including reduction of expired shelf life products)**

There are many implementation steps involved with a hazardous waste minimization program. The program must be designed to efficiently and effectively select, analyze, and activate waste minimization elements that will benefit the over-all operations while maintaining cost effectiveness. Before Delta could implement their hazardous waste minimization program, it became necessary to gather information about each process generating hazardous waste (quantity, toxicity, compliance issues, feasibility and cost.) Therefore, one of the key objectives in the selection and implementation of a hazardous materials tracking system was that the selected system have the ability to effectively track information about hazardous waste streams and the processes that generated the wastes.

Delta determined that to begin with, the reduction of expired shelf life products would be the beginning of the Waste Minimization Program. Delta currently has 342 products out of 794 materials that have shelf lives. Many of these materials in the past would expire before use and the cost of disposal for materials that never reached production was estimated at $250,000 for 1995. Delta is committed to driving down the cost of materials that expire on the shelf, and the EMIS will provide detailed information about each occurrence of those products that have the potential of expiring before use.

- **Improve Waste Disposal Cost and Data Tracking**

One of the attractive benefits of automating the hazardous materials and waste information at Delta was to identify the various costs associated with the handling, storage and disposal of hazardous wastes. Delta desired to find a method of tracking the "real" cost of the various materials used by the TOC. This cost is not only the purchase price of materials, but the transportation, handling, storage costs, and environmental fees as well as the cost of disposing of by products from processes using these materials. The material containers will be bar coded and tracked to the production operations and ultimately tracked through the disposal process. By determining how each item is disposed of and the disposal costs associated with the material, Delta can then determine the life-cycle costs of materials and choose candidate materials for substitution or elimination.

- **Controlling Employee Access to Chemicals and Tracking Employee Exposure**

Because the materials are uniquely bar coded and tracked by the EMIS as individual items in the data base, Delta can track each container to an individual user, process, location, and type of operation. Delta can determine the amount of specific materials used and analyze the data from many different perspectives. Employees that have histories of allergies, reactions or other medical conditions that would prohibit use of certain materials can be monitored by the system and informed of products that contain chemicals that they should avoid. The data base will also provide histories of materials and the components of these materials so that employees can be better safeguarded.

- **Analyzing all Costs of Materials, Material Distribution, Waste Generation and Disposal**

One of the primary focus areas for Delta was the capture of cost information for materials, waste transportation, disposal, environmental fees, taxes, and the allocation of these costs to the business unit responsible for the cost generation. The shop business units are most capable of making process changes for cost avoidance but the business units had no data regarding the "real cost" of materials. The EMIS is capable of capturing the cost associated with individual containers, the cost for purchase, material handling, taxes, environmental fees, waste transportation, disposal and allocating these costs to individual departments. Once the "real costs" are transferred to the shop business units then the shop management can make informed decisions about material substitutions, and better control procedures can be implemented.

- **Increased MSDS Data Accuracy for Internal and External Regulatory Compliance**

Delta desired to implement a system that would provide electronic management of Material Safety Data Sheets (MSDS's) that are required for internal and external regulatory compliance issues. The Chemical Management Program offered a centralized point of entry for all materials into the TOC. By centrally receiving materials, the MSDS's from manufacturers could be checked for accuracy and for most current information. Any changes in formulation or characteristics of materials could be verified at the point of entry and new information could be disseminated to all employees electronically.

Another objective for Delta was the accuracy of information for regulatory reporting. The use of an automated system for capturing the most current information from product safety data sheets provided a means to automate the various environmental reporting requirements at the TOC. A list of ingredients for each material could be accessed and summarized by process, shop, business unit, and location. This data tracking would assist in screening out unauthorized materials and provide process analysis by listing the chemicals utilized within the process.

Program Features:

- **Chemical Review Committee**

The purpose of the Chemical Review Committee is to ensure that for all materials brought into the workplace, all pertinent regulatory information (VOC content, HAP content, exposure levels, etc.) would be collected; that no non-compliant materials would be brought into the workplace; and that current MSDS's would be available to personnel, before a product is available for employee use.

- **Centralized MSDS depository**

Delta has made the transition from hardcopy MSDS manuals to a digital imaging system. Personnel are able to call an 800 number and get current MSDS's faxed to them. This system has eliminated the problems and expense encountered by Delta involved in updating the MSDS volumes at hundreds of locations in Atlanta and across the country.

- **Tier 1 Chemical Supplier**

Delta reviewed the ways in which Chemicals could be managed at Delta to determine what was the best option:

1. Continue with the present inventory control system and facilities.
2. Employ a third party to manage Delta's chemicals.
3. Develop a new management system in-house with Delta personnel outside of the present Material Services Department.
4. Build new facilities at Delta to handle the increasing compliance demands for chemical storage.

5. Define a program that incorporates several of the above plans.

Delta looked at all the options and concluded that two options were available:

1. Develop a new management system in-house with Delta personnel outside of the present Material Services Department and build new facilities to handle compliance concerns.
2. Employ a third party to manage Delta's chemicals off site of Delta's facilities.

Delta's final decision was to employ a third party due to the liability concerns of storing large quantities of hazardous materials and the capital investment required to upgrade present storage facilities.

One component of Delta's plan was to construct a new chemical staging facility, This will serve as a staging area for chemical material being delivered to the TOC from Delta's Tier 1 supplier. In doing this, Delta was able to free up 14,000 square feet of warehouse space which could be used for other requirements. Additionally, approximately 22,000 square feet of outdoor storage space was also made available. This new facility was designed and constructed in three months, is approximately 5,000 square feet, and meets all National Fire Protection Association (NFPA) requirements.

Identification and selection of a chemical management contractor was a task that involved several groups at Delta. Delta's Purchasing Department played a large part in this process because it's major functions that would be turned over to an outside contractor. This contractor would have to meet the standards that Delta was requiring from all third party sources. Purchasing made the first contacts with possible Tier 1 suppliers to develop a short list of qualified candidates. Each of these candidates was given a detailed scope of work and requested to submit a final proposal of how they would aid Delta in reaching our goal of Chemical Management. Each company was graded on a matrix of several areas of importance to Delta.

Interface LLC Chemical Management was selected because it best fit the requirements of price, flexibility, regulator and aviation experience, chemical management background and financial ability.

- **Selection and Installation of EMIS Software**

Delta made the decision to implement an Environmental Management Information System and began the process of reviewing various systems for implementation. Delta had decided that the following criteria were the basis of selection:

1. Compatibility with existing platforms (Windows based PCs running on a Novel Network)
2. Ability to interface with legacy main frame Information Systems (General Ledger, Material Purchasing & Distribution)
3. Ease of system maintenance and upgrade
4. Ability to track container level inventories from "gate to grave"
5. Image based MSDS as ready reference
6. Provide environmental regulatory reports for specific compliance items
7. The ability to use existing data type conventions and process procedures
8. Flexibility of design and a user friendly interface
9. Customizable reports and data manipulation
10. Price competitive

Modern Technologies Corporation's LINDEN Environmental Management Information System (LINDEN™) was selected because it best fit the above criteria of all the systems evaluated.

The initial phases of installation of LINDEN occurred in January of 1996 at Delta's Atlanta Technical Operation Center. The installation involved coordination with Delta's Information Technologies

Department and TransQuest, Delta's system support vendor, to select a server with the capability of hosting the database and making the connection of various client PCs in and around the TOC. The Interface chemical warehouse was connected to the server via a 128K ISDN line to insure that this critical data link would receive priority attention. Training for the LINDEN system took place in January at the TOC and involved both Delta and contractor personnel.

- **Chemical Crib / Pharmacy Distribution System for Dispensing Materials & Collecting Wastes**

Another planned feature of the overall chemical management program is a centralized materials distribution system located in and around various work center areas. The distribution cribs will manage "just-in-time" stocks of the common materials required by the work center. Employees will requisition materials from the crib in their work area. The inventories of materials in the cribs will be monitored, minimum and maximum stock levels will be determined, and the cribs will be automatically re-stocked when a minimum level is reached. By instituting this program, Delta can reduce the amount of material in each work center while insuring that each shift has just enough material for production.

The cribs will also be utilized for a central collection point for all empty containers, waste product, and items that are no longer usable. Delta will be able to collect the waste streams, consolidate all the crib waste, and insure that a smooth flow of waste materials is established to the waste treatment facility. The data collected from the cribs will contribute to the analysis of the waste streams and provide valuable information for waste minimization and pollution prevention efforts.

- **Shelf Life Maintenance / Inventory Control**

Past performance on disposal of unused expired products brought to the forefront the need for an enhanced automated shelf life maintenance program that would augment Delta's existing shelf life procedures. The EMIS relies on individual, bar coded container tracking numbers which link the container number to all the information associated with the product, including the shelf life information. As different lots and batches of materials are brought into the TOC, the shelf life for each lot is tracked by the system and is printed on the bar code container label in accordance with Delta and FAA procedures.

Program Implementation:

- **Define Objectives & Scope of Program**

There are three basic objectives of Delta's Chemical Management Program:

1. Supply chemical materials to end users as required and in a timely manner.
2. Insure that all Federal, State and Delta regulations are being complied with.
3. Obtain annual material consumption reduction of 10% over 1995 baseline.

- **Senior Management Approval and Support**

No program of this size can be completed without Senior Management Approval. As approval alone is not enough to make a program successful, Senior Management must also give great support to the goal of Chemical Management. Delta's Senior Management was briefed on this idea of Chemical Management in January of 1995, approval of the program was given at the end of June 1995 with the full support required to make the program a success.

- **Identify and Allocate Necessary Internal and External Resources**

Every area of Delta would be affected by the new Chemical Management Program, from Aircraft Maintenance, Airport Customer Services, Purchasing, Material Services, Tooling, Facilities, Accounts Payable to Information Technologies. Additionally, resources outside of Delta would be affected, from Delta's chemical suppliers (Tier 2 Suppliers), Delta's Tier one supplier (Interface LLC Chemical Management), to TransQuest Information Solutions, Delta's hardware and LAN support vendor. Key personnel from all effected areas of Delta were asked to become part of an implementation team to address all the concerns that this wide reaching program would effect. The core team members that made up the implementation team were from:

Environmental Compliance (Chemical Management -- Project Manager)
Automation Business Analyst (Automation Requirements)
Tooling Analyst (Tooling Requirements)
Facilities (New Facilities Project Manager)
Purchasing (Materials Buyer)
Program Development (TransQuest Project Manager)
Hardware Management (TransQuest Site Manager)
Members of several Departmental Safety Committees which have day to day activities with affected Departments
Finance Personnel from Accounts Payable, Tax, Accounting (Automation requirements for Accounting System's feeds)

Several outside resources would be required for complete implementation of the Chemical Program. These outside resources included:

Interface LLC Chemical Management (Tier 1 Chemical Supplier)
Modern Technologies Corporation (EMIS Software Systems Support)
General Contractor for improvements and new facilities
Local Regulators (Fire and Building Inspectors)

- **Identify Data Needs & Reporting Requirements**

One of the important criteria of the EMIS software package was the system's ability to capture the data elements critical for Delta's internal and external reporting requirements. The LINDEN system possessed the ability to report all the constituents of each product and to capture the maximum and minimum quantities on site for any given day for any regulated chemical. The chemical and physical properties of these chemicals was also stored in the system allowing Delta to access a variety of information for data analysis. Recently the local Fire Marshal requested a list of materials that had an NFPA rating of "4" for Fire, Reactivity, and Health. The Delta Environmental Compliance Office was able to write a custom query through the EMIS and produce this report in a matter of minutes.

- **Development of Chemical Approval Board**

Because the Chemical Review Committee is charged with ensuring that materials used at Delta comply with FAA, EPA and OSHA regulations, it is comprised of representatives from each of these groups. Initially, the Committee had to review materials already in use at Delta and had additional representation from the Maintenance, Operations and Purchasing departments for this purpose. As an on going program, all new chemical materials are reviewed by this committee before materials can be used.

- **Inventory of Existing Stock & Transfer to Tier I Supplier -- Purge of Hidden Hazardous Waste**

A part of the transition to a Tier I Supplier involved transferring existing Delta inventory from the TOC to the Interface Chemical Warehouse. Delta had stock for many of the materials that were

needed for everyday operations stored in and around the TOC. Removing materials that were outdated, obsolete, or partially used involved a purge of many materials to the waste treatment area. The remaining materials were transferred to the Tier I supplier for redistribution through the new program.

- **Layout of Delivery Mechanisms, Routes, Chemical Cribs, User Authorizations, etc**

  To insure control over the materials being used throughout the TOC, Interface Chemical Management is not only warehousing and delivering materials to the TOC's chemical staging building but also to all shop and hangar locations. A complete routing system has been developed which acts as a "Milk Run" for distribution of chemicals. Each location where materials are delivered is set up with the using shop to insure that all environmental and fire regulations are being complied with. Along with this, only enough chemicals for a 24 hour period or less is supplied to the using shop. Each location's chemical cabinets or process tanks are bar-coded and are scanned as materials are dropped at these locations. This data is available to Environmental Compliance staff for review and emission reporting needs through LINDEN on a real time basis. Additionally, materials which are not authorized for use on a specific process can be controlled through Delta manned Chemical Cribs/Pharmacy locations.

- **Integration Between Purchasing, Corporate Safety, Environmental Compliance and Cost Tracking Data Systems**

  Key to the success of the EMIS implementation was integration with existing Management Information systems for accounting, purchasing, and Corporate Safety. The goal was to be able to not only attribute purchasing costs to the end user but also be able to identify additional costs associated with waste treatment, storage and disposal, and propagate those costs to the individual cost centers that generated them. Similarly we would then be able to identify cost savings offered by alternatives which would reduce the total cost of handling the material.

- **Common Pitfalls**

  In a program of this size underestimating the complexity of the program is very easy to do. The time in which to complete this program's implementation was estimated to be twelve to eighteen months, in reality this timeline will be approximately twenty four to thirty months for full completion. Many of the Information Systems which had to be integrated with LINDEN proved to be more of a project than expected and required more time and money to complete. The transfer of Delta's chemical inventory became a large project in itself. Many materials were not usable and were out of shelf life which required Interface Chemical Management to do double duty to make sure materials were available to supply demand. Several of the Tier 2 chemical vendors were not comfortable in supplying materials to Interface which added to supply problems. With help from Delta's Purchasing Department these problems have been handled and now Tier 2 vendors better understand the program. Working with end using shops has proved to be easy and very hard at this same time. Some shops have embraced the program with open arms while others have looked at the program with distrust. These problems will eventually work themselves out as shop personnel and management become confident with the on time delivery of needed materials to their shops.

Program Benefits/Successes (expected & realized):

- **Inventory Control / Reduction in Overall Consumption**

  One of the immediate realized benefits of the EMIS was the ability to capture accurate data on the quantity and components of the TOC's inventory. The Tier I Supplier records every request, transfer, and issue of chemical materials to the end-use shop and can quantify for any given time frame the amount of material and the ingredients of the materials that are in-use. This information is particularly

useful for Environmental Compliance because it is the beginning of the process of pollution prevention and material minimization. High volume processes can be identified and analyzed for potential environmental, mechanical, or material process changes that will result in lower, overall consumption.

- **Improved Accuracy in Environmental Reporting & Accountability for Hazardous Materials**

  The increase in the quality of the data being gathered by the EMIS contributes to the accuracy of all environmental reporting events. Data can be accumulated on the composition of all materials entering the TOC and reformatted and compared by a variety of methods to complete environmental reporting requirements.

- **Improved MSDS Tracking and Access**

  Another benefit of the hazardous materials tracking system is a renewed emphasis on the accuracy of information and the availability of this information. The manual MSDS approval process took time and lacked an efficient means for identifying when products changed formulation, when new products were introduced, or when updates were made to the content of a MSDS. The Delta Chemical Supplier is now the single source for products that enter the TOC and has put in place management processes to identify new or modified MSDS to Delta's Corporate Safety Office. The materials tracking system contains scanned images of the original manufacturers' safety data sheets for each product and can track the history of products via archiving of out-dated information. Employees can access the system and access health and safety information by simply scanning the bar code identifier for the container and linking to the scanned MSDS.

- **Reduced Liability Exposure: EPA/OSHA/NFPA**

  One of the expected benefits of the Interface Chemical Management and EMIS implementation will be to reduce the overall liability exposure from the various regulatory agencies that involve chemical materials. For example, the "on-line" access to MSDSs and the hazard information for each material utilized at the TOC will increase Delta's ability to respond to the requirements of OSHA's Hazard Communication Standard for information dissemination. Historical information about products that were used at the TOC can be stored electronically and recalled to recreate information trails for environmental and safety reports. Data can be accurately tracked to demonstrate compliance initiatives with regulators. By removing large quantities of hazardous materials and moving to a true Just In Time (JIT) delivery system the TOC will reduce the quantity of information reported on EPCRA and other reports, and lower the physical liability of accidents and spills.

Conclusions:

Given Aerospace NESHAP requirements for emissions control, FAA requirements for tracking chemical shelf life, and the myriad of other regulations dealing with chemical usage, implementation of a EMIS is, at the very least, a good business decision. The system should be capable of calculating chemical usage to the individual constituent level and have the ability to compile SARA Tier I, and II reports. The system should also be able to provide valuable information for making waste management and minimization decisions. Separate EMIS and tracking systems should be avoided in order to alleviate redundant operating procedures. Additionally, the chosen system should be able to take advantage of previously-gathered process emissions data for various media and categories (e.g. fugitive air emissions, wastewater, landfill, etc.), either specific to one facility or standard process emission factors.

In today's corporate environment, cost-benefit analysis for the environmental <u>and</u> financial benefits should be performed when an environmental purchase is being considered. An effective EMIS can pay for itself, when compared to the time required to manually compile records for emissions estimations and SARA 312

reporting, and inefficient waste disposal methods. Furthermore, such an implementation allows the environmental staff to focus on pro-active rather than reactive environmental activities.

ELIMINATION/REDUCTION OF OZONE DEPLETING SUBSTANCES AND "EPA 17" MATERIALS IN F100 WORLDWIDE MAINTENANCE MANUALS

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Abstract

The maintenance manuals (Technical Orders) for the F100 family of military jet engines comprises approximately 163 series of volumes with approximately 118,000 pages of instructions. A program to eliminate all ozone depleting chemicals (ODC) and reduce or eliminate large use quantities of EPA 17 materials from these Technical Orders was performed. A database was developed to manage the program status and material usage and replacement documentation for each applicable usage within the manuals, as well as generate many of the formal contractual reports. The review process efficiency was dramatically increased by digitizing the manual pages, using keywords to locate the ODC and EPA 17 materials, and categorizing the technical application parameters. This database permitted multiple substitutions, eliminated redundancy, and led to a better understanding of the process based on how the information about the material usage was grouped. As an example, greater than 1800 locations of ODC materials were originally identified; ultimately it was found, using the database, that all of the uses could be categorized into less than 30 different applications. It was generally found that most of the ODC material uses were substituted without testing of alternatives, since substitutions could often be based on similar uses of the alternative in other applications.

Introduction

The F100 turbofan engine powers all F-15 fighter planes and a majority of the F-16 fighter aircraft as well. Approximately 5800 F100 engines have been placed into service worldwide. Mission readiness of these aircraft are vital to the national security of many countries, including the United States. Maintenance procedures are a critical part of the readiness requirements.

Maintenance of jet engines, including the F100, involves highly complex turbomachinery, precision tolerances, critical controls, and component material compatibility with various chemical operations. Maintenance involves not only large amounts of technical procedures, but a high degree of confidence in the effectiveness of the procedure, since safety of flight is a major consideration. The maintenance operations are performed at various Air Force locations in the United States and also in many other countries at foreign military bases. Ozone depleting substances have been eliminated in many manufacturing processes throughout the aerospace community, including manufacturing and overhaul and repair operations for jet engines; however the inertia in changing the requirements and the documentation which controls the processes where these materials are used is substantial. The purpose of this program was to change the procedures which mandated the use of ODCs and substitute materials and processes which still allowed the maintenance operations to be effective.

The Clean Air Act Amendments of 1990 restrict the production of ODCs, particularly Class I ODCs which are the most detrimental. The National Defense Authorization Act of FY93, PL 102-484, Section 326, prohibits any new contract award, as well as certain contract modifications to existing contracts, after January 1, 1993 if the contract mandates the use of a Class I ODC. In addition, the Under Secretary of the Air Force for Acquisition (SAF/AQ) Policy 93M-011 required the Air Force to eliminate the use of Class I ODCs, or provide a timely plan to do so, by April 1994.

As a result of Executive Order 12856 the U.S. Air Force was required to replace or identify replacements for ODCs and certain other hazardous materials used in maintenance operations rapidly. Pratt & Whitney was tasked with removing all mandatory requirements to use ODCs within the F100 family of engine Technical Orders (T.O.s). This involved assessment and changes to approximately 163 series of manuals, and encompassed over 100,000 pages of technical procedures, the bulk of which needed to be completed within about 6-8 months.

The program was conducted in two phases. Phase I was to eliminate ODC materials. Phase II was to replace/reduce usage of EPA 17 materials. For the ODC phase the goal was simple - all mandatory references to ozone depleting substances were to be eliminated, either by eliminating the process/material or by substituting a new material or process in its place. The criteria for replacement substances was: no class I ODC content, and preferably no EPA-17 content nor significant increase in toxicity. For the EPA 17 effort complete elimination of all EPA 17 materials is of course not reasonable, but the goal is to replace and/or reduce the requirements for EPA 17 material usage in a manner which balances the need for environmental compliance, worker safety, and cost reduction associated with procurement, usage, and disposal of EPA 17 containing substances.

This effort is being funded by the Air Force under contract F41608-95-D-0082 and is administered by Terrence Albach at the San Antonio Air Logistics Center, LPFE group.

Program Description

It was realized prior to initiating the review that to individually analyze each page within the T.O. series for the use of ODC and EPA 17 materials would not be cost effective or feasible in a timely manner. To facilitate the review process the T.O. pages were scanned and digitized by the TIEM division of the Air Force at San Antonio Air Logistics Center. Upon digitization of the documents keywords could then be used to locate the locations where ODC and EPA 17 materials were being used. For example, MIL-C-81302 (CFC 113) is an ODC and all locations where MIL-C-81302 was present on a T.O. page were then able to be easily found, including tables and figures. The documents which noted the location of the ODC and EPA 17 materials were called Chemical/Process Lists (CPLs). A CPL was generated for each of the T.O. manuals which contained at least one ODC or EPA 17 material. A total of 1852 ODC uses and 8764 EPA 17 uses were identified by the CPLs.

ODC Elimination Effort

Prior to the review and assessment phase of the program a Program Management Plan was prepared which established the program boundaries, the mechanism for documenting the ODC and EPA 17 uses, and outlined the procedure for generation of the published changes. One of the key decisions was to address only "mandatory" uses of the materials, i.e. uses for which no alternative was offered in the T.O.s. Some locations where an ODC was mentioned, such as consumable lists and uses where other materials were designated as alternatives were not replaced under this program.

A total of 166 mandatory ODC uses were documented using the CPLs. An additional 13 mandatory uses were identified without the use of CPLs. The additional discoveries were due to certain CPLs which were not available for manuals due to a major revision or merging operation at the time of the digitization process. During discovery of the mandatory ODC uses, information about the location of the operation, the process and chemical information, and related process information was entered into a Microsoft Access database. The design of the database permitted grouping of the various ODC processes to determine which processes could be solved with the same replacement. It also was used as a program management tool and as the source of data used for reporting requirements. A list of the major categories of uses is shown below in Table 1.

Table 1. Major Categories of ODC uses in F100 Technical Orders

CATEGORY OF USAGE	NUMBER OF USES
Exhaust Nozzle Bearing Cleaning	17
Augmentor Light Off Detector Cleaning	12
High Voltage Electrical Connector Cleaning	54
Sensor Cleaning	29

There were four possible options for treating the mandatory uses of ODC materials: (1) eliminate the process, (2) replace the ODC with another material or process already in the T.O. in a different location, (3) replace the ODC with a P&W approved material or process not in the T.O., or (4) approve an alternate material via component supplier usage, engine depot usage, or testing and qualification by this program.

The nozzle bearings used on the engine permit the actuator assemblies to smoothly control the movement of the nozzle during engine power transients. The bearings are made from stainless steel (typically 17-4PH or 440C) and cobalt alloy (typically Stellite 6B). The previous method of cleaning the bearings was to use 1,1,1-trichloroethane, often ultrasonically assisted. Since the bearings could not be disassembled this method was suitable to removal of cleaning solvent by evaporation. An alternate method was found in the commercial practices manual, which is a general procedures manual published for maintenance of commercial airline engines built by P&W. It was discovered that bearings of similar construction and composition were approved for cleaning in an ultrasonic alkaline cleaning process which used a dewatering oil subsequent to cleaning and rinsing to prevent corrosion staining of the bearings. This process was implemented, without testing required, as a change to the existing F100 nozzle bearing procedure in 17 locations encompassing 4 separate T.O. manuals.

By far the largest category of mandatory ODC uses was cleaning of high voltage surfaces via handwiping. Typical components in this category were the generator rotor and stator housing, exciter, ignitor, and the ignition connection joints. Both CFC 113 and 1,1,1-trichloroethane were previously used to wipe the surfaces upon assembly following maintenance actions. The ODC materials effectively cleaned residual oil or other contamination and dried quickly to permit immediate assembly. The replacement process replaced the ODCs with isopropyl alcohol or a dielectric solvent (Electron). A step to blow dry the part was added as an option if immediate assembly was required after using the dielectric solvent. The qualification of the two alternate solvents was based on commercial practice with similar components and manufacturing practice with the suppliers of the generator and ignition systems. Material compatibility issues had been previously addressed so implementation was again performed without any required testing.

Other processes in which an ODC material was replaced were: cleaning of rigid tubing, cleaning of coking deposits from augmentor light-off detector lens, activation of adhesive patches, cleaning prior to welding of components, lubrication for drilling in locations where contamination could not be permitted by machining fluids, cleaning of thermocouples and other sensor connections, removal of residual adhesive, removal of residual dry lubricants, cleaning prior to painting, as well as general purpose wipe cleaning. The key to this phase of the program was the qualification of alternatives without extensive testing. This was accomplished by identifying alternatives already available and used either by the original equipment manufacturer or in equivalent circumstances in commercial practice.

Only two processes required testing of alternative materials. One was for repair of braided cable assemblies while the components were hot, which required use of a non-flammable solvent. The second application was to replace the use of CFC 113 used in borescoping operations. Testing on these applications has not been completed. Both of the substitution processes will probably use highly fluorinated compounds, which have no flash point, but mimic the properties of the ODCs previously used.

Of the 179 mandatory uses of ODCs 23 were solved by eliminating the process; 151 were solved by substitution with an alternative within the T.O. or through P&W/supplier approved processes; and 5 required further testing to approve an alternative process.

EPA 17 Replacement/Reduction Effort

The EPA 17 phase of the program does not mandate the elimination of all EPA 17 substances as did the ODC phase. Since the scope of the EPA 17 effort is much larger no replacement effort will be performed until the completion of the discovery and prioritization efforts are completed. These two efforts are documenting the location of all mandatory uses of pure EPA 17 materials as well as products formulated to contain EPA 17 substances. The EPA 17 phase of the program has recently been initiated. Although the full assessment has not been completed it appears as though the number of mandatory uses of EPA 17 materials will be an order of magnitude greater than with the ODC effort. Processes, databases, and lessons learned from the ODC phase will be incorporated into the EPA 17 phase.

Since elimination of all EPA 17 materials is impossible under the scope of this program a prioritization document will be prepared which will document the different amounts of EPA 17 materials used in various processes and recommend a replacement strategy which is both realistic and will achieve maximum reduction with the available funds. Based on historical experience with the T.O.s it is anticipated that the metals reduction effort will focus on elimination of cadmium (typically plated coatings for corrosion protection) and lead (typically used for solid film lubrication), and on reduction of nickel and chromium as used in plating operations.

The major amounts of EPA 17 solvent usage for the F100 are from methyl ethyl ketone, perchloroethylene, toluene, and xylene. Theses materials are commonly found in paints, masking materials, vapor degreasers, and are used as handwiping solvents. Reduction/elimination of these materials will also be to assure compliance with the Aerospace NESHAP.

CLEANING: METHODS AND MECHANICAL SYSTEMS

TESTING AND QUALIFICATION OF HFE CLEANING AGENTS IN VAPOR DEGREASING APPLICATIONS

by

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Abstract

There is no satisfactory replacement for vapor degreasing in many metal and precision parts manufacturing and cleaning tasks, including a variety of electronics printed wiring assembly, printed wiring board and component applications.

This paper describes a new, environmentally friendly, second-generation vapor degreasing process that uses a hydrofluoroether (HFE). The new process can permanently replace both 1,1,1-trichloroethane and CFC-113 in a wide variety of cleaning applications vital to the industry, as well as chlorinated solvents such as methylene chloride, trichloroethylene (TCE), perchloroethylene and HCFC-141b.

Importantly, this new fluorochemical-based process operates very satisfactorily in unmodified, modern vapor degreasing equipment, or in slightly modified older but well-maintained equipment. Thus, this alternative may offer the possibility of an eleventh-hour rescue for many organizations that delayed converting or couldn't afford the equipment necessary to use other alternatives to ozone-depleting solvents. It also is extremely attractive for those whose first alternative choice has not fully met their expectations, or whose circumstances, designs and requirements have changed.

From the equipment operator's perspective, HFE processes are run identically to a conventional vapor degreasing process in which the parts are immersed in the boil sump, rinsed in the next sump and then quickly dried in the vapor.

HFE process results to date can be summarized as follows:

- HFE processes have been satisfactorily implemented in several completely unmodified pieces of conventional vapor degreasing equipment.
- HFE cleaned routine production parts at least as well as HCFC-141b, TCE or aqueous cleaning does in current operations.
- No compatibility problems were encountered with the HFE process.
- HFE process cycle times were equal to or less than those used in production with HCFC-141b or TCE, and far shorter than those for aqueous cleaning.

- HFE solvent emissions were much lower than those from HCFC-141b or TCE.
- Preliminary economic analysis suggests that cleaning costs for the new process are competitive with or lower than those of other cleaning processes. These conditions are thought to be typical of other, similar manufacturing operations.

Introduction and Industry Status

For developed countries which are signatories to the Montreal Protocol, the end of 1995 ended lawful manufacture of 1,1,1-trichloroethane (methyl chloroform) and CFC-113, the principal ozone-depleting solvents. Further, in some markets, HCFC-141b can no longer be used for cleaning, except in certain narrowly defined applications.

This phaseout date has been known for several years, but surveys as late as mid-1995 revealed that many industrial manufacturers had not yet switched to non-ozone depleting cleaning processes. Shortage of capital funds has been cited as a primary reason for procrastination on the part of many companies. For most of those who were late to address the problem of solvent change, there is now a desperate, in some cases business-threatening, need for an alternative that can be quickly adopted.

For many industrial cleaning tasks, there is no satisfactory replacement for vapor degreasing. Co-solvent processes using organic solvents and perfluorocarbons (PFCs) were developed for use in such applications. However, due to their long atmospheric lifetimes, PFCs have been seen only as interim solutions. This paper describes a new, environmentally friendly co-solvent/fluorocarbon vapor degreasing process that appears capable of permanently replacing CFC-113 and 1,1,1-trichloroethane in a wide variety of industrial cleaning applications.

A New, Low Capital Cost Co-Solvent Cleaning Option

New, highly (but incompletely) fluorinated liquid compounds with attractive characteristics, including hydrofluoroethers (HFEs) and hydrofluorocarbons (HFCs), are now becoming available for use as long term replacements for ozone-depleting solvents in cleaning applications. This paper describes the commercial-scale prove-out of HFE/co-solvent vapor degreasing, an alternative that offers the possibility of replacing a poorly performing or otherwise unsatisfactory non-ozone-depleting cleaner. This process can also serve as an eleventh-hour rescue for those organizations which delayed finding or couldn't afford the equipment necessary for using most ozone-depleting solvent replacement processes.

A co-solvent cleaning process is one in which the cleaning and rinsing solvents are of significantly different composition. For example, in semi-aqueous systems cleaning is done with organic solvents, similar in many respects to those used in fluorinated

liquid/co-solvent processes, and water is used for rinsing. In the co-solvent cleaning process described in this paper, cleaning is accomplished primarily by the organic co-solvent, and rinsing is effected by a fluorochemical.

Typically, in co-solvent systems, the boil (wash) sump contains a mixture of approximately equal volumes of co-solvent and fluorochemical rinsing agent, though the process operates successfully over a wide range of boil sump compositions. The rinse sump normally contains essentially 100% fluorocarbon rinsing agent.

Fluorochemical rinsing agents may be either miscible or immiscible with the organic co-solvent. For example, perfluorocarbons are immiscible with most organic solvents, while hydrofluoroethers are generally miscible with common solvents, except for longer-chain hydrocarbons. Hydrofluorocarbons may fall into either category.

Unlike the cleaning solvents traditionally used for vapor degreasing, co-solvent cleaning and rinsing agents have zero ozone depletion potential and essentially no global warming potential. There are virtually no volatile organic compound (VOC) emissions from the co-solvent process.

A solvent wash/fluorochemical rinse co-solvent process operates in precisely the same way as a conventional vapor degreaser. In fact, HFE/co-solvent processes can be operated in unmodified, modern vapor degreasing equipment designed for use with ozone-depleting solvents such as CFC-113, HCFC-141b and 1,1,1-trichloroethane. Other equipment can be simply and inexpensively modified to run the process.

From the equipment operator's perspective, the co-solvent process is conducted identically to a conventional vapor degreasing process in which the parts are immersed in the boil sump. The presence of solvating agent (co-solvent) in the boil sump does not change the way the process is run. Appendix 1 shows a simplified schematic representation (not to scale) of a conventional vapor degreaser like the ones used for the co-solvent cleaning applications described in this manuscript.

The only practical difference between vapor degreasing with ozone-depleting solvents and co-solvent cleaning is that the co-solvent constitutes approximately half of the boil sump. Because the co-solvent is low in volatility (*i.e.*, it has a low vapor pressure), there is little tendency for it to exist in the vapor phase, and thereby be condensed into the rinse sump. Ignoring the effects of dragout (which are usually minor), the rinse sump normally contains close to 100% fluorochemical rinsing agent.

Referring again to the diagram in Appendix 1, co-solvent process operation can be summarized as follows. Dirty parts are immersed into the boil sump, which contains a mixture (usually a solution) of co-solvent and fluorochemical rinsing agent, typically about equal volumes of each. Soils are dissolved primarily by the co-solvent, though the fluorochemical contributes to some degree, particularly with certain soils.

After being cleaned in the boil sump, the parts are immersed in the rinse sump, which contains nearly 100% fluorochemical, in this case HFE. The rinse sump is normally kept a few degrees cooler than the vapor. The primary function of the rinse sump is to remove the fluorochemical /co-solvent mixture and the soil dissolved in it. Eventually, the boil sump soil loading increases sufficiently that the co-solvent must be recycled or replaced.

Following immersion in the rinse liquid, the parts are moved into the vapor phase for a final rinse with fluorochemical condensate (there is essentially no co-solvent in the vapor). Finally, the parts are raised into the freeboard zone, where any remaining HFE evaporates from the parts and returns to the sump (as vapor or condensate). At this point, the cleaning cycle is complete and the parts are clean and dry.

Case Histories

Two case histories are presented on the following pages. One of the companies described, Omnirel Corporation, is a contract electronics assembler. The second case history describes a co-solvent process installed at Aurora Bearing Company.

HFE / Co-Solvent Cleaning at Omnirel Corporation

Omnirel, located in Leominster, Massachusetts, USA, is a manufacturer of single- and multi-chip semiconductor and integrated power modules. Omnirel operates four vapor degreasers using ozone depleting solvents, most recently HCFC-141b. Omnirel's plan has been to convert to no-clean fluxes for a portion of its soldering business. The semiconductor process uses fluxless solder, but the parts must be cleaned for degreasing purposes. Omnirel decided to evaluate co-solvent vapor degreasing in order to investigate whether the process could offer a low- or no-capital backup to no-clean fluxes. 3M and Petroferm, the vendors who are cooperating to supply HFE/co-solvent process chemicals, provided on-site technical expertise to support the startup.

Omnirel Equipment

A Baron Blakeslee MSR-120 vapor degreaser running HCFC-141b was drained and refilled with chemicals for the new process. The MSR-120 is representative of machines which have been used by the thousands for 1,1,1-trichloroethane or CFC-113 cleaning of a broad variety of electronic, precision and gross metal parts in many different industries; see Appendix 1 for a simplified schematic. This particular vapor degreaser had 100% freeboard and standard cooling coils operating at 4°C (40°F). The machine was not equipped with freeboard chillers. One of the primary goals of the test was to determine whether the co-solvent process could be satisfactorily implemented in a standard vapor degreaser without any modification whatsoever, a goal which was successfully met.

Boil sump dimensions (l x w x h) of the MSR-120 are 30 cm by 25 cm by 33 cm. Rinse sump dimensions (l x w x h) are 30 cm by 25 cm by 30 cm. Overall equipment dimensions (l x w x h) are 68 cm by 45 cm by 110 cm. The total fluid volume is 53 liters, with 18 liters in the boil sump, 23 liters in the rinse sump and the remainder in the water separator and associated piping.

Before beginning the defluxing process, the vapor degreaser boil sump was filled with a 60/40 (by volume) mixture of Solvating Agent 24* and HFE 7100* (about 11 liters of Solvating Agent 24 and about 7 liters of HFE 7100). The rinse sump and water separator were filled with neat HFE. The power was turned on, and the boil sump was heated to its desired operating temperature of 71°C (160°F). The rinse sump temperature was 38°C (101°F).

Omnirel Parts Cleaned and Experimental Procedures

Several types of electronic assemblies were cleaned, along with a variety of other parts. The results were good, generally comparable to those normally obtained with ozone-depleting solvents, and with HCFC-141b in particular. Cleaning tests were performed side-by-side in the HFE/co-solvent system and in essentially identical equipment with HCFC-141b. The electronic assemblies tested had been soldered with RMA solder paste using a standard reflow profile.

One type of assembly cleaned was an industrial power module with surface mount power MOSFETs, high voltage diodes, and precision thick film resistors. The substrate was aluminum with a 3-mil polyimide insulator. Wire bonding is performed after cleaning. Another assembly was a power supply circuit for medical analytical equipment. It contains a ceramic substrate with surface mount components, connectors, and a polyimide flex cable with a connector. A third assembly was a typical FR4 substrate with surface mount components on both sides.

In the HFE/co-solvent cleaning process, the assemblies were immersed in the boil sump, transferred to the rinse sump, held in the vapor until condensation stopped, and then raised slowly past the cooling coils, held briefly in the freeboard, and taken out of the equipment. Some parts were held over the boil sump and sprayed with HFE condensate using the spray wand before they were transferred to the rinse sump.

In the HCFC-141b process, the assemblies were sprayed with solvent from the spray wand, immersed in the clean (rinse) sump, removed from the clean sump and sprayed again, held in the vapor space, lifted into and held in the freeboard area, then lifted from the equipment. All the assemblies from both processes were visually clean. Analysis of the results indicates that the two cleaning processes performed equivalently.

* HFE 7100 is 1-methoxy-nonafluorobutane ($C_4F_9OCH_3$). Solvating Agent 24 is a specially-formulated cleaning composition containing long-chain aliphatic esters and propylene glycol alkyl ethers.

The emissions data show that the HFE loss rate is sufficiently low that the process offers attractive economics. In idling emissions testing, the loss rate was similar to laboratory results previously obtained with this type equipment, approximately 0.3 kg/hr-m^2. This compares very favorably with the same equipment running HCFC-141b, which gave emissions under similar conditions of approximately 1.4 kg/hr-m^2. Further, dragout losses are much less (in some cases five times less) for HFE 7100 than for HCFC-141b.

Aurora Bearing Company Experience with the HFE / Co-Solvent Process

Aurora Bearing, located in Aurora, Illinois, USA, manufactures a complete line of standard rod end and spherical bearings They also design and manufacture special bearings to meet a variety of applications that require custom engineered units or special materials. Known for high quality products and strong commitment to customer service, the firm serves nearly every major industrial and aerospace market. These markets include packaging machinery, machine tools, business machines, agricultural and off-highway vehicles, commercial transportation, high performance racing vehicles, military equipment and commercial aircraft.

Aurora's standard cleaning equipment included an aqueous cleaner and a vapor degreaser running TCE (trichloroethylene). The TCE vapor degreaser was used to clean specially plated parts that the aqueous cleaner attacks. For most parts, the aqueous cleaning system cleans well but the cleaning cycle is long due to the long drying cycle required. Prior to installing the HFE/co-solvent process, Aurora Bearing had tested several different cleaning processes to find a suitable replacement for the chlorinated solvent and the aqueous system. All those tests had been unsuccessful. By contrast, the HFE/co-solvent process has proven fully satisfactory.

Aurora Equipment

An old Phillips vapor degreaser which Aurora had previously used for Freon® was removed from storage to run the HFE co-solvent process. This vapor degreaser has two sumps that are each 30 cm x 33 cm x 33 cm (l x w x h). The sumps are separated by a split weir about 5 cm wide. The machine does not have a water separator, but instead has a desiccant tank that the condensate passes through. There is also a condensate reservoir which is used to feed a spray wand that was removed for the present work. The rinse sump can be recirculated as required to filter the fluid. Ultrasonics, heating and temperature control are also available on the rinse sump. The machine has primary condensing coils operating at -18°C. The freeboard is 125%. There are no freeboard chillers. The opening at the top of the machine is 70 cm x 30 cm (0.22 square meters).

The boil sump was charged with approximately equal volumes of SA-70* and HFE 7100* (see Table 1 for a description of the properties of these materials). The rinse sump and rinse sump piping were filled with HFE 7100. Crest drop-in ultrasonics (250 watts, 40 kHz sweep frequency) were placed in the boil sump so they would be available if needed. The boil sump operating temperature was 65°C (150°F). The rinse sump temperature was adjusted to 55°C (130°F).

Table 1

Selected Properties of HFE/Co-Solvent Process Chemical Ingredients

Property	HFE 7100	Solvating Agent 70	Boil Sump Mixture
Boiling Point, °C (°F)	60 (140)	230 (450)	Selectable
Freezing Point, °C (°F)	-135 (-210)	<-18 (<0)	<-18 (<0)
Flash Point, °C (°F)	None	>100 (>200)	None
Density (g/ml)	1.50	0.88	Variable
Ozone Depletion Potential (ODP)	0	0	0
Global Warming Potential[a] (GWP)	500	0	NM[b]
Kauri-butanol Value (K_b)	10	>200	>100

Notes: a) CO_2 = 1; 100-year ITH
b) NM = Not Meaningful

Aurora Parts and Cleaning Parameters

Aurora has cleaned a variety of bearings and bearing assembly parts in the co-solvent system. Individual parts may be cleaned several times during the various manufacturing steps. An initial cycle time of 5 minutes in the boil with ultrasonics, 5 minutes in the rinse with ultrasonics and 1 minute in the vapor was chosen. Parts with oil or grease contaminants constitute the majority of those processed through the Aurora machine. Some parts have residue from water-based cutting fluids; these are rinsed with water before being put through the HFE/co-solvent process.

3M and Petroferm provided on-site technical expertise to support the startup. The system has been operating under the full control of Aurora personnel for several months and is performing well. Aurora people have optimized the cleaning cycle at 3 minutes in the boil sump with ultrasonics, 3 minutes in the rinse sump with ultrasonics and 1 minute in the vapor zone. Emission data show that losses are approximately 0.09 kg/hr-m^2 including any fluid dragout.

* HFE 7100 is 1-methoxy-nonafluorobutane ($C_4F_9OCH_3$). Solvating Agent 70 is a specially-formulated cleaning composition containing long-chain aliphatic esters and propylene glycol alkyl ethers.

Summary and Conclusions from Omnirel and Aurora Bearing Experience

The Omnirel and Aurora Bearing HFE/co-solvent cleaning test results can be summarized as follows:

- The HFE/co-solvent process was dropped into completely unmodified, conventional vapor degreasing equipment, where it operates fully satisfactorily.
- Routine production parts are cleaned as well in the new process as they were with HCFC-141b, TCE or aqueous cleaners.
- No compatibility problems were encountered with the HFE process.
- Cycle times were equal to or less than those used in production with HCFC-141b or TCE, and far shorter than those for aqueous cleaning.
- HFE emissions were much lower than from HCFC-141b or TCE emissions.
- The co-solvent process would also function using hydrofluorocarbons (HFCs) as the fluorochemicals.
- Cleaning costs for the new process are competitive with or lower than those of other cleaning processes.

The test program described here demonstrated that co-solvent vapor degreasing can replace ozone depleting solvents or other chlorinated solvents in conventional vapor degreasers. It can also economically replace poorly performing aqueous cleaners. Minimal, if any, vapor degreaser modification is required, and the process offers good performance in a variety of cleaning applications. The HFE/co-solvent process appears to be a viable, long term, low-capital cost solution for many cleaning problems.

Note: For questions or comments, the authors can be contacted at Petroferm Inc., at fax 904-261-6994 or on the Internet at Kevin Petro @ aol.com

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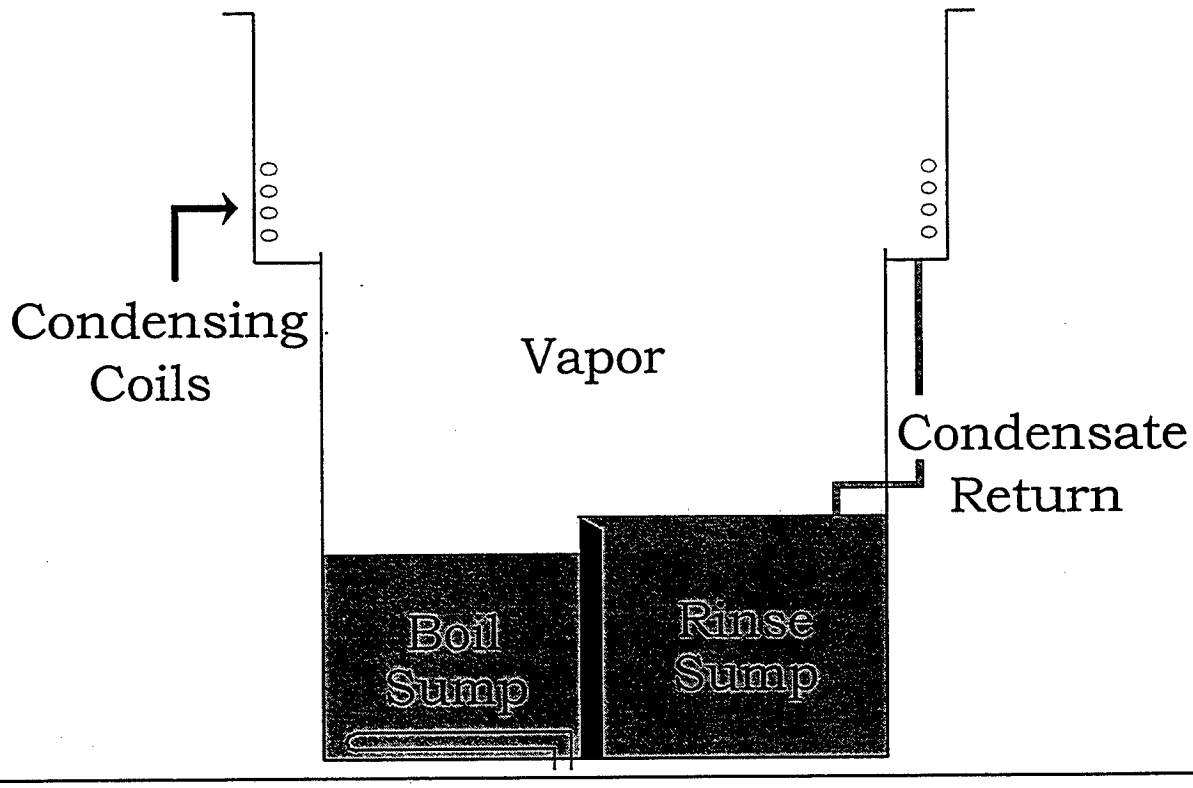
APPENDIX 1

TYPICAL
VAPOR DEGREASING EQUIPMENT



Non-ODS Handwipe Cleaner for Precision Cleaned Space Shuttle Main Engine Hardware

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ABSTRACT

Various assembly, test, and handling operations are performed upon precision cleaned Space Shuttle Main Engine (SSME) hardware after the final required cleanliness levels have been verified. This cleanliness level must be maintained throughout these operations to ensure the successful function of the SSME during test and flight. Historically, the same solvents used to perform the cleanliness verification of precision cleaned hardware have also been used for handwipe operations. These solvents were trichlorotrifluoroethane (CFC-113) and 1,1,1-trichloroethane (TCA). World-wide environmental regulations halted the production of these and other ozone-depleting substances (ODSs) on December 31, 1995. A variety of aqueous and solvent candidates were reviewed and evaluated to identify an acceptable handwipe replacement for CFC-113 and TCA.

BACKGROUND

The proper functioning of the Space Shuttle Main Engine is critically dependent upon specified cleanliness levels, which are established and verified during final precision cleaning operations. Violations of these requirements during post-cleanliness verification operations, such as engine assembly, testing and miscellaneous handling operations could lead to the blockage of critical orifices in the propellant flow streams and/or uncontrolled ignition reactions with the oxidizer propellant. Either or both of these events could cause engine failure. Various contamination-control techniques are utilized to protect against contamination. However, particles and/or hydrocarbons that may inadvertently be introduced during handling operations must be removed to maintain the established level of cleanliness. Historically, the same solvents, trichlorotrifluoroethane (CFC-113) and 1,1,1-trichloroethane (TCA), used for final precision cleaning and verification have also been used for handwipe cleaning during various assembly, test and handling operations. These two solvents, along with a number of other materials containing chloride and bromide, were categorized and are regulated as Class 1 ozone depleting substances (ODSs) by the 1990 U.S. Clean Air Act (CAA). In accordance with the amended 1994 U.S. CAA, the manufacturing of these materials was banned as of January 1, 1996. This required the identification and implementation of alternate cleaning agents. Over 200 aqueous and solvent candidates were identified and approximately 55 cleaners were tested for SSME final cleanliness maintenance handwipe operations as potential replacements for CFC-113 and TCA.

TEST PROCEDURES

Evaluation Strategy

A multitude of cleaners have been introduced to the market as replacements for ODSs. To ensure a successful evaluation program, a defined list of criteria for an acceptable non-ODS handwipe cleaner for SSME final cleanliness maintenance operations was established. Applicable engineering documents were reviewed to determine specified program requirements of a handwipe cleaner, while all assembly, test, and handling activities at the Rocketdyne Canoga Park, Stennis Space Center (SSC), and Kennedy Space Center (KSC) locations were reviewed to determine the practical requirements.

These reviews resulted in the identification of the following handwipe cleaner criteria:

- Little or no residue on cleaned surface upon evaporation
- Acceptable volatility to promote evaporation without facilitated drying
- Compatibility with SSME metallic and non-metallic materials
- Effective at the handwipe removal of known contaminants
- Compliant with all applicable Environmental, Health and Safety Regulations, including
  - No flashpoint to eliminate fire potential
  - Compliant with all applicable local regulations
  - Approved by the EPA Significant New Alternatives Program (S.N.A.P.)
  - Little or no ozone depleting potential
- Available for use currently or in the near future
- Acceptable to users

A systematic approach to this evaluation was developed to minimize cost while maximizing the effectiveness of laboratory resources. This approach evolved into the three phased Non-ODS Handwipe Cleaner Evaluation Decision Tree diagrammed in Figure 1.

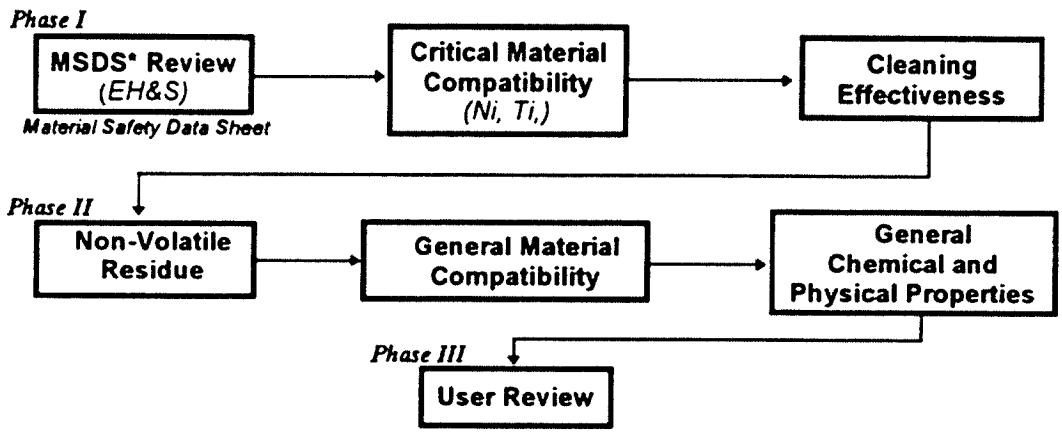

Figure 1. Non-ODS Handwipe Cleaner Evaluation Decision Tree

This systematic down-select approach is similar to a previous Rocketdyne study used for evaluating aqueous immersion cleaners (Reference 1). The order of the tests in each phase took into account cost, time and the results of previous evaluations (References 1, 2.) The tests requiring the least amount of time were completed early in the evaluation. The applicable tests, whose use in previous studies eliminated a significant number of candidates, were also used in the early phases. The more restrictive and costly tests were evaluated in the later phases. Environmental, Health and Safety compliance, compatibility with two critical materials, and the effectiveness of the candidates as handwipe cleaners were evaluated during Phase I. A candidate that failed any of the individual tests of Phase I was eliminated from consideration, and not evaluated during any other test in that phase or any subsequent testing phase. Phase II testing included a measurement of non-volatile residue (NVR); other material compatibility (non-metallic materials and metallic alloys); and a series of tests to determine or confirm some general chemical and physical properties. Phase III involved user review and acceptability, and was actually conducted simultaneously with Phase II.

Phase I

MSDS Review

The Material Safety Data Sheet (MSDS) and any relevant technical literature for each candidate was reviewed for compliance with appropriate federal, state and local environmental, health and safety regulations. These included local California air district regulations, the Environmental Protection

Agency's (EPA) Significant New Alternatives Program (S.N.A.P.) and the U.S. CAA, as well as all applicable OSHA toxicity requirements. All potential and pending regulations and restrictions were also considered. In summary, to satisfy the numerous environmental, health and safety issues, a candidate had to meet the following stipulations to continue in the evaluation process:

- No carcinogenic (or suspected carcinogenic) compounds
- Low toxicity (Applicable OSHA Personal Exposure Limit, PEL, must be within levels that can be met with minimal engineering controls and/or personal protection equipment)
- Non-ODS
- No flashpoint
- No pending or anticipated federal, state or local regulation.

The MSDS and technical literature for some cleaners also listed general physical and chemical properties as well as material compatibility information. A cleaner was rejected during this phase if it had an acidic pH, a very slow or low evaporation rate, or gave off strong or offensive odors. To minimize duplication of effort, any listed compatibility information was compared against the list of metallic and non-metallic materials of which the SSME is composed. Any noted incompatibility with the SSME materials also eliminated a cleaner from consideration.

Critical Material Compatibility

Many critical SSME hardware components are produced with nickel (Ni), nickel base alloys and titanium (Ti) alloys. Cleaners, as well as other processing compounds used at Rocketdyne, undergo two screening tests to verify compatibility with these metallic alloys. Compatibility with Ni was determined by a sulfur embrittlement test, while a stress corrosion cracking evaluation test was utilized for Ti compatibility.

Nickel Compatibility - The test specimens for this test were two inch lengths of the commercially pure nickel alloy, Nickel 200 (Ni 200) seamless tubing, with 0.15 inch O.D. and 0.015 inch wall thickness. The tubes were first ultrasonically cleaned in acetone for 1 - 5 minutes, then boiled in deionized water for 1 - 5 minutes. After drying, each specimen was crimped at one end, forming a "test tube." The Ni 200 test tubes were filled, at least half way, with the candidate cleaner at the intended use concentration. The cleaner was then sealed in the tube by crimping the open end. Highly volatile cleaners (e.g., solvents) were allowed to evaporate prior to sealing. For each candidate, a control "test tube" was prepared under the same conditions, except the tube was empty. Each sealed Ni 200 test tube was encased and sealed in a 300 series stainless steel "test tube" of a slightly longer length and diameter. Sealing of the 300 series test tubes was also accomplished by crimping. (see Figure 2.) The control sample was tested first by placing it horizontally in an air atmosphere furnace, and heating for 10 ± 2 minutes at 1300 ± 25 °F. In a subsequent furnace load, the tube containing the cleaner was heat treated in the same manner. A full circular cross section of each tube was mounted, polished and etched in preparation for metallographic examination. An 100X examination of each mount was performed to determine the presence or absence of intergranular attack (IGA), as compared to the control. Any IGA measured greater than 20% (i.e., 0.003 inches) of the Ni 200 tube wall thickness was recorded as evidence of nickel incompatibility. The test was repeated, at least once, if evidence of IGA less than 20% was observed.

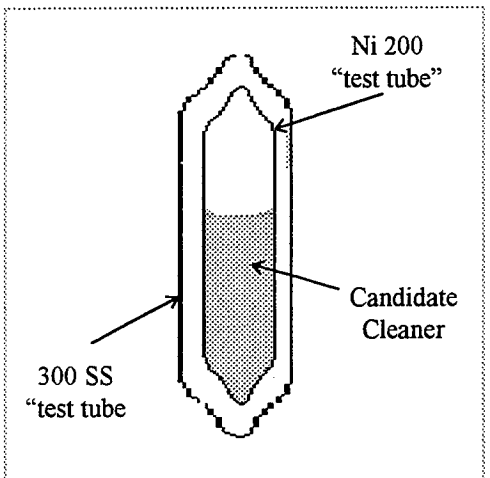

Figure 2. Ni Compatibility Specimen

Titanium Compatibility - The compatibility of cleaners with this metallic alloy was determined by utilizing an elevated temperature stress-corrosion cracking test. Standard Rocketdyne test specimens, measuring 1 ± 0.2 inches X 6.9 ± 0.01 inches, were cut parallel to the transverse direction of 0.045 - 0.050 inches thick, rolled 5Al-2.5Sn Ti alloy (AMS 4910) sheet (see Figure 3).
The panels were cleaned, conditioned and etched by a 10 - 20 minute immersion process in a heated (270°F) scale conditioning solution (47%/wt. sodium hydroxide, 1%/wt. sodium dichromate, remainder deionized water), followed by a 3 - 5 minute immersion process in a heated (85°F) HNO_3-HF descale solution (63 - 70% HNO_3, 5± 1 NH_4F, balance deionized water).

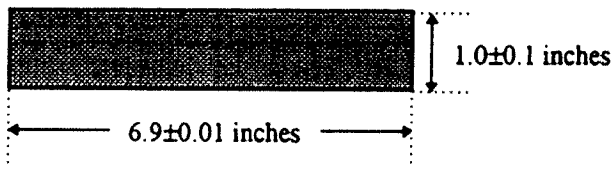

Figure 3. Ti SCC Test Panel

Three panels were used for each cleaner candidate. Each panel was carefully loaded into a bent beam apparatus made of stainless steel (see Figure 4). The calculated outer-fiber bending stress, when loaded, was 87 - 90 KSI. All loaded panels were handwiped with a clean lint-free cloth, moistened with acetone, to remove any extraneous contamination, including fingerprint oils. One of the three coupons for each cleaner was coated with the cleaner and allowed to air dry for 24 hours. The second panel was coated immediately prior to entry into the furnace, while the third stressed coupon was left uncoated as a control specimen. The coupons were placed in an air atmosphere furnace at 1000°F for 4 hours. After cooling to ambient temperature, the specimens were cleaned as necessary, and examined at 30X for cracks. Then using the guided bend apparatus each specimen was bent around a 10T diameter mandrel and again examined at 30X for cracks. A cross section through the bend of each specimen was taken. These samples were then mounted, polished and etched in preparation for metallographic examination. Each mount was examined at magnifications up to 200X to detect the presence or absence of cracks. If no cracks were observed, the cleaner was considered compatible with 5Al-2.5Sn Ti alloy.

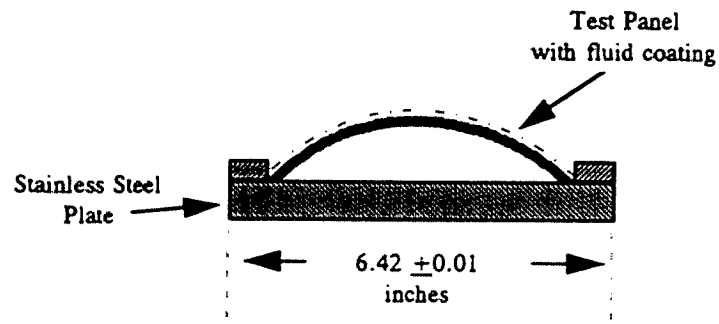

Figure 4. Ti SCC Test Panel Apparatus

Cleaning Effectiveness

Cleaning effectiveness, or the ability to remove contamination utilizing a handwiping technique, was the third property evaluated during Phase I. Most contamination of SSME hardware is a result of fabrication, and the compounds and materials applied to hardware during those fabrication operations. These compounds and materials, otherwise referred to as "production support materials" (PSM), are not a part of the final hardware product, and must subsequently be removed. The test contaminants used for the cleaning effectiveness tests are representative of the various Rocketdyne PSM classes and chemical compounds. These materials are listed in Table 2.

TEST CONTAMINANT	DESCRIPTION
CIMSTAR 3700 by Cincinnati Milacron	Semi-synthetic water-soluble machining coolant containing mineral oil, di- and tri-ethanolamines, aminomethylpropanol and a synthetic lubricant;
Houghto Draw 3105 Oil by E. F. Houghton & Co.	Highly chlorinated drawing compound was containing 10-30% mineral oil.
Alum-Tap Tapping Fluid by Winfield Brooks	Non-sulfated aluminum cutting fluid containing a light napthenic oil and tetrachloroethylene.
Cool Tool by Monroe Fluid Technology	Non-sulfated, non-silicated cutting and tapping fluid containing a heavy paraffinic oil distillate compound.
DTE 24 by Mobil Oil	A machining coolant composed of a petroleum distillate oil.
Rust Foil L-492 Preservative Oil by Franklin Oil Co.	Solvent-dispersed corrosion preventive coating containing aliphatic hydrocarbons and mineral oil.
MolyKote Metal Assembly Paste ("Molylube", "MolyG") by Dow Corning	A anti-seizing and gasket sealing compound composed of a MoS_2-filled petroleum-based grease.
Braycote 236 by Castrol Inc.	Petrolatum-based o-ring lubricant.
Krytox 240AC Grease) by Dupont	Oxygen-compatible perfluoroalkylether lubricant with TFE filler.
Stick Wax 140 by Castrol Industrial North America	A machining aid made of a blend of solid lubricating aliphatic hydrocarbon waxes.
Bio-Pen P6R by Ardrox Inc.	Detergent-based, visible, solvent-removable penetrating dye penetrant
Bio-Pen P6F-4 by Ardrox Inc.	Fluorescent, water-washable dye penetrant
Bio-Pen NQ-1 Developer by Ardrox Inc.	IPA and silica dye developer
Micronic 882 by Bray Oil Co. *(MIL-H-83282)*	Synthetic hydrocarbon hydraulic fluid containing triphenylphosphate
Dykem Spray SP-1100 by Dykem Corp.	Solvent-based blue machining ink containing nitrate cellulose.
Sharpie Marker #30002 by Sanford Corp.	Red water-resistant permanent marking pen.
China Marker 165-T by Empire Berol Corp.	Red water-resistant marking pencil.
Hydro Marker 665-T by Empire Berol Corp.	Red water-soluble marking pencil.
Ultragel II by Echo Ultrasound	Low sulfur, non-silicated glycerin based ultrasonic couplant
Scotch Industrial #470 Electroplating Tape by 3M Inc.	Vinyl plastic plating maskant tape with translucent synthetic rubber adhesive
Polyken #221 Tape by The Kendall Co.	Polyethylene coated cloth packaging tape with natural rubber adhesive

Table 2. Test Contaminants

The handwipe cleaning effectiveness of each cleaner was determined by assessing its ability to remove each contaminate from a standard Rocketdyne test panel, composed of Ni alloy 718 (AMS 5596), measuring 3.00 ± 0.03 inches X 6.00 ± 0.03 inches X 0.04 ± 0.01 inches. The panels were cleaned to a bright, uniformly polished, water break-free condition using deionized water and Scotch-brite abrasive cloth per MIL-A-9962, Type III, Grade A. The initial weight of each cleaned panel was measured after being allowed to dry. The liquid, grease and wax materials were applied evenly over 70 - 75% of one side of each panel, while the sprays, markers, and tapes were directly applied to the panels. The contaminated panels were conditioned by heating for 1 hour at 200°F. After cooling to room temperature, the contaminated side of each panel was handwiped for about 1 minute with a clean cheesecloth moistened with the candidate cleaner at the intended use concentration. If not visually clean, the moistened-cheesecloth handwiping process was repeated up to two more times. The necessity for a subsequent wipe with a water-moistened cloth to remove cleaner residue was also noted during the inspection for visual cleanliness. Upon reaching visual cleanliness or a maximum of three removal attempts, the surface condition of the panel was evaluated and the ease of soil removal was rated. Surface condition was determined by inspecting for visual cleanliness and a water break-free surface. The amount of effort used to clean the panels was estimated on a relative scale: Easily removed, Removed with average effort, or Difficult to remove. The final weight of the panel was determined after the final water break free inspection had been performed. These tests were repeated in triplicate. The average final surface cleanliness condition, the number of required cleaning cycles, and estimated effort was reported.

Phase II

Non-Volatile Residue (NVR)

The non-volatile residue (NVR) of a cleaner indicates the amount of contamination the cleaner could potentially leave on a "cleaned" surface upon evaporation. This residue could have the same detrimental effect on the performance of the SSME as contamination resulting from other materials. The NVR measurement was performed upon a 500 ml sample, after being filtered through a 10 micron pore size filter. The filtrate was evaporated to approximately 10 - 20 ml using a rotary evaporator. This volume was then transferred to a clean, constant-weight (within 0.3 mg) 30 ml weighing dish, which had been previously weighed to the nearest 0.1 mg. The cleaner was allowed to continue to evaporate down to a volume of approximately 5 ± 0.5 ml. The weighing container dish and its residual contents were placed in a clean, dust-free, constant-heat oven at 110 ± 5°F for a minimum of 1 hour. After complete evaporation, the dish was allowed to cool to room temperature in a desicator, and then weighed to the nearest 0.1 mg. The dish was returned to the constant temperature oven for 30 minutes, allowed to cool and weighed again to the nearest 0.1 mg. If the difference between the weights was greater than 0.3 mg, the 30 minute heating period was repeated until the difference between successive weighings was 0.3 mg or less. The original weight of the dish was subtracted from the final weight. If the weight was greater than 10 mg, the level set with the control solvents CFC-113 and 1,1,1,-TCA, the cleaner was rejected.

General Material Compatibility

The SSME is composed of a wide variety of materials, many of which may be handled during the assembly, test and flight operations. The compatibility of the cleaner candidates with all these materials were considered. Information concerning compatibility with the metallic and most of the non-metallic materials of the SSME were obtained either from literature searches or the cleaner manufacturer. Details of the testing procedures were also obtained if the compatibility test performed by the manufacturer was not in accordance with a standard industry test method. If no information was found concerning the compatibility of certain materials with a candidate cleaner, then an evaluation using a general immersion test was performed.

Metallic Alloys - Corrosion by immersion was the testing procedure used to evaluate compatibility with metallic alloys, if other compatibility results were not available for a cleaner. Test samples, measuring approximately 1.00 inch X 3.00 inches by 0.625 inches were made from one or more of the appropriate representative alloys:

- Cobalt base alloy per AMS 5608
- 2024 aluminum alloy per QQ-A-250/4
- Nickel base alloy 718 per AMS 5596
- Copper OFHC, per RB0170-047 or QQ-C-576
- 4130 alloy steel per MIL-S-18729, Condition A
- Iron base alloy 903 per RB0170-196
- 440C alloy per RB0160-063 or AMS 5618 (heat treated)
- 21-6-9 stainless steel per AMS 5595

Two panels of each material requiring evaluation were cleaned using an acetone-moistened cloth to remove all grease and ink markings. The samples were then cleaned using an Scotch-brite abrasive mat (per MIL-A-9962, Type III, Grade A) dampened with deionized water until a bright, uniform polished, water-break free surface was obtained. If used, the 4130 and alloy 903 panels were immediately dried with gaseous nitrogen (GN_2) to prevent corrosion. One sample of each material type was reserved as a control for comparison purposes. The other panels were placed in a clean glass petri dish containing sufficient quantity of the cleaner, at the intended use concentration, such that at least 3/4 of each sample was immersed in the fluid. The vessel and its contents were covered and allowed to remain at ambient temperature for 24 $\pm$ 1 hour. For highly volatile cleaners (e.g., solvents), the 24 hour immersion process was performed in a sealed container to minimize evaporation. The panels were then withdrawn from the candidate cleaner and rinsed with deionized water. The test panels were dried for approximately 1 hour at 200 $\pm$ 10 degrees. After cooling to ambient temperature they were visually inspected at 100x to 200x for any evidence of etching, pitting or other corrosion as compared to the control panels.

Non-metallics - Numerous non-metallics are used throughout the SSME including sealants, gaskets, o-rings, adhesives, protective coverings, structural composites, etc. Many manufacturers provided compatibility data of their cleaners with the more common non-metallics materials, such as PTFE (Teflon®), butyl rubber, nitrile (Buna-N®) rubber, neoprene, fluoroelastomers (i.e., VitonA®), silicone rubber, polyimides (i.e., A-Vespel®). As with the metallic alloys, if compatibility data was not available either from the manufacturer or literature, a standard immersion compatibility test was conducted . Specimens of the appropriate materials, measuring approximately 3.00 inches X 1.00 inches were cut from bulk samples. The dimensions (length, width and thickness), as well as the weight and hardness of each specimen were measured and recorded. The specimens were immersed in the candidates for 1 hour at room temperature. A visual inspection of all specimens was performed immediately after removal from the cleaner. Any notable signs of deterioration or change, such as softening, cloudiness, etc., as compared to the control was noted as evidence of incompatibility. The specimens were allowed to air dry for approximately 5 - 10 minutes. The final length, width, thickness, weight and hardness were measured. Again, any significant differences were noted as indications of incompatibility.

Oxygen Compatibility - Oxygen, a highly reactive material, is the oxidizer propellant used for powering the SSME. Due to its very sensitive level of reactivity, it is a requirement to evaluate all materials which may come in contact with this propellant. Oxygen compatibility of the handwipe cleaner candidates was performed by mechanical impact in accordance with NASA Handbook (NHB) 8060.1B Test 13. Both the liquid and residue form of all qualified cleaner candidates were evaluated. Twenty test cups were filled with enough volume of the cleaner candidate liquid to measure 0.050$\pm$0.005 inch thick. These samples were tested in liquid oxygen (LOX) at an impact energy of 10 kg-m. For evaluation of the cleaner residue, twenty standard nickel alloy 718 disks were dipped into each cleaner and then allowed to dry. These samples were subjected to mechanical impact testing in 8800 psi LOX at the same 10 kg-m impact energy as used on the liquid samples. The cleaner was recorded as "LOX-compatible" if none of the twenty liquid samples and none of the twenty residue samples "reacted" (i.e., chemically changed or transformed as denoted by an audible noise, electronically and visually detected flash, or obvious charring

of the sample or supporting equipment). If one sample of either set of twenty did react, then 40 additional samples were tested. All forty of these samples would have to complete the testing without reaction to deem the cleaner compatible with LOX.

General Physical and Chemical Properties

Phase II testing concluded with a series of general property tests. The properties evaluated depended upon the chemical composition of the cleaner. A matrix of the general requirements for the physical and chemical properties tested as compared to the type of cleaner candidate evaluated is provided in Table 3.

PROPERTY (and Test Method)	AQUEOUS BASED CLEANER	SEMI-AQUEOUS BASED CLEANER	SOLVENT BASED CLEANER
Appearance by visual inspection	X	X	X
Flashpoint by ASTM D92 or other open-cup test method	X	X	X
Chloride Content by ion chromatography	X	X	X
Boiling Point by ASTM D86	X	X	X
Density by ASTM D941	X	X	X
Viscosity by ASTM D445	X	X	X
pH by any calibrated method	X	X	--
Identification of Organic Constituents by IR analysis		X	X
Distillation Range by ASTM D86	--	--	X

Table 3. General Physical And Chemical Properties

These properties were used as part of the receiving inspection process to maintain proper material control and ensure hardware quality upon implementation of the cleaner on SSME production hardware.

Phase III

User Evaluation

This phase of testing is a continuous one. All properties, material compatibility or other considerations identified by the users were evaluated during this Phase. In conjunction with the evaluation, a series of status briefings was presented at the respective use sites, including various assembly operations at the Rocketdyne Canoga facility, Test Operations at SSC, and Flight Operations at KSC. Feedback during these briefings has resulted, to date, in the performance of two additional compatibility tests.

The evaluation review performed at one of the user sites revealed that two adhesives, although not required, are handwiped as part of general contamination control: a polyurethane adhesive used as part of a non-removable protective shell for certain SSME hardware; and a neoprene rubber adhesive used to bond Teflon-covered Buna-N gaskets to ABS hardware flange covers. A request was made by a user to evaluate material compatibility of these adhesives with the cleaner candidates. Each adhesive was tested by the same procedure previously described for other non-metallic materials. Again, any significant differences, as compared to the control, CFC-113 and TCA, were noted as indication of incompatibility.

The user survey will continue to be distributed on a periodic basis, All resulting information will be reviewed and analyzed. Additional testing based upon the results of the analysis will be performed as necessary.

RESULTS

Of the fifty-five cleaners evaluated, 52 were not evaluated past Phase I testing: 38 failed due to unacceptable information listed on the MSDS or technical literature (i.e. environmental, health or safety concerns, material incompatibility, or unacceptable chemical or physical property data); 11 failed due to incompatibility with nickel and/or titanium; and 2 failed due to limited cleaning effectiveness at removing Rocketdyne production support materials/contaminants. The manufacturer of one cleaner halted production during Phase I testing, which eliminated it from consideration. Two cleaners were not evaluated past Phase II due to unacceptable NVR levels. The remaining cleaner passed all the Phase II and III tests. The purpose of this evaluation was to identify handwiping cleaners that met the specific requirements detailed in this report, and not to give endorsement to the quality of any cleaner. The results of Phase I, II and III are summarized in Attachment 1.

CONCLUSIONS

A detailed evaluation program, involving the testing of over 200 candidates, resulted in the identification of Vertrel XF, ($C_2H_2F_{10}$), a hydrofluorocarbon (HFC) fluid produced by Dupont, as the most viable candidate currently available for critical handwiping procedures used on SSME hardware after final cleanliness verification. This solvent meets all the necessary and established requirements for these cleaning operations. The Rocketdyne Environmental Health and Safety (EH&S) department has reviewed and approved this fluid for all appropriate SSME handwipe applications. Vertrel XF showed similar, if not superior, cleaning capability for removing a variety of contaminants used on SSME hardware as compared to the previous standard cleaning fluids CFC-113 and TCA. This fluid evaporates quickly and is has no flashpoint. Vertrel XF is compatible with the all the materials of the SSME, including oxygen at ambient and high pressures. This solvent also meets the required cleanliness levels, as measured by non-volatile residue (NVR) and particulate size limitation, for safe and efficient engine operation.

Vertrel XF has been implemented into the SSME production system by approval for use as a type IV hydrofluorocarbon material to the Rocketdyne material specification RB0210-030, "Fluorocarbon Fluid". Its use for handwiping operations is regulated through the Rocketdyne process specification RA1110-016, "General Precision Cleaning", which is applied to the SSME program by reference in the SSME Program final cleanliness contract specification, RL10001, "Specification For Cleanliness of Components For Use in Oxygen, Fuel, and Pneumatic Systems".

ACKNOWLEDGMENTS

The author wishes to acknowledge and thank M. Fritzemeier and A. Brown for technical support and editorial advice, as well as C. Schack and M. Somerville for their dedication and diligence in performing various tests in support of this project.

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Attachment 1. Phase I, II and III Test Result Summary

CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS					
			PHASE I		PHASE II		PHASE III	
A500 Biodegradable Cleaner/Degreaser	Stoner	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
APC Formula Cleaner	Marking Methods, Inc.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ✓ ⊗(c)	N/T		N/T	
Acetone		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Amberclean L12	Innovative Organics	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ✓ ✓	NVR General Material Compatibility Chemical & Physical Properties	⊗(d) n/t n/t	N/T	
Amberclean STR3000	Innovative Organics	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Aqua Solv 860	M & T Harshaw	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Brulin SD 1291	The Brulin Corp.	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Clean-N-Dri	Clean Room Products	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	

Notes: ✓ = Passed requirements stipulated in this report, ⊗ = Failed requirements stipulated in this report, n/t, N/T = Not Tested

Phase I (a) Unacceptable EH&S concern, material compatibility issue, or chemical/physical property information listed on MSDS or in technical literature

(b) Failed Ni and/or Ti compatibility testing

(c) Ineffective at removing ≥50% of the tested contaminants, or Required a subsequent water wipe

Phase II (d) NVR of >10mg/500ml

CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS			
			PHASE I	PHASE II	PHASE III	
Citrus Fresh	Chemco	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Citrus Base Cleaner	3M	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
CC-1000 Hydrocarbon Dispersant	Charles A. Crosbie Labs, Inc.	Solvent (Blend)	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Citrex	Inland Technology Incorporated	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Cyclohexane		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Dykem Special Blue Cleaner	Dykem	Aqueous	MSDS Review Critical Material Compatibility ***Production Halted by Mfr.***	✓ ✓ n/t	N/T	N/T
Daraclean 211	Grace	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ✓ ⊗(c)	N/T	N/T
Daraclean 292XX	Grace	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
D-Greeze 500 Recyclable	Solvent Kleen	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T

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(c) Ineffective at removing ≥50% of the tested contaminants, or Required a subsequent water wipe

Phase II (d) NVR of >10mg/500ml

CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS					
			PHASE I		PHASE II		PHASE III	
DOT 111/113	Delta-Omega Technologies, Inc.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
D.S. Wipe Solvents (103, 104, 105)	Dynamold Inc.	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
EB-AK Cleaner	Jim Cappello Associates	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Electron	Ecolink	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Ethyl acetate		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Flo-Shine	Southend Janitorial Supply	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Formula 409	Clorox	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Generation 2000 Citri-Solv	Generation 2000	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	

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Phase II (d) NVR of >10mg/500ml

CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS					
			PHASE I		PHASE II		PHASE III	
Generation 2000 Multi-Kleen	Generation 2000	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Glass & Plastic Cleaner	The Texwipe Co.	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
HCFC 123 (C_2FCl_2)	Allied-Signal	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
HCFC 141b (C_2FCl_2)	Allied-Signal	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
HCFC 225 ($C_3F_5Cl_2$)	Asahi	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Hurri-Safe All Purpose Industrial Strength Cleaner	O.C.S. Manufacturing	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ✓ ✓	NVR General Material Compatibility Chemical & Physical Properties	⊗(d) n/t n/t	N/T	
Isopropyl alcohol		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
M-Pyrol (C_5H_9NO)	ISP Technologies	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	

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Phase II (d) NVR of >10mg/500ml

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CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS			
			PHASE I	PHASE II	PHASE III	
OS-10 (methyl siloxane)	Dow Corning	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
OS-20 (methyl siloxane)	Dow Corning	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
PF 5060 (C_5F_{12})	3M	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Perchloroethylene (tetrachloroethylene)		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Precision Clean Cleaner / Degreaser	LPS Laboratories, Inc.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T	N/T
QED	Ecolink	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
RK-60	World Laboratories	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T	N/T
Resque 2	DM Laboratories Corp.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T
Rosstech Safety Solvent	Global Tech	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T	N/T

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CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS					
			PHASE I		PHASE II		PHASE III	
Sil-Clean	Amtex Chemical	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Simple Green	Sunshine Makers	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Solv-It	Four Star Chemical	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Spray White	Allied Kelite Div., Witco Corp.	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Supersolv L	Allied Kelite Div., Witco Corp.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
TexClean 100	The Texwipe Co.	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Trichloroethylene (TCE)		Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Turco Eco-Solv	Turco Products, ATOCHEM	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	
Turco 6820	Turco Products, ATOCHEM	Semi Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	⊗(a) n/t n/t	N/T		N/T	

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Phase II (d) NVR of >10mg/500ml

CLEANER NAME	MANUFACTURER	CLEANER TYPE	TESTING RESULTS					
			PHASE I		PHASE II		PHASE III	
Turco Meteor	Turco Products, ATOCHEM	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
V.A.C. (Volatile Aqueous Cleaner)	*	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Vari-Kleen	Allied Kelite Division, Witco Corp.	Aqueous	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ⊗(b) n/t	N/T		N/T	
Vertrel XF (C_5F_{10})	Dupont	Solvent	MSDS Review Critical Material Compatibility Cleaning Effectiveness	✓ ✓ ✓	NVR General Material Compatibility Chemical & Physical Properties	✓ ✓ ✓	User Evaluation	✓

* *(A cleaning solution composed of deionized water, isopropyl alcohol, ammonium hydroxide, Surfnol 61 Surfactant by Air Products, Inc., and Aerosol OT-75 Surfactant by American Cyanamid)*

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REPLACEMENT OF HAZARDOUS SOLVENTS FOR HANDWIPING OPERATIONS IN GAS TURBINE ENGINE MANUFACTURING

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Abstract

A substantial amount of hazardous solvents, primarily methyl ethyl ketone (MEK) and isopropyl alcohol (IPA) are used in the manufacturing of components used in gas turbine engines. Although many cleaners have been approved for general tooling and fixture cleaning, specialty applications still consume a significant quantity of the solvents. This is especially significant since the hazardous waste volume is much greater than the solvent itself, because a large amount of applicators and disposable shaping implements are used in removal of un-cured rubber and are also discarded as hazardous waste. A program was performed which eliminated the need for these solvents in hand wiping operations during manufacturing of stator airfoil assemblies. Both an aqueous and a non-hazardous hydrocarbon solvent were identified for operations involving braze surface preparation, preparation of surfaces prior to bonding of various rubber materials, removal of excess un-cured rubber, and general cleaning. The aqueous hand wiping operation is used in preparation for brazing and also bonding of several types of rubber to both metallic and non-metallic substrates. The hydrocarbon cleaner is used to shape un-cured rubber for aerodynamic sealing of shroud and airfoil interfaces. The substitutions resulted in no material property or performance debit, no additional cost to the process, substantial reductions in hazardous waste disposal volume and costs, and reduced worker exposure to hazardous solvents.

Introduction

The manufacturing of jet engine components involves a large number of chemical processes which generate very significant quantities of hazardous and non-hazardous waste. Many of the components require cleaning prior to subsequent operations such as welding, brazing, bonding, and heat treatment. In addition the machining processes in the manufacture of components and assemblies requires local cleaning of surfaces. During the assembly process surfaces must be cleaned locally and the simplest option is to hand wipe the affected area.

One family of components which require a large amount of handwiping is stator assemblies. Most of the stator components are assembled from numerous pieces. An inner circular shroud, either as a single piece or multiple pieces, and an outer shroud are connected together by many airfoils. For the stators which operate at lower temperatures the airfoils are attached mechanically to the outer shroud. The airfoils are attached to the inner shroud with a high strength oven cured silicone rubber. The joints between the airfoils and shrouds are filled with rubber to make the component aerodynamically smooth. The silicone rubber fillets which transition the airfoils to the inner shroud must be mechanically shaped using a fluid to achieve the required smoothness and transition. This rubber can be shaped with a variety of solvents, but typically isopropyl alcohol (IPA) is used. The outer fillet is typically composed of a one-part red RTV rubber. This rubber has been traditionally shaped with methyl ethyl ketone (MEK). Isopropyl alcohol cannot be used since in inhibits the cure of the RTV rubber used for stators. This mandates the use of a hazardous air pollutant in the manufacturing process.

For high temperature stators the airfoils are brazed to the inner and outer shrouds to form rigid assemblies capable of extended high temperature exposure. A second example is brazing of blade rub strips into the interior surface of an engine case. The strip is a porous metallic or honeycomb structure and is used to achieve a good seal at the tip surface of the compressor blades. The surfaces to be bonded

must be clean to achieve complete wetting and adhesion of the braze. The surfaces to be brazed must be cleaned to permit good wetting of the braze alloy; thus the structural integrity of the components are subject to the quality of the hand cleaning operation. Typically IPA and MEK are used to clean the surfaces.

Additional handwiping processes under the scope of this program were turbine vane brazing and cleaning of turbine vanes prior to application of a ceramic sealing rope using RTV rubber. Some turbine vanes have an anti-rotation tab brazed on to prevent the vane segments from rotating. The surface must be cleaned prior to brazing to permit full braze coverage and adhesion. In addition if very high temperature sealing of turbine vanes is required then occasionally a Nextel ceramic rope is attached to the vane with RTV rubber. The surface of the vane must be cleaned before application of the RTV rubber and the excess rubber must be removed after bonding of the ceramic rope. Presently IPA is used to clean the surfaces and MEK is used to remove the excess rubber.

Evaluation Methods and Results

Although there were specific technical requirements for each process described above certain common requirements for qualification of alternate cleaners were mandated by the manufacturing facility where the cleaners were used. One of the most significant requirements restricted the composition of the cleaners. The Pratt & Whitney (P&W) plant where these particular cleaners were to be used did not permit cleaners containing phosphates or terpenes due to local discharge and disposal regulations. Cleaners initially selected for evaluation varied widely in composition, and included isoparaffinic hydrocarbons, water based glycol ethers, petroleum fractions, and blends of the above. Initially many cleaners were considered, however seven cleaners were down selected after a review of the associated material safety data sheets for certain hazardous components and for flash point. A list of the seven cleaners evaluated is shown in Table 1.

Table 1. Cleaners Selected for Evaluation

CLEANER	MANUFACTURER
D99	Tiodize
SD 1291	Brulin
MP 1793	Brulin
Aqua-Safe	Brulin
EZE 662	Calgon
Envirosolv 655	Fine Organics
Evasol	Mag Chem

Testing performed included material compatibility testing [stress corrosion on titanium 8-1-1, hot corrosion on (steels, nickel alloys, and cobalt alloys), non-metallic compatibility], odor evaluation, skin reaction, lap shear, peel strength, evaporation rate, and general cleaning capability.

For material compatibility on metals testing to confirm stress corrosion cracking (SCC) resistance and hot corrosion resistance was required. Stress corrosion testing consisted either a two point bend titanium stress corrosion on Ti 8-1-1 using a method similar to ASTM G39 or a u-bend specimen tested in accordance with ASTM F945. Testing was performed at 900°F. The hot corrosion testing was performed by exposing a small amount of cleaner on various metallic substrates representative of engine materials (e.g. certain steel, aluminum, magnesium, nickel, and cobalt alloys) for 8 hours at temperatures typical of the maximum experienced in gas turbine engines. Any cleaner causing attack greater than 0.0002 inches deep on any alloy was rejected. Non metallic materials were also evaluated with the cleaners. Hardness change and volume change (swell) were measured for various exposure times on selected elastomers, rubbers, and polymers. Other material compatibility tests were employed to evaluate

the aqueous cleaners for corrosion of tool steel. This was accomplished by spraying the cleaner on a carbon steel panel and placing it in a humidity cabinet at 120°F and 98% relative humidity for 72 hours.

The only cleaner eliminated for material compatibility problems was the Tiodize D99, which failed the hot corrosion test on AMS 4037 (2024-T3 aluminum), AMS 5536 (Hastelloy X), AMS 5544 (Waspaloy), and AMS 5608 (Haynes 188). Attack on these alloys was greater than the 0.0002 inch maximum limit. No cleaner was rejected due to any adverse skin reaction; however the odor of the Brulin SD 1291 was very offensive and thus was rejected for further consideration.

Since no gross contamination is encountered during cleaning of components prior to bonding and brazing only light soils and fingerprints needed to be removed. This was evaluated by the effectiveness in removing SAE 1010 light oil and fingerprints. Both visual and water break criteria were used to determine the effectiveness of the cleaning. Of the remaining cleaners the Aqua-Safe was by far the best for removal of light oil and fingerprints. A single wipe was sufficient to remove most or all of the contamination. The Envirosolv 655 and Brulin MP 1793 were poor at removal of fingerprints and light oil. The Aqua-Safe was pursued for further work and it was determined that a 4% concentration was the optimum concentration for removal of contamination and minimization of cleaner residue.

Peel testing to quantify adhesion of RTV 159 red rubber on anodized aluminum was performed to compare the Aqua-Safe to the baseline MEK. The peel test was based on ASTM D903. The test involves bonding of the RTV rubber to a chromic acid anodized (CAA) aluminum strip approximately one inch wide. A metal screen is encapsulated within the RTV and upon cure of the material the screen is pulled such that the rubber is either torn cohesively or peels away from the surface, or a combination of the two. Both peel strength and percent cohesive failure were measured. It was shown that the samples prepared with 4% Aqua-Safe were substantially superior to the baseline MEK samples; the samples prepared with the Aqua-Safe demonstrated complete adhesion to the substrate. In this test a silicone primer was not used and the Aqua-Safe demonstrated that the priming operation can be eliminated for the RTV 159 rubber.

Lap shear testing of Visilox V-612 A/B oven cured rubber on anodized aluminum showed that the 4% Aqua-Safe cleaner significantly enhanced the bonding as compared to the baseline MEK. In this test, performed per ASTM D816, CAA aluminum panels were cleaned either with MEK or 4% Aqua-Safe, primed with silicone primer, and bonded together with the rubber. The panels are separated in shear and the cohesive strength and percent cohesion are measured. As with the peel strength samples the Aqua-Safe demonstrated superior adhesion to the primed substrate; at least 98% cohesion was demonstrated. Lap shear testing was also performed on primed carbon-filled polyetherimide (Ultem) substrates. The bond, using Aqua-Safe, was not as good as with the aluminum, but met the minimum requirements for the application. It was expected that the material would not bond as well to the Ultem as with anodized aluminum.

Results of the peel strength and lap shear testing is shown in Table 2.

Table 2. Results of Rubber Bonding Trials

CLEANER	RUBBER	PEEL STRENGTH*	LAP SHEAR STRENGTH**	% COHESIVE FAILURE
Spec. Req't	RTV 159 (no primer)	45		
	Visilox V-612 A/B (primer)		450	90
	Visilox V-622 (primer)		140	90
MEK	RTV 159 (no primer)	25.3		0
	Visilox V-612 A/B (primer)		498.6	90
	Visilox V-612 A/B (primer)		323.3†	90†
Aqua-Safe (4%)	RTV 159 (no primer)	66.7		100
	Visilox V-612 A/B (primer)		510.7	98
	Visilox V-622 (primer)		180	100
	Visilox V-612 A/B (primer)		295†	90†

* Measured in pounds per inch of width
** Measured in pounds per square inch of cohesive/adhesive force
† Testing performed on carbon-filled polyetherimide

Evaluation of the 4% Aqua-Safe demonstrated that it could be used to shape the RTV 159 and Visilox V-612 A/B rubber, however the process took two to three times as long as the present process using MEK and resulted in a greater usage of the q-tips used to form the rubber fillets. Based on these results it was determined that a non-aqueous cleaner would be needed to remove the excess rubber, shape the fillets, and clean the tooling used to mix and apply the un-cured rubber. It was found that EZE 662 was the best of the alternate cleaners for accomplishing these steps. The EZE 662 shaped the un-cured rubber as well as the MEK and did not inhibit the cure of the RTV rubber.

Exposure of the concentrated and 4% Aqua-Safe had no measurable effect on silicone, fluorosilicone, or fluorocarbon rubbers. The EZE 662 did cause certain elastomers to swell significantly and soften upon extended exposure, but for short duration exposure the effect was both reversible and within specification limits. Results are shown in Table 3.

Table 3. Effect of Cleaners on Elastomer Materials

CLEANER	SUBSTRATE	EXPOSURE TIME	HARDNESS CHANGE*	VOLUME CHANGE (%)
Spec. Req't	Silicone rubber		-10 max.	+15 max.
	Fluorocarbon		-5 max.	+5 max.
	Visilox V-622		-5 max.	+5 max.
Aqua-Safe (4%)	Silicone rubber	22 hours	-1	+2.2
	Fluorocarbon	22 hours	-3	+0.4
	Visilox V-622	22 hours	-3	+1.0
	Carbon-filled polyetherimide	2 hours	-1	
EZE 662	Silicone rubber	22 hours	-13	+118
	Fluorocarbon	22 hours	-1	+1
	Visilox V-622	22 hours	-18	+73
	Carbon-filled polyetherimide	2 hours	-1	
	Silicone rubber	5 minutes	none	+30
	Visilox V-622	5 minutes	none	+5
Isopropyl Alcohol	Silicone rubber	5 minutes	none	+3

* Measured with Shore A Durometer

Shop Trials

Results of the shop trials at the manufacturing facility using the cleaners in the manufacturing processes were consistent with the results of the laboratory trials. The Aqua-Safe dried within the required times (15-30 minutes) needed for further processing of the parts. The Aqua-Safe demonstrated excellent bonding for both the RTV and oven cured rubbers. The EZE 662 was found to remove excess rubber easily and clean up the tooling very well. The only unexpected effect of the EZE 662 was a slight amount of rubber residue left adjacent to the fillet - an adjustment in the visual inspection criteria was required, but no adverse functional effect was detected. Brazing trials on both the turbine vanes and case rub strips were successful using the 4% Aqua-Safe solution, even when a substantial excess of cleaner was used and was not permitted to completely dry. This demonstrated the robustness of the cleaning solution and process.

Specifications for the Aqua-Safe and EZE 662 were generated. The cleaners were essentially "drop in" replacements for the MEK and IPA, so no processing changes were required for the new materials.

Conclusions

It was found that the Aqua-Safe, a water based cleaning fluid, effectively removed light soils and other contamination in various hand wiping operations. For metal and rubber bonding it was found to be equal to or superior to conventional solvent wiping. EZE 662 was shown to remove excess un-cured rubber similar to MEK and to clean rubber application tooling equally well.

A significant cost saving was documented for replacement of the cleaners, primarily in a dramatic reduction in potential solid hazardous waste (MEK contaminated rags, q-tips, etc.). Additionally, an improvement in environmental health and safety could be realized by elimination of the toxic and flammable solvents.

THE ELIMINATION OF METHYL CHLOROFORM SOLVENT USED FOR THE CLEANING OF PROPELLANT CONTAMINATED TOOLING DURING THE PRODUCTION OF THE SPACE SHUTTLE SOLID ROCKET MOTORS

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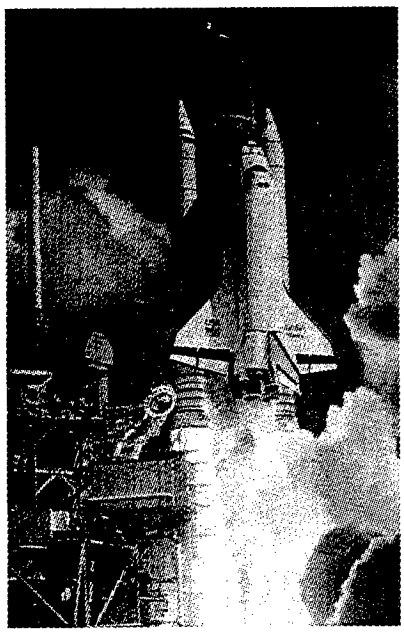
ABSTRACT



The Thiokol Corporation, Space Operations, Mix/Cast Work Center uses methyl chloroform as a cleaning solvent throughout the reusable solid rocket motor propellant production process. Testing to select and qualify suitable replacements for methyl chloroform has been performed. This effort was initiated to comply with amendments to the Clean Air Act that ban production of methyl chloroform after January 1, 1996.

The two solvents selected for methyl chloroform replacement are Ionox BC® and PF Degreaser®. Selection and qualification testing evaluated propellant/motor integrity, materials compatibility, safety, cleaning effectiveness, combustion sensitivity, and environmental effects. Test results showed that all presently used production materials were compatible with Ionox BC and PF Degreaser, and that propellant properties/motor integrity and bond strengths were as good as, or better than, those obtained from methyl chloroform cleaning processes.

INTRODUCTION

During the process of manufacturing propellant for the Space Shuttle reusable solid rocket motor (RSRM), the Mix/Cast Work Center uses methyl chloroform (TCA) as a cleaning solvent throughout the propellant production process. Propellant–contaminated tooling constitutes the majority of the cleaning requirements. Propellant, in its uncured state, has the consistency of smooth peanut butter, and in its cured state it has the consistency of a pink pearl eraser. Space Shuttle propellant is a composite of hydrocarbon compound (Table 1). It was the direction of the work center to find a widely available solvent that would not require significant changes to current production facilities and processes.

Screening testing was concerned with a selection process to evaluate possible "drop–in" replacements. The criteria for acceptability in the selection process was based on:

- Compatibility ..... Chemical stability with propellant and support materials
- Personnel Safety ..... Safe to use in propellant area and as a hand–wipe solvent with operator exposure (Industrial Safety)

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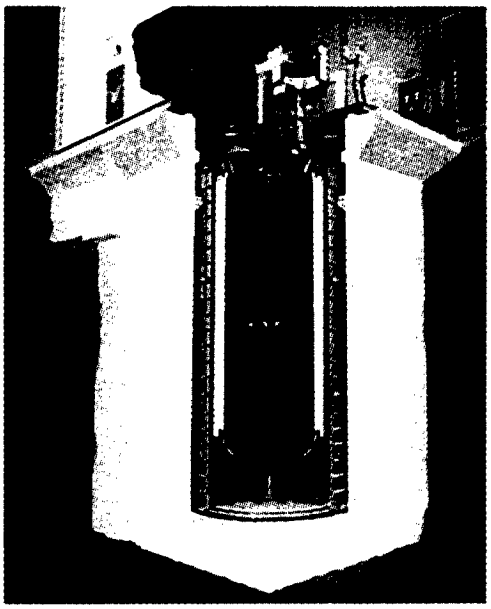
Table 1. Space Shuttle Solid Propellant

Hydrocarbon Composites Propellant Composition
Aluminum Powder (fuel): 9.7 - 16.3% Ammonium Perchlorate (AP) (oxidizer): 69 - 71% HB Polymer, Polybutadiene (binder): 9 - 16% Iron Oxidize Fe (catalyst): 0.3 - 3.0% Epoxy Curing Agent (curative): 1.8 - 2.7

Propellant Mixing



Propellant Casting

- Cleaning Effectiveness ..... Solubility and amount of nonvolatile residues that are left behind after cleaning

- Bonding Studies ..... Effect on bonding surfaces

Table 2 contains a list of solvents that were proven effective in breaking down propellant. This simple screening process using small samples of propellant and critical process materials, made evaluating many different solvents possible.

Evaluation of this data produced two solvents selected for TCA replacement in the Mix/Cast Work Center: Ionox BC and PF Degreaser. This paper discusses the engineering test plans (ETPs) and certification test plan (CTP) that provide data to show that the production process and product quality were unaffected by the substitution of PF Degreaser and Ionox BC for TCA. Qualification testing evaluated propellant performance/motor integrity, materials compatibility, safety, cleaning effectiveness, combustion sensitivity, and environmental effects.

Table 2. Final 11 Candidate Solvents

Solvent	Chemical Family	Compatibility			Personnel Safety	Flash Point (°F) (TCC)	Effective Cleaning Method
		Propellant	Silastic J	NBR			
Purasol BL	Lactic acid ester	Yes	N/A	Red color	Skin, oral intake TLV: 5 ppm	174	Manual and soak
PF Degreaser	Hydrocarbon	Yes	N/A	N/A	Skin, eyes	144	Manual
Ionox BC	Alcohol	Yes	N/A	N/A	Skin, eyes	165	Manual and soak
IBHK	Isobutyl heptyl ketone	Yes	N/A	Yellow color	Respiratory, skin, eyes	184	Manual and soak
KNI 2000	Pine terpene	Yes	N/A	Yellow color	Skin, eyes, combustible rags	148	Manual and soak residue
Tekusolv	Limonene aliphatic mixed	Yes	N/A	Red color	Skin, eyes, respiratory	142	Manual release/ bond
Axtrel 9100	Aliphatic hydrocarbon	Yes, off-gassing	N/A	N/A	Skin sensitizes, eyes	200	Aggressive manual
KNI 1000	Light terpene	Unstable	Swelling of sample	Swell/ yellow	Skin, eyes, combustible rags	144	Manual
X-Caliber	Methyl pyrolidone limonene	Exotherm	Swelling of sample	Red color	Acute health	155	Aggressive manual/soak
MNP	Methyl pyrolidone	Exotherm	N/A	Yellow color	Acute health	199	Manual
Citrex	Methyl pyrolidone limonene	Exotherm	N/A	Red color	Acute health	144	Manual/ soak
TCA (1,1,1)	Halogenated hydrocarbon	Yes	Swelling of sample	Yellow color	Skin, eyes, respiratory	--	Aggressive manual/soak

Note: N/A = The solvent had no effect on the material.
☐ Shaded areas indicate characteristics that were critical in either selecting or eliminating that particular solvent.

DISCUSSION

Propellant/Motor Integrity

Five-gal propellant mixes were conducted using tooling and equipment recently cleaned with either solvent. Potential solvent spill situations were simulated by adding one tablespoon of solvent directly into the mix.

Propellant tests included both cured and uncured propellant properties. Specimens were made up of RSRM propellant and critical bond materials. The flight-critical features that were investigated are: propellant-to-liner, propellant-to-inhibitor, inhibitor-to-nitrile butadiene rubber (NBR), propellant burn rate tests, and initiator process bonds.

Test results for propellant burn rate and mechanical properties, documented in Table 3 and 4, demonstrate that these replacement solvents did not have an effect on the propellant's ballistic and mechanical characteristics. All the test results were within the pass/fail and flag criteria of the CTP.

Additional tests were conducted simulating a worst-case situation. An example of this is found in Table 5 where the solvents were applied directly to the bores of 5-in. center perforated motors which were test fired. As the results indicate there was very little variation in the burn rate of the motors.

Table 3. Propellant Uncured Properties and 5-in. CP Burn Rates

	Percent HB Polymer	Total Solids (%)	Percent AP	Percent Al Plus Iron	LSBR (in./sec)	5-in. CP (in./sec)
CTP/TP-H1148 Mix	86.79	85.91	69.59	16.32	0.553	0.3669
Flag Criteria	85.5 to 89.5	85.5 to 86.5	69.33 to 69.79	16.24 to 16.64	0.553 ± 0.023	0.355 to 0.371
Material Evaluation Average (std dev)	86.73 (0.124)	85.98 (0.0578)	69.54 (0.0602)	16.44 (0.0635)	0.5563 (0.0042)	0.3656 (0.0027)
CTP/TP-H1178 Mix	85.49	81.93	68.91	13.02	1.051	0.9229
Flag Criteria	84.3 to 86.3	81.50 to 82.50	69.0 ± 0.5	13.0 ± 0.3	1.052 ± 0.078	0.886 to 0.972
Material Evaluation Average (from two mixes)	85.30	81.96	68.88	13.08	1.069	0.9411

Note: Flag criteria represent Space Shuttle production history.

Table 4. Cured Propellant Mechanical Properties

	TP-H1148		TP-H1178	
	Maximum Stress (psi)	Strain at Maximum Stress (%)	Maximum Stress (psi)	Strain at Maximum Stress (%)
Loaf 1	119	33.0	217	31.6
Loaf 2	121	34.1	219	34.8
Loaf 3	119	33.3	217	32.4
Pass/Fail Criteria	80 minutes	30 minutes	140 minutes	25 minutes
Flag Criteria	96 to 129	31 to 42	182 to 240	26 to 38

Note: Pass/fail criteria represent Space Shuttle specification requirements.

Table 5. Propellant Bore Wipe Test Results

Solvent	5-in. CP Burn Rate (in./sec at 625 psia and 60°F)		
	No Wipe (production)	Solvent Wipe	Difference
TCA	0.3626	0.3618	0.0080
Ionox BC	0.3613	0.3625	0.0012
PF Degreaser	0.3630	0.3632	0.0002
Ionox BC + Dry Wipe	0.3624	0.3642	0.0018
PF Degreaser + Dry Wipe	0.3644	0.36648	0.0040

To ensure the integrity of critical bondlines in the Space Shuttle booster motors, many bondline specimens were made and tested. Each specimen built duplicated actual production processes and production worst-case conditions. TCA and methyl ethyl ketone (MEK) were used as baseline solvents in these tests. The test results showed very little variation, and in some cases the new solvents provided a stronger bond (refer to Table 6 and 7). These results demonstrated that the replacement solvents will maintain

Table 6. Initiator Fabrication Bonding (no aging)

Bonding Surfaces Tensile (psi) (standard deviation)	Cleaning Method						
	No. 1 MEK	No. 2 Ionox	No. 3 PF	No. 4 I+1hr	No. 5 P+1hr	No. 6 I+pr	No. 7 P+pr
Case to Liner	256.5 (19.1)	257.4 (12.4)	273.1 (19.0)	267.2 (10.0)	255.8 (13.6)	262.5 (19.9)	261.9 (15.0)
Case to Insulator	577.2 (30.2)	560.5 (20.8)	582.5 (7.1)	564.0 (19.8)	614.0 (32.2)	647.5 (6.2)	660.6 (40.7)
Liner to Nozzle	193.8 (11.9)	190.2 (7.7)	206.6 (18.2)	178.8 (4.6)	188.6 (29.7)	188.0 (6.1)	203.8 (48.8)
Liner to NBR	200.0 (12.0)	185.0 (12.8)	199.6 (5.3)	187.9 (8.5)	195.8 (14.2)	200.9 (11.4)	206.5 (17.1)
Environmental Plug to Nozzle	726.6 (6.2)	673.4 (4.8)	696.6 (2.4)	602.9 (130.1)	697.1 (67.1)	755.3 (90.2)	727.6 (94.2)

1—MEK baseline using current cleaning method and processing dry times as outlined in Table 2 in ETP-1361
2—Ionox BC with dry wipe
3—PF Degreaser with dry wipe
4—Ionox BC with dry wipe and a 1-hr dry time
5—PF Degreaser with dry wipe and a 1-hr dry time
6—Ionox BC with dry wipe and current process dry time
7—PF Degreaser with dry wipe and current process dry time

Table 7. Average Propellant Witness Panel, Inhibitor Tensile Cup, and Liner Peel Tests

Test Sample	1	2	3	4	5	6
TP-H1148/Liner Peel (pli)	8.3	8.8	8.4	9.3	8.7	8.4
Pass/Fail Criteria	4.0 to 12.0 pli					
Flag Criteria	5.5 to 10.4 pli				100% propellant failure	
TP-H1148/Liner Tensile (psi)	114	115	117	117	117	117
Pass/Fail Criteria	67 psi minimum					
Flag Criteria	94.7 to 145 psi					
TP-H1148/Inhibitor Tensile Cups	145 psi		97% deep propellant, 3% thin propellant film failure			
Pass/Fail Criteria	65 psi minimum					
Flag Criteria	114 to 163 psi		Failure modes can not exist within the bond line			
TP-H1178/Liner Peel (pli)	9.5	9.7	9.3	9.5	100% propellant failure	
Pass/Fail Criteria	4.0 to 12.0 pli					
Flag Criteria	6.0 to 10.7 pli					

bondline integrity. In all cases studied, either Ionox BC or PF Degreaser (usually both) produced acceptable bond strengths similar to TCA or MEK. During certification testing, all the test results where within Space Shuttle specification requirements and also the production historical database.

MATERIAL COMPATIBILITY

Testing showed Ionox BC and PF Degreaser are compatible with currently used processes and process materials. Acceptable compatibility includes: chemical stability tests using differential scanning calorimeter

(DSC), accelerating rate calorimeter (ARC), materials soak swell/hardness test, and metal corrosion tests. No thermal or chemical issues were identified from the DSC and ARC testing.

Issues that surfaced during soak swell testing were mostly a specific process material degradation nature related to repeated material exposure to solvent. In these degradation cases, only one solvent was a problem on a specific material, i.e., materials affected by Ionox BC were not affected by PF Degreaser and vice versa. Examples of this phenomenon are urethane RP6442, which was chemically affected by Ionox BC, but not by PF Degreaser; and RTV 732, which was chemically affected by PF Degreaser but not by Ionox BC (Table 8).

Tests performed on metal corrosion and paint-to-steel bondlines demonstrate that Ionox BC and PF Degreaser are compatible for cleaning metal tools. Metal corrosion tests show no specific concerns, and paint-to-steel bond specimens showed no statistical difference in bond strength (Table 9) when compared to TCA data.

SAFETY

A Mix/Cast operations facility hazards analysis was performed to determine and evaluate the potential industrial safety hazards resulting from implementing the two new ODC-free solvents: Ionox BC and PF Degreaser. The main concern with the use of these two new solvents in the Mix/Cast Work Center is changing from a noncombustible solvent (TCA) to combustible solvents. The new cleaners were evaluated relative to electrostatic discharge (ESD), combustible liquids classification Class IIIA, handling/storage, and potentially increased combustion sensitivity when used in friction or impact situations.

Two tests were devised to identify any new ESD hazards in Mix/Cast operations caused by using the replacement solvents to clean nonconductive materials. These tests were accomplished by measuring: 1) the increase/decrease in generated charge while extracting pull-rods made from or coated with nonconductive materials from propellant and 2) the electrical property degradation of materials following cleaning with the above noted solvents and TCA as a control. The materials tested were selected by reviewing all live Mix/Cast operations and identifying those materials that currently come in contact with propellant and are cleaned with TCA.

PF Degreaser is a very nonpolar liquid and thus generates ESE on nonconductive materials during handwipe operations. Ionox BC is the most polar of the solvents tested. As a result of these findings, the applications where each solvent will be used were analysed for electrostatic energy (ESE)/ESD concerns. It was determined that both solvents can be used in current propellant manufacturing processes for the RSRM program with the exception of using PF Degreaser to clean cured Silastic J Rubber® and virgin Teflon®. Table 10 provides data on the tests that were designed to evaluate the ESD.

The production facilities were evaluated in terms of introducing Class IIIA combustible liquids into the facilities and processes. Table 11 displays the flammability/safety characteristics of the production processes. Although the solvents are classified as combustible, they can be safely used and stored in the live propellant areas. The solvents are safe to the environment and to personnel exposed to normal processing conditions. It was concluded that the ventilation systems needed to be improved in one facility. The rest of the facilities and equipment are already rated for explosion-proof conditions, which is more than adequate for Class IIIA combustible liquids. Class IIIA combustible liquids, by definition, have flash points between 140° and 200°F and are not classified as flammable liquids. Facilities where these liquids are used do not

Table 8. General Results of Material Compatibility

Material	Affect on Material			Comments	Use/Facility
	TCA	PF	Ionox		
Propellant	C1,C2,C5	B2	C2,C1,B5	Ionox made propellant spongy	All areas
HB Polymer	--	B5	B5	Ionox is higher in density than HB polymer	Propellant/all areas
ECA	--	B5	B5	Solvents appear to have little affect	Propellant/all areas
Ammonium Perchlorate (AP)	--	B2	B2	AP soaks up solvents	Propellant/all areas
NBR Gloves	C1,C4	B1	C1,C3	Ionox behaved like TCA on glove	General cleaning/all areas
PVC Gloves	C3,C4	B2,C5	C3,C5	PVC gloves can be used for very short-term exposures	General cleaning/all areas
TYVEX® Suits	--	A,B1	A,B1	Solvents soaked in, but did not dissolve the material	Safety equipment/ M-325, casting pits
Cured Inhibitor	B1,B2	C1,C2	B2	PF soak into material more than Ionox	Motor/casting pits
Uncured Inhibitor	--	B2,B5	B2	PF removes uncured inhibitor better than Ionox	Motor/casting pits
Cured Liner	C1,C2	C1,C2	B2	Similar to inhibitor. HC polymer is polar in nature	Initiator, igniter fab/M-325
Buna-N O-ring	B1,B3	A	A,B1	Affected most when surface is cut	Tooling, facilities/all areas
Neoprene Gasket	B1,B3	B1,B2	B2	Solvents had little visual affect	Forward core/casting pits
Epoxy Adhesive	B1	A2	A2,B1	Ionox should work on uncured adhesive removal	Inhibitor repair, initiator fab
EPI® Bond	--	A	A	Generally, solvents have little affect on hard materials	Tooling repair
Double Bubble®	--	A	A	Hard; similar to EPI bond	Tooling repair/ M-27, casting pits
Sta Bond®	C5,C3,B2	B2	C3,B2	Material is rubbery. Ionox softens rubber materials	Forward core, tooling/ M-12, other
Swift D®	C1,C2,C5	B1,C2	C5,C2	Similar to Sta Bond	Forward core, tooling/ M-12, other
Elcocoat®	B5	A	C5	No affect if not visually removed	Forward core fin plugs/ M-12
Ren-Co-Thane® RP6401	B1,B4	A	B1,B5	Ionox attacks urethanes. If exposures are limited Ionox can be used to clean	General tooling/ M-320, all areas
Ren-Co-Thane RP6402	B1,B4	A	B1,B5	Ionox followed by a dry wipe could work in most urethane cleaning	General tooling/ M-325, all areas
Ren-Co-Thane RP6442	B1,B4	A	B1,B2,C5	Ionox should not be used to soak the ball valve bladder	Ball valve, general tooling/ M-325, all areas
Ren-Co-Thane RP6444	B1,B4	A,B2	B2,B3	Urethane 6444 resists Ionox's breakdown the best of those tested	Ball valve, general tooling/ M-325, all areas
NBR Rubber	C1,B5,C3	A2	C2,B5,B3	Sample tested was uncured	Motor, tooling/all areas
Neoprene Rubber	B1,B2,B3	A2,A5	A2	Solvents are less aggressive than TCA	Tooling/all areas
Cured Silastic J®	B4,B1	B2,B1	A2	PF is similar to TCA on Silastic J	Grain former/ M-320, casting pits

A—Little/No Effect
B—Moderate Effect
C—Major Effect

1—Swelled
2—Softened
3—Deformed

4—Hardened
5—Dissolved

Table 8. General Results of Material Compatibility (cont)

Material	Affect on Material			Comments	Use/Facility
	TCA	PF	Ionox		
Permitex®	C1,C3,B5	C1,C3,C2	A,B2	Permitex is an RTV material	Gasket sealer, maintenance/ M-314
Cured RTV	B1,B1,B5	C1,C2,C3	A	PF will swell RTV, like TCA, with exposure	Casting tooling, cores/ all areas
Uncured RTV	C3,C5	C2,C5	A,B5	PF interferes with RTV cure	Tooling prep/M-12, M-27
Black Velostat®	C5,C3	A1	B1,B3	TCA dissolves velostat. Ionox and PF are better than TCA	Container or covering/ all areas
Pink Poly®	--	A1	A1	Solvents may remove the conductive coating	Container or covering/ all areas
Follower Plate Plastic	--	A	A	No effect detected	Follower plate tool/M-320
PVC Pipe	--	A	A,B2	Ionox dissolves vinyls	Witness panel fabrication/ M-325
Polyethylene Sample Container	--	A1	A	Sample container can be cleaned with either solvent	Propellant samples/ M-2X, M-19A, M-325
Scotch Brite®	--	A,B5	A	PF dissolves some part of Scotch Brite's surface	General usage/all areas
Yellow Vinyl Tape	C1,C3,C5	B3,B5	C1,C3,C5	Both solvents affect the tape and backing with time	General usage/all areas
Reinforced Tape	--	B1,B3,B5	C1,C3,C5	Tapes can be wiped, but should be dry wiped to remove residual solvent	General usage/all areas
Vacuum Putty	C1,C3,C5	C1,C3,B5	A	Ionox had no visual effect	Casting tooling/ M-27, casting pits
Conoco HD-2® Grease	C2,C3,C5	B2,B3,B5	A5	Ionox had no visual effect. PF softens the edges like TCA	Metal tools/ casting pits, M-184
Virgin Teflon®	--	A	A2	No visual effect	Tooling/all areas
Glass-Filled Teflon®	--	A	A	No visual effect	Tooling/all areas
Delrin®	--	A2	A2	Similar to nylon in nature	Tooling/all areas
Nylon®	--	A2	A2	No visual effect	Tooling/all areas
Conductive Table Top	A	A	A	No visual effect	Facilities: M-325 and M-320
Plexiglass	--	A	A	No visual effect	Tooling, covers/all areas
Conductive Floor Wax	C1,C2,C5	A	B1,B2,B5	Ionox softens/dissolves conductive floor wax in a short time	Conductive facility floor wax
Shoe Sole	C1,C2	A2	C1,C2,C3	Shoe soles swell with Ionox, but will restore shape with time	All areas
Plastic Spatulas	A	A	A	No visual effect. Similar to TCA	Propellant areas
Phenolic Nozzle	--	A4	A4	The solvents seem to harden the material some how	Initiator fab/M-325
Royalstat® R69	--	A	A1,B2	Solvent exposure over time will degrade the conductive properties	Propellant areas

A—Little/No Effect
B—Moderate Effect
C—Major Effect

1—Swelled
2—Softened
3—Deformed

4—Hardened
5—Dissolved

Table 9. Steel-to-Paint Tensile Value (psi)

Solvent Average/Std Dev	Set 1	Set 2	Set 3	Set 4	Set 5
TCA	344.2/29.0	405.8/51.6	292.5/193.2	317.5/43.4	312.6/51.5
Ionox BC	319.5/39.7	337.7/11.5	359.6/17.3	373.3/68.4	331.3/62.1
Ionox BC + 1 Hour Dry Time	319.9/28.9	334.5/29.3	355.0/62.2	341.9/31.1	361.2/16.4
Ionox BC + Dry Wipe	260.9/42.0	371.4/35.9	396.4/22.0	354.4/52.9	374.5/31.0
PF Degreaser	337.7/70.0	293.3/27.2	329.2/49.2	267.8/68.2	340.2/40.2
PF Degreaser + 1 Hour Dry Time	303.9/16.8	331.0/28.6	370.7/13.3	315.8/17.7	313.5/106.2
PF Degreaser + Dry Wipe	364.7/28.9	384.6/42.7	396.4/20.1	325.5/37.0	333.7/42.4

Note: All samples were tested at 75°F and 0.5 in. per minute.

require special electrical equipment per Article 500 of the National Electrical Code. A hazardous area electrical classification or adequate ventilation will be necessary in the areas where these liquids are stored or handled at temperatures above their flash points. Ventilation is considered adequate if it is sufficient to prevent accumulation of significant quantities of vapor-air mixtures in concentrations below the lower flammable limits of the solvent.

Finally, the hazards analyses identified two concerns: handling/storage and actual process usage of the new solvents. The handling issue will be addressed through awareness training and personnel protection. The storage issue pertains to storing combustible liquids in various quantities from bottles to bulk gallon storage tanks. Changes/modifications will be made in the current procedures and facilities to ensure that operations are performed in accordance to the General Safety and Health Manual and the National Fire Code. An example of such a change is that solvent bottles that are not in use are to be stored in a flameproof storage cabinet.

Process usage involves analysis of potential friction and impact situations, e.g., out-of-place propellant on facility flooring. Thiokol Mix/Cast facilities have six main types of flooring: aluminum (conductive), concrete/cement, Stone Hard Epoxy, Selbuclad Epoxy, and Unideck Epoxy. Testing was included to evaluate the changes to sensitivity that Ionox BC and PF Degreaser would have when combined with ammonium perchlorate (AP), main grain propellant, igniter propellant, and the various floor types. Allegheny Ballistics Laboratory (ABL) sliding friction and Russian Detonation Deflagration test (DDT) tests were performed to determine the degree the new solvents would affect the sensitivity. There was not any change in material sensitivity to friction when using these new solvents to clean AP or propellant from these floor materials. It is recommended that Stone Hard Epoxy flooring not be used in an AP facility.

CLEANING EFFECTIVENESS

In addition, cleaning demonstrations were set up to evaluate the ability of Ionox BC and PF Degreaser to clean in four cleaning operations. These applications were the 600-gal mixer, M-27 bubbler tank, M-320 soak tank, and M-27 spray station. Actual facilities were used in the case of the mixer and spray station. A subscale bubbler and soak tank were used due to the costs and contamination concerns involved in using the actual equipment.

Table 10. ODC Solvent-Dampened Rags Wipe Test/ESE Bulidup (volt range)

	Silica-Filled EPDM	Silastic J RTV	NBR J-Leg	Hypalon-Painted TPS	Cured Castable Inhibitor
Baseline Dry Wipe Only	+580	0	+500	0	+3k
	610	-13,300	0	-930	0
TCA Dry Wipe	400	-6,000	0	-510	300
	-680	-20,000	-70	+20	0
PF Degreaser Dry Wipe	600	-5,500	40	-2,000	480
	-630	-20,000	30	-4,700	0
Ionox BC Dry Wipe	0	+30	+30	20	80
	0	-30	-20	-10	0

Table 11. Sovent Flammability/Safety

Tests	PF Degreaser	Ionox BC	Comments
Flash Point (°F) (tag close cup)	144	165	MSDS
Flash Point (°F) (open cup flame)	165.2	184.4	Average at Utah
Flash Point (°F) (open cup spark)	214	246	10 kV ignition source
Conductivity pS/M	4 - 5,778	19,433,050	TCA = 42,906
ESD	Nonpolar liquid, generates a charge on nonconductive materials	No ESE concern—excellent solvent to prevent ESE/ESD	TCA causes some ESE concerns because it evaporates so quickly
Flammability—Solvent Spray Demonstration	No fire with spark test; only fire was with a mist spray in flame test	No fire with spark test, only fire was with mist spray in flame test	Solvent must be contaminant-free and below the solvent's flash point
Compatibility	Yes with propellants and all materials, except Scotch Brite pads	Yes with propellants and all materials	Scotch Brite exotherms at 224°F with PF
Soak/Swell/ Hardness	Effects: RTV, vacuum putty, Silastic J	Effects: urethanes, Ren-Co-Thanes	
Chemical Exposure	RIS TLV: 300 ppm Worst case: 36.5 Mix bowl cleaning	RIS TLV 100 ppm Worst case 22.1 Bubbler tank	Results taken from cleaning demo
SBAT—Contaminated Waste (°F)	175 with TP-H1178	200 with Rympiecloth® and propellant	Avoid direct sun, use airtight waste containers
Facility Temperature (°F)	Mixers (130)	Casting pit (124)	Not to be on surfaces above 140
Environmental	No concern	No concern	Burn propellant/solvent waste

Two teams of operators using the new solvent cleaned two 600-gal mixers at the end of a production mixing campaign. Several conclusions were made from the operators comments:

- The odor that is associated with cleaning a mixer with TCA was greatly improved with the use of the two new solvents, but the operators preferred the PF Degreaser. Refer to Table 11 for actual solvent exposure/concentration levels.
- PF Degreaser was a much better solvent for cleaning the warm tooling (101°F) with uncured propellant contamination. PF Degreaser cleaned the tooling easier and faster than

Ionox BC. PF Degreaser left the tooling shiny clean and Ionox BC left the tooling surface with a dull, filmy look.

- The current cleaning process uses approximately one quart of TCA to clean the mixer head. Using the new solvent required approximately 8 ounces to clean the mixer head.

The results of the subscale bubbler and soak tank demonstration showed that Ionox BC was the more aggressive solvent for cleaning the different types of tooling that are normally cleaned in one of the solvent tanks. PF Degreaser did clean the propellant contamination from the tooling; however, more effort was required on the part of the operator. Another observation that was made during the Ionox BC portion of this test was that the Ren–Co–Thane bladder used in the 8–in. ball valve became slippery and hard to handle when soaked in Ionox BC. It was found in the soak/swell tests that Ionox BC degrades Ren–Co–Thane and urethane. It was concluded that either Ionox BC or PF Degreaser could be used in the bubble/soak tanks depending on the types of tooling being cleaned and the amount of effort/time that can be spent cleaning the tooling. It is recommended that PF Degreaser be used in the soak tank where the ball valve is cleaned and that Ionox BC be used in the bubbler where casting tooling is cleaned.

The results of the mix bowl spray station demonstration show that Ionox BC is the best solvent for spraying through the wand and cleaning the 600–gal mix bowls. Ionox BC and PF Degreaser responded just the reverse from that of the mixer cleaning test. Ionox left the stainless steel bowl shiny and clean and PF took considerably more effort to clean the bowl. The temperature of the bowl was 72°F and the propellant had started to cure. As a result of the data collected (flammability of solvents in spray application), the following conclusions can be made:

- Ionox BC is the more aggressive solvent for cleaning partially cured propellant from tooling that is at ambient temperature.
- Ionox BC and PF Degreaser can be safely sprayed from the M–27 spray wand if the spray does not mist or exceed a flow rate of 3.2 gal/min. The solvent that is to be sprayed must be free of contaminants and should not be heated.

To show how effective Ionox BC and PF Degreaser can be in cleaning, Fourier transform infrared (FTIR) wipe tests for were performed. FTIR test results give a relative indication of how well a selected solvent removes propellant and grease contamination in a given situation. In these FTIR tests, a Teflon (filter) test cloth soaked in reagent–grade TCA was used to remove residual contamination from a solvent–cleaned material surface. This Teflon cloth was then used as the test sample in an FTIR analysis. Many variables can affect the quantitative FTIR test results (e.g., cleaning technique used, surface area wiped, number of times wiped, etc.). Therefore, FTIR test results only show relative contaminant residue contents that were detected on the test cloth as compared to TCA.

FTIR test results show either PF Degreaser or Ionox BC were acceptable in all applications as a replacement for TCA. Also, residual propellant is still present on many of the nonmetal materials. A second solvent wipe with the replacement solvents is recommended.

A test was performed to determine the nonvolatile residues left on D6AC steel that has been contaminated with Conoco HD–2 grease. Initial results showed that Ionox BC is not a good solvent for removing grease. The steel specimens were contaminated with grease, then hand cleaned with PF Degreaser and TCA using the double–wipe method. The steel specimens were then flushed with TCA. The flushed solvent was captured and evaporated. The NVR was weighed and calculated to mg/ft^2. The NVR results were 4.00 mg/ft^2 on the TCA–cleaned specimens and 0.61 mg/ft^2 on the PF Degreaser–cleaned specimens.

ENVIRONMENTAL IMPACT/DISPOSAL

To show Ionox BC and PF Degreaser are environmentally safe, Environmental Engineering conducted a study to evaluate the methods that would be required to dispose of production waste due to using PF Degreaser and Ionox BC. State and federal regulations were incorporated into the study to ensure that Thiokol could, and would, properly dispose of the solvent waste generated in the Mix/Cast Work Center.

Both Ionox BC and PF Degreaser are considered nonhazardous by the Environmental Protection Agency. However, contaminants added to these solvents during use could cause them to be hazardous. The evaluation looked at the solvents used in cleaning propellant contaminated tooling and parts. The conclusions are based on analytical work that was perform to evaluate the reactivity of waste materials:

- Solvent Spills: All spills must be reported to Safety as required by Thiokol policy. Solvent contaminated with propellant that is classified as reactive has a reportable limit of 100 lb on spills.

- Solvent–Contaminated Nonhazardous Waste (solid): This material could be placed in Thiokol's own landfill if properly controlled and monitored.

- Propellant Contaminated Solvent (soak tank): This material should be filtered to separate the propellant solids from the liquid. The solids would then go to the burning grounds and the liquid would go for off–site disposal as a nonhazardous waste at a price of approximately $100 per drum, including transportation.

- Propellant and Solvent Contaminated Waste (rags, etc.): These rags and other debris would be sent to the burning grounds for disposal as reactive waste.

- Solvent and Propellant Contaminated Water: This mixture is assumed to be low in propellant and, therefore, nonreactive. Under this assumption, this waste would be disposed of off–plant as nonhazardous waste at approximately $100 per drum. An alternative to this option is disposal at the Waste Water Treatment Plant (M–705). This option would require trial runs and testing to determine actual process requirements and would cost about $1.10 per gallon.

- Solvent Contaminated With Hazardous Waste (flammable, asbestos, etc.): Asbestos–contaminated solids can be disposed of on–site in the asbestos trench. Solvents contaminated with flammable solvents will most likely be disposed of as hazardous waste or in some cases the waste may be processed through Thiokol's sewer treatment plant.

SUMMARY

All testing was performed successfully. For each test, at least one of the two solvents performed acceptably for use in each of the propellant production facilities. Methyl chloroform is noncombustible, which definitely is a safety advantage in many applications. Ionox BC and PF Degreaser are Class IIIA combustible liquids with closed cup flash points of 165° and 144°F, respectively. Although the two solvents are classified as combustible liquids, results indicated that these solvents can be safely used in the Mix/Cast area processes.

Results of the testing indicate that either of the two solvents could be interchanged in approximately 98% of the processes without compromising process safety and hardware quality. Thus, both solvents were qualified for use in the propellant production processes, and their respective use in any building or process will be controlled by shop planning.

THE GSFC COMBINED APPROACH OF ODC STOCKPILING AND TRIBOLOGICAL TESTING TO MITIGATE THE RISKS OF ODC ELIMINATION

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ABSTRACT

In response to the elimination of production of several Ozone Depleting Chemicals (ODCs) which have been widely used in successful space flight mechanism cleaning and lubricating procedures, GSFC developed and implemented an overall philosophy of mitigating the risks to flight hardware during the transition phase to ODC-Free cleaning procedures.

One leg of that philosophy is the initiation of a several tier testing program which will deliver increasing amounts of information over the next few years, starting with original surface analysis comparisons between ODC and various ODC-Free cleaning technologies. The other leg is the stockpiling of an appropriate amount of ODC solvents such that all short term GSFC missions will be able to stay with or revert to heritage cleaning and lubricating procedures in the face of life issues.

While tribological testing, mechanism life testing and space-flight experience will ultimately bring us into the 21st century with environmentally friendly means of cleaning long-life precision mechanism components, many satellites will be launched over the next few years with a number of important tribological questions unanswered. In order to prepare for this challenge, the Materials Engineering Branch in cooperation with the Electromechanical Branch launched an intensive review of all ongoing missions. The failure risk was determined for each long-life mechanism based on a number of parameters, including a comparison of flight solvents used to clean the heritage/life test hardware.

Also studied was the ability of the mechanism manufacturers to stockpile ODCs based on state laws and company policies. A stockpiling strategy was constructed based on this information and subsequently implemented.

This paper provides an overview of the GSFC ODC elimination risk mitigation philosophy as well as a detailed examination of the development of the ODC stockpiling plan.

INTRODUCTION

For many years, the successful heritage of most long life lubricated mechanisms for satellites has been based on cleaning procedures which utilize the chlorofluorocarbon solvent CFC-113 and 1,1,1,-trichloroethane (1,1,1-TCA). Most satellites require long life lubricated mechanisms for successful orbital operation up to 10 years. Spacecraft use reaction wheels, momentum wheels, antenna gimbals, solar array drives, gyros and despin mechanisms for control and power acquisition. Satellite instruments require spatial scan mechanisms, spectral scan mechanisms and focus mechanisms for scientific and earth observations. In order to qualify a lubricated mechanism, a successful mechanism life test for up to 5 years or an orbital heritage for 10 or more years has to be successfully accomplished.

ELIMINATION OF OZONE DEPLETING SOLVENTS

In 1993, GSFC discovered that the Montreal Protocol had mandated the termination of CFC-113 and 1,1,1-TCA solvent production at the end of 1996. In September 1994, a workshop was held in Denver to assess the state-of-the-art of new ODC-free cleaning process development, requirements imposed by the Montreal Protocol and the requalification status of heritage lubricated mechanisms (Ref. 1). The workshop entitled "Non-Ozone Depleting Chemical Cleaning and Lubrication of Space System Mechanical Components for Multi-Year Operations", was sponsored by Aerospace Industries Association, The Aerospace Corporation, Air Force Space and Missile Systems Center, International Cooperative For Ozone Layer Protection, Instrument and Bearing Working Group, Draper Laboratory, NASA, Honeywell, Inc. and EPA.

The workshop discovered that most bearing manufacturers, spacecraft mechanism suppliers and satellite instrument fabricators had or were about to remove ODC solvents from their cleaning processes which had been qualified for long life space mechanisms. To resolve the requalification problem of heritage mechanisms, the workshop recommended stockpiling CFC-113 and 1,1,1-TCA to extend the use of heritage mechanisms, repeat life testing to requalify mechanisms cleaned with ODC-free solvents and conduct

generic lubricant life studies with ODC and ODC-free solvents in an attempt to show that ODC-free cleaning processes did not degrade lubricant life and therefore eliminate the necessity for requalification. Short life satellite and rocket lubricated mechanisms were not included because they could be requalified quickly with a short duration life test. Aircraft mechanisms were not included because they are redundant and receive periodic maintenance.

INADEQUATE TIME FOR MECHANISM REQUALIFICATION

After the Denver Workshop in September 1994, GSFC tribologists had to define stockpile needs for all the long life mechanisms on GSFC satellites and persuade the project managers to purchase a stockpile of CFC-113 and 1,1,1-TCA solvents. In early 1995, GSFC discovered that manufacturing of CFC-113 and 1,1,1-TCA was scheduled to be terminated by the suppliers in April 1995 instead of December 1995.

The Materials Engineering and Electromechanical Branches proposed a stockpiling plan to the Engineering Directorate, Flight Projects Directorate and the Office of Flight Assurance in March. With the support of project management, resource management, procurement, safety logistics and all GSFC flight hardware contractors, the survey team reviewed CFC-113 and 1,1,1-TCA usage in manufacturing all long life lubricated mechanisms.

ODC/ODC-FREE SOLVENT USAGE SURVEY QUESTIONS

In order to provide a reasonable estimate of GSFC stockpiling needs, it was necessary to develop a database of cleaning procedure information from all current GSFC projects. One of the main objectives was to ascertain which mechanism suppliers were either still using ODC cleaning procedures or were in the process of switching from ODC to ODC-free processes but had not completed the qualification process for the new procedures.

Long life lubricated mechanism suppliers were asked the following survey questions:

1. Which company supplied the bearings?
2. Which ODC and ODC-free cleaning solvents were used for each mechanism?
3. What is the distribution of your ODC and ODC-free cleaned bearings in flight, life test and heritage mechanisms?
4. Which solvents were used to clean the long life mechanisms that were qualified by life tests or successful flight heritage?
5. What requalification is being planned after you switched to ODC-free cleaning solvents?

6. Are you stockpiling ODC solvents in order to continue ODC solvent cleaning until ODC-free cleaned mechanisms are requalified?
7. Who is your executive responsible for environmental policy decisions?

CRITERIA FOR STOCKPILING ODC SOLVENTS

If the mechanism had a successful space flight heritage or had completed a life test and if the bearings and hardware had been cleaned with an ODC-free solvent, the mechanism was qualified and ODC solvent stockpiling was unnecessary.

Many companies are under extreme public pressure to neither use nor stockpile ODCs and it would be impossible for them to comply to a GSFC request to keep ODCs at their facility. Mechanisms being built by those companies which were able to and agreed to stockpile ODC's were eliminated from GSFC's stockpiling list.

However, all precision bearing manufacturers have implemented ODC-free cleaning methods in the past few years for all of their bearings. Therefore, even if the mechanism manufacturer was using the heritage cleaning procedure for the current flight unit, the overall cleaning history of the mechanism bearings was quite likely different due to the changes in the bearing manufacturers cleaning methods. Unless life testing had been completed with ODC-free cleaned hardware, stockpiling and requalification were planned.

Space mechanisms that operate at slow speed or possess a stop/start motion operate in the boundary lubrication regime. Moving metal parts are in constant contact during boundary lubrication and therefore sensitive to surface chemistry changes. Stockpiling ODC solvent was accomplished in order to maintain ODC solvent cleaning until requalification was completed for ODC-free solvent cleaned hardware.

The newly developed low outgassing synthetic hydrocarbon (Pennzane) will accept boundary lubrication additives and has great potential. Several GSFC mechanisms have been lubricated with Pennzane and are being life tested but only one mechanism has flown. Stockpiling was accomplished for these mechanisms so that the low outgassing Braycote 815Z or Krytox could be used as a replacement if the Pennzane lubricated mechanisms fail life testing.

The perfluoropolyalkylethers (PFPE) like Braycote 815Z or Krytox oils will not dissolve boundary additives and have been found to autocatalytically break down to form solid polymers in the presence of bare iron surfaces (Ref. 2 and 3). CFC-113 is the solvent used for PFPE cleaning.

Preliminary data has shown that ODC-free cleaning methods have accelerated the PFPE breakdown process. All long life mechanisms which had or were continuing to use a PFPE lubricant were candidates for ODC stockpiling. Stockpiled CFC-113 solvent will be used until ODC-free solvent cleaned mechanisms can be requalified by life testing.

CFC-113 AND 1,1,1-TCA SOLVENT STOCKPILE

The list of long life lubricated satellite mechanisms and the satellite instruments with their associated solvent stockpile quantities are shown in Table 1, ODC/ODC-Free Cleaning Survey.

The first column lists the GSFC project and satellite. The second column identifies the spacecraft long life lubricated mechanisms. The third column lists the instruments on the satellite. The fourth column identifies the qualification status, potential failure status, heritage status, stockpiling status and other information used to identify stockpiling needs. The fifth column shows examples of solvent stockpile quantity computations. The sixth column lists the CFC-113 solvent quantity selected for each mechanism. Column seven lists the quantity of 1,1,1-TCA selected for each mechanism. The lubricant, cleaning processes, qualification status and project schedule were compared with the criteria for stockpiling in order to select the quantity of solvent to stockpile. The quantities are listed in column six and seven. With only a few months to stockpile, GSFC stockpiled 1055 gallons of CFC-113 and 122 gallons of 1,1,1-TCA.

Since the stockpile was purchased in May 1995, CFC-113 has been used by Miniature Precision Bearing, Aerospace Corp., Lockheed-Martin Sunnyvale, Wedeven and Assoc. and Marshall Space Flight Center for the generic study of ODC-free cleaning effects on lubricant life. The Bearing Consultants used CFC-113 for bearing failure analysis. Barden used CFC-113 to process flight bearings like the bearings that are flying. Hubble Space Telescope (HST) needed 250 gallons of CFC-113 to fabricate additional gyros in December 1995 but was able to purchase the solvent from warehouse stocks. If Goddard has need for four more future applications like HST, the GSFC stockpile will be gone.

GENERIC LUBRICANT LIFE MEASUREMENTS

The NASA Chief Engineer's Office is sponsoring a generic study of ODC-free cleaning processes on lubricant life. Marshall Space Flight Center is leading the NASA study. Aerospace Corp., Lockheed Martin Sunnyvale and Lewis Research Center are conducting the studies. One of the

early results showed that UV/Ozone and super critical carbon dioxide cleaned bearings reduced the Krytox life below CFC-113 cleaned bearings by 49% and 70%, respectively, during parched elastohydrodynamic bearing testing (Ref. 4).

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TABLE 1
ODC/ODC-Free Cleaning Survey

PROJECT	Spacecraft Mechanism	Satellite Instrument	CFC - 113 Stockpiling Rationale	CFC - 113 Stockpile Computation Gal.	CFC - 113 Stockpile 4/26/95 Gal.	1,1,1 TCA Stockpile Gal.
LANDSAT 7	X- Band Antenna Gimbals		1 of 2 Life Tests	0.5 x 50 = 25	25	6
	Solar Array Drive		Failures - New	0.5 x 50 = 25	25	6
	Reaction Wheels Assy.		Heritage			
				LANDSAT 7 Total	50	12
HST	Fine Guidance System		Fabrication of Bearings & Mechanism		40	
	Reaction / Momentum Wheels				0	
	Solar Array Drive				0	
	Gyros				0	
	CATS				5	
	FSS / BAPS Ring Gear / CDU / 10 Latches				0	
	SI Latches		Retain Flight Heritage		5	
	SAC		Short Life / Seldom Lubed		5	
	ORUC LIS/FSIPE		Short Life		5	
		NICMOS			55	14
		STIS			55	14
		ACE			110	28
				HST Total	280	56
EOS - AM	Solar Array Drive		In Life Test	0.5 x 80 = 40	40	10
	High Gain Antenna Gimbal		In Life Test (No Heritage)	0.5 x 80 = 40	0	10
	Reaction Wheel Assy.		No Life Test or Heritage		50	
	Earth Sensor Assy.				20	
	Inertial Reference Unit		NAVY Stockpiling at Kearfott		20	
		CERES	In Life Test		0	20
		MISR	JPL Stockpiling		0	
		MOPITT			0	
		MODIS	8152 Heritage		20	
				EOS - AM Total	150	40

TABLE 1
ODC/ODC-Free Cleaning Survey

PROJECT	Spacecraft Mechanism	Satellite Instrument	CFC - 113 Stockpiling Rationale	CFC - 113 Stockpile Computation Gal.	CFC - 113 Stockpile 4/26/95 Gal.	1,1,1 TCA Stockpile Gal.
EOS - PM	Reaction / Momentum Wheels				40	
	Solar Array Drive				0	
	Gyros				0	
	High Gain Antenna Gimbal				0	
		AIRS	JPL Stockpiling		0	
				EOS - PM Total	**40**	**0**
ACE	N/A	N/A			0	
				ACE Total	**0**	**0**
METSAT	Solar Array Drive				10	
	Reaction Wheels Assy.				400	
	Gyros				?	
		AVHRR	ITT Stockpile		0	0
		HIRS	ITT Stockpile		0	0
		SBUV	Ball Stockpile		0	
		AMSU			0	
				METSAT Total	**410**	**0**
XTE	Solar Array Drive		Passed Life Test		0	
	Antenna Gimbal		Passed Life Test		0	
	Momentum Wheels		In Life Test		0	
		ASM			15	
		HEXTE			15	
				XTE Total	**30**	**0**
TRMM	Solar Array Drive		In Life Test		0	
	Antenna Gimbal		In Life Test		0	
	Momentum Wheels		In Life Test		0	
		VIRS	In Life Test & Bearing Stockpile		0	
				TRMM Total	**0**	**0**
SMEX	Momentum Wheels				0	
	Gyros				0	
				SMEX Total	**0**	**0**
TOMS	Momentum Wheels		In Life Test		0	

TABLE 1
ODC/ODC-Free Cleaning Survey

PROJECT	Spacecraft Mechanism	Satellite Instrument	CFC - 113 Stockpiling Rationale	CFC - 113 Stockpile Computation Gal.	CFC - 113 Stockpile 4/26/95 Gal.	1,1,1 TCA Stockpile Gal.
	Gyro				0	
		TOMS	1 of 3 Instrument Failure		55	9
				TOMS Total	**55**	**9**
SSBUV		SSBUV	Instrument Failure		0	5
				SSBUV Total	**0**	**5**
AXAF		XRS			0	
				AXAF - XRS Total	**0**	**0**
GGS	Despin Platform		Passed Life Test		0	
				GGS Total	**0**	**0**
GOES	Solar Array Drive				0	0
	Momentum Wheel Assy.		Heritage		0	0
	Gyro (DIRA)		Northrop		40	
		IMAGER	ITT Stockpile & Life Test		0	0
		SOUNAR	ITT Stockpile & Life Test		0	0
				GOES Total	**40**	**0**
				Lubricated Mechanisms Total	**1055**	**122**
BLDG. 29	Quadex Cleaner				275	0
				BLDG. 29 Total	**275**	**0**
				Estimated Margin	**55**	**0**
				Total Volume Gal.	**1385**	**122**
				Total Weight lbs. †	**18,088**	**1,338**
				Total Cost ‡	**$ 208,013**	**$ 1,245**

† CFC-113 = 13.06 lbs/Gal. ; 1,1,1-TCA = 10.97 lbs/Gal.

‡ CFC-113 = $11.50/lb. ; 1,1,1-TCA = $0.93/lb.

Adhesion Performance of Solid Film Lubricants on Substrates Cleaned with Environmentally Compliant Cleaners

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Solid film adhesion testing was used to determine the effect different environmentally compliant cleaners have on the adhesion properties of solid film lubricants used for several NASA programs. In an action to remove ozone depleting chemicals from aerospace processes, a replacement cleaner must be identified that does not affect the adhesion of solid film lubricants used on flight critical NASA hardware. ASTM D2510-83 Standard Test Method for Adhesion of Solid Film Lubricants was used to evaluate the cleaners. Two different lubricants - Inlox 88 and Boosterlube - were tested using various commercially available cleaners. Inlox 88 is produced by E/M Corporation and is a liquid oxygen compatible lubricant used in the Space Shuttle Main Engine, and Boosterlube is a new lubricant being implemented for use on the Space Shuttle Solid Rocket Booster. These lubricants were selected because of their specific use on flight critical NASA components. Results of this testing are presented in the paper.

INTRODUCTION

Due to growing environmental concerns, cleaners containing stratospheric ozone depleting subtances are banned from future use. NASA, its contractors, and industry are forced to adapt cleaners that meet new environmental standards. NASA/MSFC oversees the operation of propulsion elements for the Space Shuttle. In addition, solid film lubricants are continually being researched and tested for use in enhancing Shuttle components and for consideration of technology transfer to industry. In the past, Freon 1,1,3 was often used to clean test samples and flight hardware prior to application of solid film lubricants. Prudence suggests that new replacement cleaners be evaluated for any changes (decreases) in adhesion of solid film lubricants, particularly those lubricants used in critical Shuttle hardware. Adhesion evaluation was performed on two solid film lubricants against five different cleaners. These candidate replacement cleaners were evaluated using ASTM 2510 - Standard Test Method for Adhesion of Solid Film Lubricants. Two solid film lubricants used in critical space related applications were tested for adhesion on panels cleaned in two aqueous and three non-aqueous cleaners. The cleaners are Formula 815 GD from Brulin & Company, Inc., Vitro-Klene followed with T4215 Additive rinse from Turco Products, Inc., TCE (Trichloroethylene), heptane, and Freon 1,1,3.

DISCUSSION

The cleaners were chosen from a list of cleaners used by a selection of NASA's contractors. These cleaners have performed nominally in a number of different applications in the space industry and industry in general. The aqueous cleaners are simple and safe to use with normal precautions when reduced in distilled water to the correct ratio. Heptane and TCE are used as received, but both have some health concerns associated with their use. Freon was used as a baseline and is not considered as a candidate cleaner due to its being barred from manufacture and sale.

The solid film lubricants used in these tests were Inlox 88 made by E/M Corp. and Booster lube, patent pending, by USBI. Inlox 88 is a liquid oxygen (LO2) compatible solid film lubricant that contains molydisulfide and graphite in a phosphoric acid binder. The cure temperature is 191 C (375 F) for 90 minutes. This lubricant is used in critical areas of the Space Shuttle main engine liquid oxygen turbopumps. Booster lube was developed as an environmentally friendly solid film lubricant for use on the SRB aft skirt shoes and mono-ball fittings. This lubricant consists of molydisulfide and boric oxide with an epoxy/silicone binder system. The carrier system is ethyl acetate which is approved for use by the EPA in the foreseeable future. Inlox 88 was chosen for this test because of its continued use in cryogenic applications. The SRB program will be implementing Booster lube in the next year. Private industry has taken an interest in this lubricant in an effort to comply with increasing environmental standards.

The plates used in the test were 1/16 inch thick 304 stainless steel that were grit blasted to a surface finish of 0.7 um. This finish closely duplicates the grit blasted finish (0.68 um) of an SRB aft skirt shoe before application of the solid film lubricant. Surface roughness measurements were done on a Rank Taylor Hobson form talysurf. For portability, the shoe measurement was taken from a section of flight shoe which was grit blasted at NASA's Kennedy Space Center using the same procedures as specified for flight hardware.

PROCEDURES

Adhesion Test Procedure

To test the adhesion of the solid film lubricants, an ASTM standard test method for Adhesion of Solid Film Lubricants was used. The standard was altered to take into account the environment that Inlox 88 is used. In this case the panels were immersed in LO2 for 6 hours to duplicate a standard chill down time before take-off of the Space Shuttle. The standard requires a 24 hour immersion time in the fluid it is exposed in. Booster lube is exposed to a high humidity environment at KSC before flight, so a 24 hour water soak is appropriate. Basically Procedure A

was used for Booster lube and Procedure C was used for Inlox 88 with the exception of immersion time. Following is the procedures used on this test series as adopted from ASTM D2510.

1. Immerse the panels to one half their length in water for 24 hours for Booster lube and in liquid oxygen (LO2) for 6 hours. Care was taken to ensure panels did not touch. In the case of Inlox 88, the panels were placed in an insulated Dewar vessel partially filled with LO2. Because of the high evaporation of LO2 it was difficult to keep the level consistent. The tape application procedure was altered to reflect this and is described below.
2. The panels were removed from their respective fluids. The Booster lube samples were wiped dry with a lint free cloth. Inlox 88 samples were removed from the LO2 and at this time the panels were scored before they could reach room temperature. This was done to promote adhesion loss through thermal cycling. After the Inlox 88 panels reached room temperature the resulting condensation was wiped off with a lint free cloth.
3. Using a stylus, two parallel scratches were created through the lubricant. These scratches were one inch apart and the length of the panel. This step was completed on the Inlox 88 coated plates as described in step 2.
4. A piece of masking tape conforming to US Federal Specification UU-T-106 was placed lightly over the panel perpendicular to the scratches half on the immersed section and half on the dry section. Tape was also applied to the fully immersed section of the Inlox 88 coated panel. The tape was rolled down with 2 passes using a 4.5 lb. roller. Minimum pressure was exerted by the operator. The specification of the roller are as follows: 1. diameter is 82.6 mm (3.25 in), 2. width is 44.5 mm (1.75 in), 3. the roller is covered with rubber 6.4 mm (0.25 in) thick with a burometer hardness of 80 and, 4. the weight of the roller is 2.04 kg (4.5 lbs.).
5. The tape was removed from the test panels in an abrupt perpendicular motion.
6. Test panels were then examined for loss of adhesion. Loss of adhesion is described as coating removal down to bare metal.

Cleaning Procedure

The cleaning procedures used below are an adaptation of procedures used by contractors and cleaning manufacturer's recommendations. The panels were cleaned in groups of three; three panels per cleaner per lubricant type. Brulin and Turco recommended their products could be used for many cleaning cycles, so all panels were cleaned with the same batch of cleaner. In the case of TCE, heptane, and Freon, a maximum of 3 panels were cleaned in each batch of the cleaner.

Cleaner	Step	Procedure	Constituents	Temp C /Time
BRULIN 815 GD	1	Ultrasonic	Brulin 815 GD 10:1 distilled water	60 max/ 10 min
	2	Rinse	Distilled water	ambient/ 4 min
	3	Hot rinse-ultrasonic	Distilled water	60 max/ 4 min
	4	Dry	Air	ambient/ N/A
TURCO	1	Ultrasonic ultra	Turco vitro clean 10 oz/gal distilled water	60 max/ 10 min
	2	Rinse	Distilled water	ambient/ 4 min
	3	Hot rinse-ultrasonic	Distilled water	60 max/ 10 min
	4	2nd-ultrasonic clean	Turco 4215 additive 3.0-3.5% in water	60 mix/ 10 min
	5	Rinse	Distilled water	ambient/ 10 min
	6	Hot rinse-ultrasonic	Distilled water	60 max/ 10 min
	7	Dry	Air	ambient/ N/A
FREON	1	Ultrasonic	Freon	ambient/ 10-15
	2	Rinse	Freon	ambient/ 10-15
	3	Dry	Air	ambient/ N/A

HEPTANE	1	Ultrasonic	heptane	ambient/10-15
	2	Rinse	heptane	ambient/10-15
	3	Dry	Air	ambient/ N/A
TCE	1	Ultrasonic	TCE	ambient/ 10-15
	2	Rinse	TCE	ambient/ 10-15
	3	Dry	Air	ambient/ N/A

Solid Film Lubricant Application Procedure

Booster lube -

1. Clean panels according to cleaner specifications and allow to dry.
2. Mix lubricant to disperse all solids to a uniform constancy.
3. Apply lubricant to test panels using a Binks spray gun with a nitrogen gas pressure of approximately 40 PSI.
4. To achieve the correct thickness of 0.5 to 1 mil, a minimum of 5 passes may be required. It is beneficial to spray test panels using increasing numbers of passes and measure thickness and uniformity before spraying test panels.
5. Cure in a preheated oven at (430 F to 480 F) for 90 minutes.
6. Air cool and seal in Capran 980 or equivalent bag.

Inlox 88 -

1. Clean panels according to cleaner specifications and allow to dry.
2. Mix lubricant to disperse all solids to a uniform constancy.
3. Apply lubricant to test panels using a Binks spray gun with an air pressure of approximately 40 PSI.
4. Spray lubricant to a thickness of .2 to .5 mils. Five passes may be required.
5. First cure at room temperature cure for 30 minutes then cure in a preheated oven at 191 C (375 F) 90 minutes.
6. Air cool and seal in Capran 980 or equivalent bag.

RESULTS

The adhesion properties of these two different solid film lubricants on 304 stainless steel are excellent. Testing shows no loss of adhesion on any test panel when using the ASTM standard test. When the tape was taken off the Inlox 88 test panels, some of the top burnished fluff coat was removed and made the tape appear gray. This is normal due to the burnishing process after the solid film lubricant has cured. The Booster lube samples did not experience fluff-coat removal because of the hardness of the solid film lubricant. With most solid film lubricant application processes these panels were grit blasted - as stated above. This grit basting creates a good anchor for the coating, making them difficult to remove. The only test this laboratory has experienced in which a solid film lubricant was removed from the substrate are tests that have high Hertzian contact stresses and/or are operated at moderate to high surface speeds. In those examples, the loss of adhesion was due to over heating of the binder system. A good example of this kind of test is the Falex Pin and Vee Block tester using ASTM 2625 B - Test Method for Endurance of Solid Film Lubricants. The use of a smooth panel may have shown a loss of adhesion, but such a test is not indicative to the application and use of solid film lubricants.

Very good information on the usability of these cleaners was obtained through this testing. As one would expect, the non-aqueous cleaners (excluding Freon) must be handled with caution due to their inherent toxicity. In large cleaning operations and even in the laboratory, these cleaners can be an environmental concern. The aqueous cleaners were more user friendly, but as can be seen by the cleaning procedures, they require several time consuming steps, more-so than is required with the non-aqueous solvents.

CONCLUSIONS

Based on the standard tests performed on panels cleaned with several environmentally friendly cleaners it can be stated that none of the cleaners have a detrimental affect on the adhesion of two different aerospace lubricants on adhesion. There does not appear to be any adhesion issue in using these evaluated cleaners for components that are grit blast and using these two aerospace quality solid film lubricants.

The Effect of ODC-Free Cleaning Techniques on Bearing Lifetimes in the Parched Elastohydrodynamic Regime

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A parched elastohydrodynamic rig was used to determine relative bearing lifetimes as a function of cleaning procedures in a series of accelerated tests. Two ODC-free cleaning procedures (super critical CO_2 and ultraviolet-ozone) were compared to a CFC-113 control. Bearings (52100 steel) were run in the counter rotating mode (equivalent to 4600 rpm) with a full complement (i.e. no retainer) and a single charge of lubricant (Krytox 143 AC). Test conditions included: an air atmosphere, 445N load, ~1.0 GPa mean Hertz stress. There was approximately a 50% reduction in life with bearings cleaned with UV/ozone and a 70% reduction in life with SFE CO_2 when compared to the Freon control. Possible reasons for these decreases in lifetimes are presented.

Keywords: bearings, cleaning, elastohydrodynamics

INTRODUCTION

For many years, CFC 113 (trifluorotrichloroethane) has been used as a solvent in the processing of ball bearings for use in space mechanisms. In addition, CFC 113 has been used as a grease plating medium and solubilizing agent for the popular series of space lubricants known as the perfluoropolyethers (PFPE). PFPE lubricants have been used extensively as lubricants for scanning devices, filter wheels and harmonic drives. Their use has been dictated by their excellent physical properties: thermal stability (*1*), chemical stability (*2*) and elastohydrodynamic behavior (*3*).

However, these fluids are particularly susceptible to catalytic degradation by a variety of different chemical surfaces, both statically and in tribocontacts. (*4*)-(*12*). These include: titanium, aluminum and iron based alloys, aluminas, fluorides, chlorides, and oxides. The Montreal protocol has mandated the phaseout of CFC 113 and other ozone depleting substances. This has resulted in a series of new bearing processing and cleaning techniques based on non-ODC chemicals. These new techniques, although adequate for cleaning, result in a series of different surface chemistries whose ramifications for bearing longevity are unknown. In 1994 a workshop was held in Denver, CO to address these issues as they relate to the cleaning and lubrication of space system mechanical components for multi-year operations (*13*).

One issue covered at this workshop was the use of alternate alkaline aqueous cleaners (*14*) for spacecraft bearings that had been presoaked in tricresyl phosphate (TCP)(*15*). TCP presoaks have been used for many years to enhance boundary lubrication for slow speed spacecraft bearings (*16*). Surface analysis indicated that the aqueous cleaning removed 60 to 85% of the beneficial phosphorus layer. Other results showed the importance of the final solvent rinse on PFPE lubricant degradation (*17*). At 345 °C in air, an iron coupon rinsed in CFC-113 caused about 25% of a linear PFPE to be degraded. In contrast, a final rinse of water caused about an 80% degradation. Tests with a linear PFPE on 440C steel in oxygen at 316 °C yielded similar results (*18*).

Recently, new cleaning protocols and solubility tests have been developed for spacecraft bearings and lubricants (*19*). These protocols recommend the replacement of CFC-113 and 1,1,1-trichloroethane with super critical CO_2 and a series of perfluorinated solvents. Although these procedures adequately solubilized PFPE fluids and cleaned bearing surfaces, the resulting surface chemistries and their effects on bearing lifetimes are unknown. Another cleaning technique, ultraviolet-ozone (*20*), has been used for many years to remove carbonaceous contamination from surfaces.

Therefore, the objective of this work was to study the effects of two ODC-free cleaning procedures on bearing lifetimes in a transient elastohydrodynamic lubrication apparatus. These procedures are: super critical carbon dioxide and ultraviolet-ozone. Results are compared with conventional CFC-113 cleaning. Test conditions included: a

dry air atmosphere, 891 N load (mean Hz stress, 1.2 GPa), effective bearing speed, 4700 rpm, room temperature and a poly (hexafluoropropene oxide) PFPE lubricant.

EXPERIMENTAL

Transient Elastohydrodynamic Apparatus (TEHL)

The overall apparatus is shown in Fig. 1. It consists of the TEHL apparatus itself, inner and outer race drive motors (the latter containing a torque sensor) and a loading mechanism. The TEHL apparatus appears in Fig. 2. The upper bearing is the test bearing. The outer race of this bearing is driven by a synchronous hysteresis motor through a toothed belt drive. A keyed bushing is press-fit into the inner race. The load ring is keyed into the bushing and a spindle, which is driven by a second synchronous motor through another toothed belt drive. This allows the bearing to be run in a counter-rotating mode, where the races spin in opposite directions such that the ball complement is stationary. The bearing is loaded axially through the load ring and the central load shaft that extends down through the spindle. A lever arm system and a scissors jack are used to load the shaft. The four lower bearings provide support and alignment. More details about rig design, instrumentation and operation appear in reference (*21*).

Bearing Measurements

A data acquisition and control system monitors test bearing health. Parameters monitored include: test bearing, housing, upper support bearing and ambient temperatures; test bearing film capacitance and conductivity; inner and outer race speeds and ball spin; relative humidity, basic speed ratio (BSR) and motor torque. Test bearing torque is calculated from a thermal model and lubricant film thickness from capacitance measurements (*21*).

Materials

The lubricant used for this study was a perfluoropolyether based on hexafluoropropene oxide (*22*). Properties for this fluid appear in Table I. Test bearings (ABEC 5) were made of AISI 52100 steel and were operated in a retainerless mode using a full complement (21 balls)(7.9375×10^{-3} m diameter, grade 10). Bearing bore was 0.04 m and the pitch diameter was 5.40×10^{-2} m.

Cleaning Procedures

Bearing balls and races were ultrasonically cleaned for 10 minutes in hexane, then scrubbed with 0.3 μm alumina powder and tap water and rinsed with deionized water. Specimens were then either: (1) UV-ozone cleaned for 30 minutes, (2) cleaned in a super critical CO_2 device for one hour at 80 °C and 225 atmospheres or (3) ultrasonically cleaned in Freon 113 for 10 minutes. Procedure (3) included a step, prior to the Freon

rinse, to simulate removal of machining oil by coating the specimens with a thin film of an unformulated super refined mineral oil (KG-80).

Experimental Procedure

Immediately after cleaning, the ball complement is weighed. Then, the ball complement is placed in a beaker of a 50/1 dilution of the lubricant in Freon 113. Each ball is removed and dried in a gaseous nitrogen stream. Then, the entire complement is weighed again and the bearing is assembled. The total amount of lubricant is recorded and is typically 3 to 6 mg. The races are not lubricated. After assembly, the complement is rotated by hand for several revolutions to distribute lubricant to the raceways. Then the test bearing is placed in the test rig. The rig is enclosed and purged with a dry air atmosphere (RH < 2%) for a minimum of 30 minutes.

The apparatus is operated in a counter-rotating mode with an inner race speed of ~ 44 Hz and an outer race speed of ~ 33 Hz. This yields an effective bearing speed of ~ 4600 rpm. Bearing temperatures (test, upper support, housing and ambient) are continuously monitored. Typical data appear in figure 3. Bearing capacitance, conductance (resistance) and motor torque are also monitored. Typical traces for capacitance and resistance as a function of test time appear in figures 4 and 5, respectively. Approach to bearing failure is indicated by a rise in capacitance and a decrease resistance. Tests are automatically terminated when preset values of test bearing temperature, capacitance or resistance are attained.

Normally, the automatic termination procedure is sensitive enough to prevent major damage to the test bearing. The test bearing races are inspected, cleaned and reused. New bearing balls are used for each test. Used test balls are retained for surface analysis.

Statistical Analysis

The bearing lifetime data was statistically analyzed (*23*) in order to establish the confidence levels for comparisons between the three cleaning techniques. The data set for each cleaning technique was first checked for normality. It was necessary to perform a (ln) transformation to yield normally distributed data sets so that the common statistical tests could be applied. The means of the transformed data sets were then compared simultaneously using a one-way ANOVA. It was found that the means were statistically different from one another at a 95% confidence level. This allowed a simultaneous comparison of the standard deviations to be performed using a Foster-Burr test. A further SNK test on the transformed means indicated that they were significantly different from each other at a 95% confidence level.

RESULTS

Test Duration

Figure 6 contains the average test times to failure for the three different cleaning procedures. These averages represent a total of 11 tests for UV-ozone cleaning, 9 tests with Freon cleaning and 11 with SFE CO_2 cleaning. As indicated, the Freon cleaned bearings ran the longest. There was ~ 50 % reduction in life with UV/ozone cleaning and ~ 70% reduction with SFE CO_2. Error bars represent one standard deviation.

Surface Analysis

Figure 7 contains a micrograph of a track on a test ball from one of the tests. Typically, as the balls establish a stable orbit, a well defined band of degraded lubricant is evident. Raman analysis on and off this track appears in figures 8(a) and (b), respectively. Inside the band, the typical Raman signature for a degraded PFPE is shown. The well known G and D peaks are evident. A complete interpretation of these spectra appears in reference *24*.

DISCUSSION

The phasing out of ODC cleaning agents has raised many concerns about the long term consequences on spacecraft lubrication systems. Almost all heritage systems had utilized Freon 113 or trichloroethane for final bearing processing. New bearing cleaning processes may alter surface chemistries in such a way as to decrease the lifetimes of bearings for critical instruments. Therefore, the objective of this research was to determine bearing lifetimes for two ODC-free cleaning processes (UV-ozone and SFE CO_2) and compare these results to that obtained by standard Freon 113 cleaning. As indicated above, both new processes adversely affected average bearing lifetimes. The 50 and 70% decreases in average lifetime were shown to be statistically significant at a 95% confidence level.

All of the bearings in these tests were operated in the parched EHL regime (*25*). This is a subdivision of starved lubrication where there is no free bulk oil in the system. The lubricant films are so thin that they are immobile outside the Hertzian contact region. Many spacecraft bearings operate in this regime because it requires the least driving torque and has the most precisely defined spin axis. The lubricant inside the Hertzian zone is not immobile and is eventually squeezed out , resulting in thinning transients which leads to lubricant film failure and subsequently to bearing failure.

As the lubricant film thins, shear rate increases and this shear energy is concentrated in smaller and smaller Hertzian volumes. Eventually, this shear energy

causes irreversible chemical changes in the lubricant film, resulting in degradation and/or polymerization (*26*). It is during this process that surface chemical effects can come into play. If the bearing surface is too active, the film degradation progression can be accelerated, resulting in earlier bearing failure. Conversely, if the bearing surface is less active, this progression can be delayed, resulting in longer duration tests.

Of course, these are greatly accelerated tests because of the limited amount of lubricant and the fact that no additional lubricant is added during the test. In addition, all tests were run in an air atmosphere. Whether these results can be extrapolated to long duration non-accelerated tests in vacuum, remains to be seen. Standard bearing gimbal tests in vacuum are now in progress. Nevertheless, the fact that statistically significant reductions in bearing lives were observed for two ODC-free cleaning processes, is a cause for concern.

CONCLUSION

Two ODC-free cleaning processes (UV-ozone and super critical CO_2) can produce residual surface chemistries that reduce lifetimes in accelerated bearing tests and may affect bearings for long-lived space missions.

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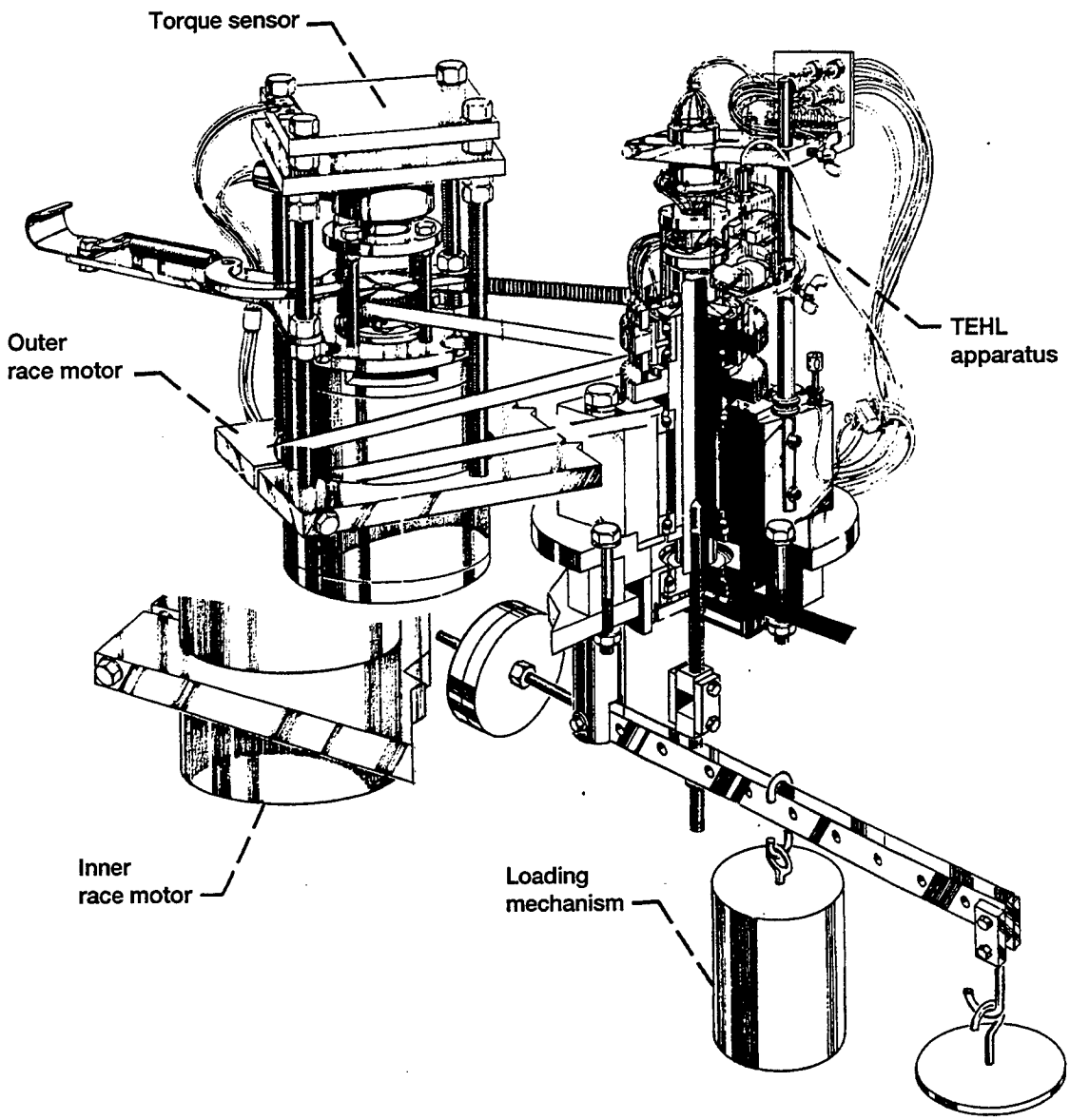

Figure 1.—Overall experimental apparatus.

E-10425 Jones 9pt/100% nm Scan of E-6259-1 Fig 1

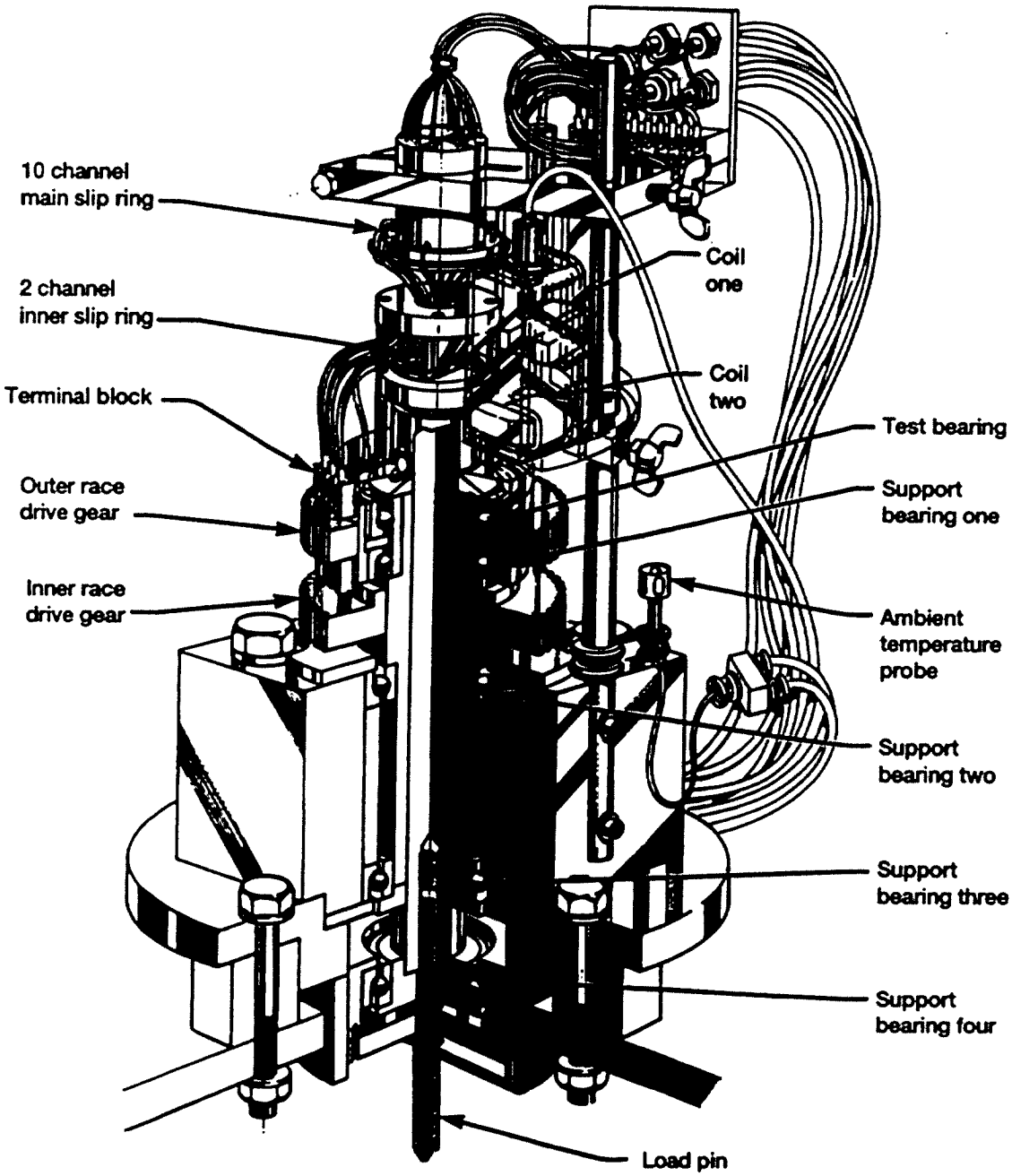

Figure 2.—TEHL apparatus.

E-10425 Jones 9pt/100% nm Scan of E-6259-1 Fig 2

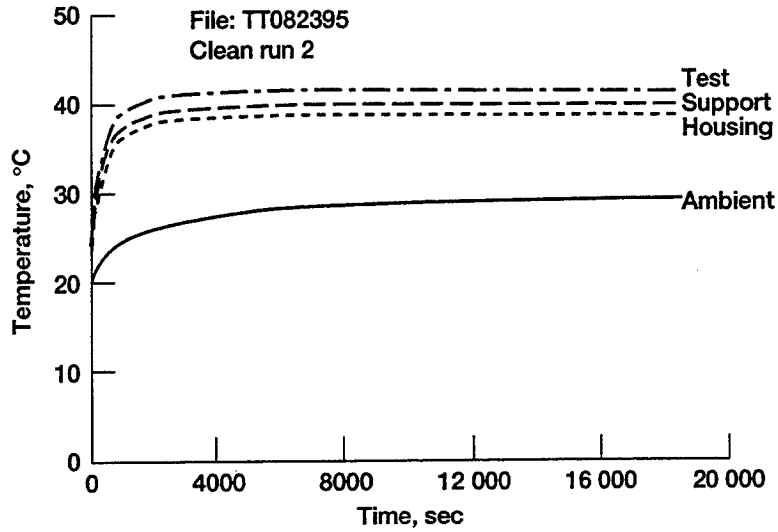

Figure 3.—Test and support bearing, housing and ambient temperatures as a function of test time.

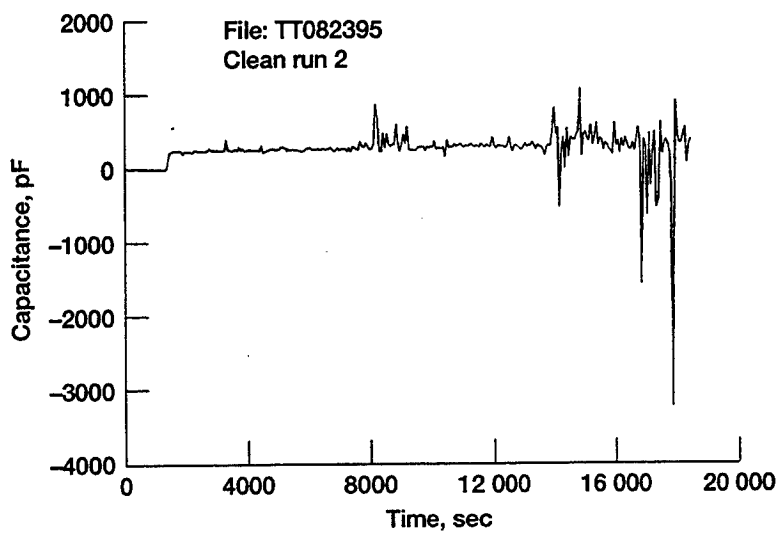

Figure 4.—Bearing capacitance as a function of test time.

E-10425 Jones 9pt/100% nm Scan

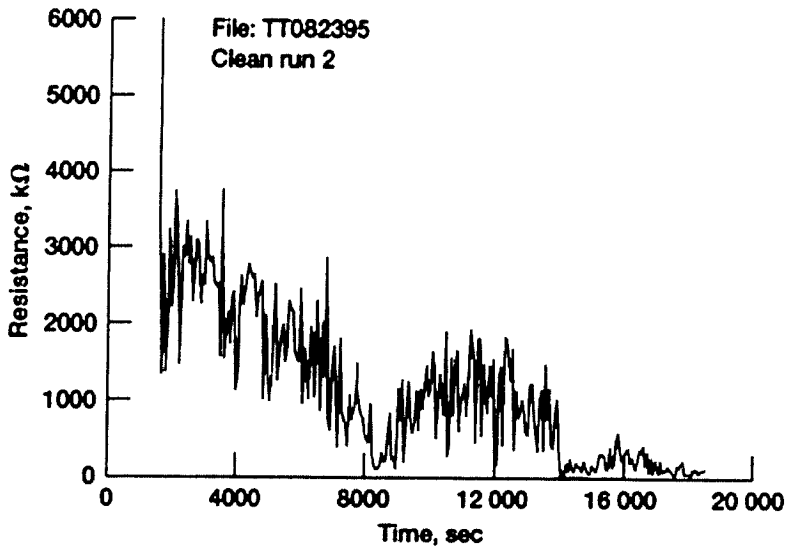

Figure 5.—Bearing resistance as a function of test time.

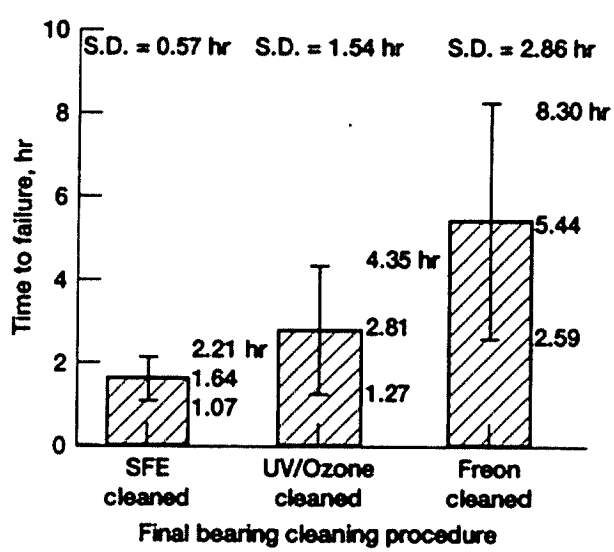

Figure 6.—Freon-free bearing cleaning summary parched EHL apparatus (air; 4500 rpm, room temperature).

E-10425 Jones 9pt/100% nm Scan

Figure 7.—Micrograph of a wear track on a bearing ball.

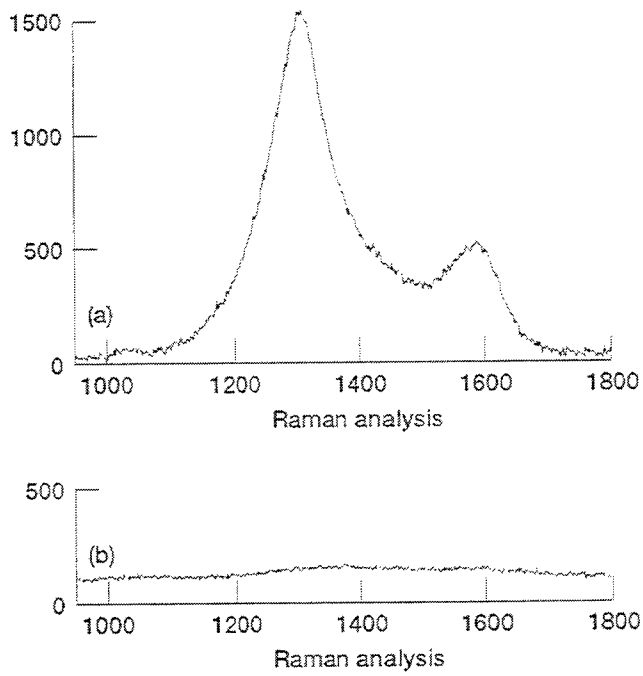

Figure 8.—Raman analysis of test ball. (a) On track. (b) Off track

E-10425 Jones 9pt/100% nm PhE

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The mandated elimination of CFC's, Halons, TCA, and other ozone depleting chemicals and specific hazardous materials has required changes and new developments in aerospace materials and processes. The aerospace industry has been involved for several years in providing product substitutions, redesigning entire production processes, and developing new materials that minimize or eliminate damage to the environment. These activities emphasize replacement cleaning solvents and their application, verification, compliant coatings including corrosion protection system and removal techniques, chemical propulsion effects on the environment, and the initiation of modifications to relevant processing and manufacturing specifications and standards.

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