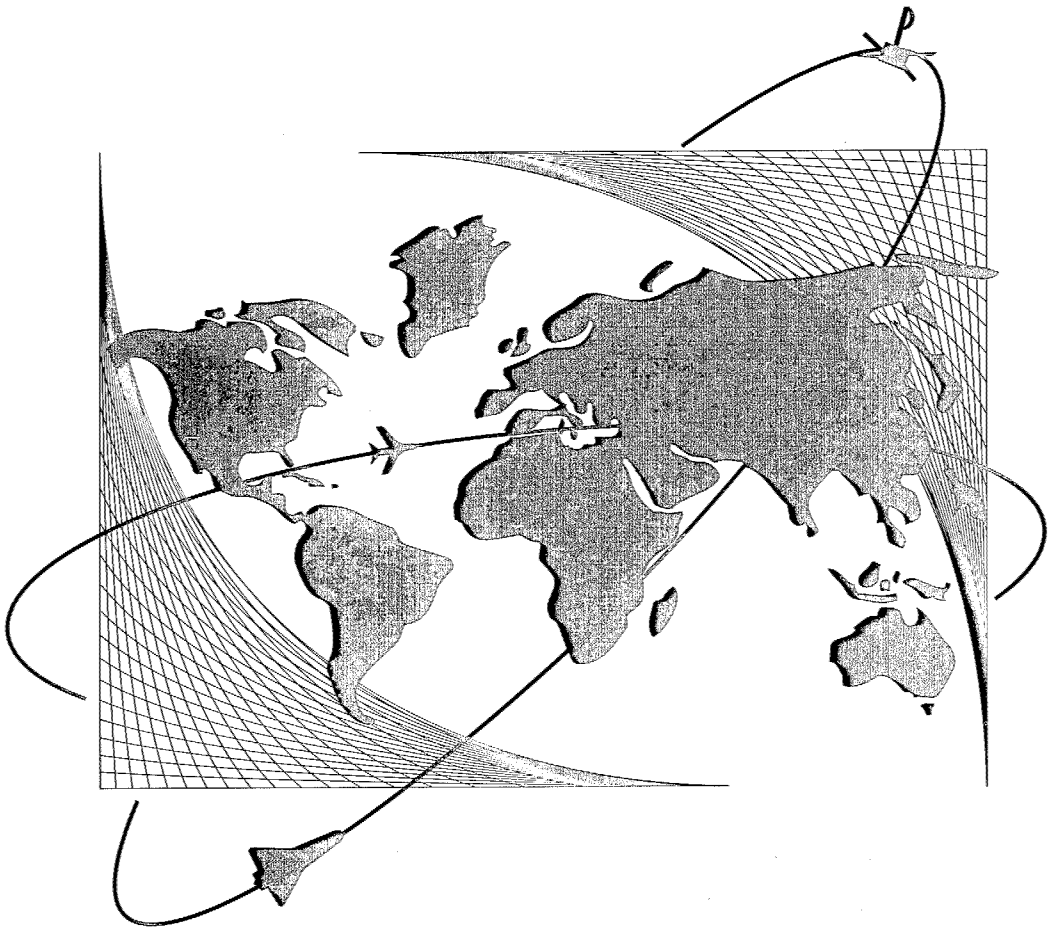
NASA/CP—1999–209258

Third Aerospace Environmental Technology Conference

A.F. Whitaker, D.R. Cross, S.V. Caruso, M. Clark-Ingram, Editors
Marshall Space Flight Center, Marshall Space Flight Center, Alabama



Proceedings of a conference held
in Huntsville, Alabama
June 1–3, 1998

April 1999

The NASA STI Program Office...in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and mission, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results...even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA Access Help Desk at (301) 621-0134

- Telephone the NASA Access Help Desk at (301) 621-0390

- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  800 Elkridge Landing Road
  Linthicum Heights, MD 21090-2934

NASA/CP—1999–209258

Third Aerospace Environmental Technology Conference

A.F. Whitaker, D.R. Cross, S.V. Caruso, M. Clark-Ingram, Editors
Marshall Space Flight Center, Marshall Space Flight Center, Alabama

Proceedings of a conference held
in Huntsville, Alabama
June 1–3, 1998

National Aeronautics and
Space Administration

Marshall Space Flight Center

April 1999

Available from:

NASA Center for AeroSpace Information
800 Elkridge Landing Road
Linthicum Heights, MD 21090-2934
(301) 621-0390

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

3rd Aerospace Environmental Technology Conference
Co-Sponsors

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
MSFC, AL 35812-9999

NASA Operational Environment Team
George C. Marshall Space Flight Center
MSFC, AL 35812-9999

Office of Space Flight, NASA Headquarters
Washington, DC 20546-0001

SAMPE Space Manufacturing Thrust Committee
P. O. Box 2459
Covina, CA 91722-8459

Aerospace Industries Association
125 Eye Street NW
Washington, DC 20005-3299

Air Transportation Association
4400 Catalina Circle
East Point, GA 30344-6511

American Institute of Aeronautics and Astronautics
370 L'Enfant Promenade SW
Washington, DC 20024-2518

ASM™, International
9639 Kinsman Road
Materials Park, OH 44073-0002

Environmental Protection Agency
86 T.W. Alexander Drive
Research Triangle Park, NC 27711-0001

National Center for Manufacturing Sciences
3025 Boardwalk Street
Ann Arbor, MI 48108-3266

The University of Alabama in Huntsville
Division of Continuing Education – Conferences
Huntsville, AL 35899-0650

3rd Aerospace Environmental Technology Conference

Table of Contents

Opening, Plenary and Closing Sessions Summary xi

Session A1: Engineering Evaluation of Materials for ODC Replacement - I

Effect of Bearing Cleaning on Long Term Bearing Life 1
T. Jett, R. Thom

Implementation Update: n-Propyl Bromide in Perspective 14
B. Kanegsberg

Session A2: Environmental Laws and Compliance Strategies

Aerospace NESHAP Compliance: Planning and Lessons Learned at Delta Air Lines, Inc. 20
I. Pearl, J. Burke, M. Hait

Storm Water Discharges from Industrial Facilities: Achieving Compliance at Kelly Air Force Base 38
P. Makowski, G. Goodman

X-33 Environmental Impact Statement: A Fast Track Approach 43
R. McCaleb, D. Holland

Title V Application Preparation at MSFC: Lessons Learned 54
J.P. Martin

Life Under the NESHAP: Experiences of the Regulators, Industry and Users 59
J. Durkee

Session A3: Elimination of Heavy Metals

Cryogenic Bonding Primer Replacement for the External Tank 66
L. Groves

Chromium Electroplating Alternatives Reference Executive Summary 83
T. Rice, B. Anderson

Zinc-Chromate Primer Alternatives for Aircraft Engine Inserts & Fasteners 88
S. Patel

Vacuum Arc Vapor Deposition Electroplating Chrome Replacement 99
J. Weeks

Health & Safety Issues of Compliant Aluminum Metallic-Ceramic Coating 104
K. Eddinger, A. Piacentino

Session B1: Workshop on Technology Challenges for Replacement Fire Suppressants

Fire Protection Considerations for Critical Electronic Equipment Facilities.....109
G. Taylor

NASA Issues Related to the Use of Halon: Past, Present, Future.....141
M. Collins

Session B2: Current Processes and Materials for Precision Cleaning

Implementation of Precision Verification Solvents on the External Tank.....144
M. Campbell

A Review of Production Cleaning Processes.....153
A. Brown, V. Douglas

Precision Cleaning and Verification Processes Used at Marshall Space Flight Center for Critical Hardware Applications.....160
S. Caruso, J. Cox, K. McGee

Aqueous Cleaning and Validation for Space Shuttle Propulsion Hardware at the White Sands Test Facility.....169
S. Hornung, P. Biesinger, M. Kirsch, H. Beeson, K. Leuders

CFC-113 Replacement Plan for the BNA Palmdale Facility.....178
E. Eichinger

Session B3: Environmentally Compliant Coating Technologies

Energetic Ingredients Processing in Liquid Carbon Dioxide.....200
R. Farncomb, G. Nauflett

Hazardous Material Minimization in Adhesives and Sealants Used in PATRIOT Missile System Maintenance.....208
R. Morgan, R. Hagler

Surface Treatment Technology.....215
J. Mitchell

Session C1: Approaches to Environmental Management - I

An Innovative Approach to Meeting Storm Water Discharge Requirements.....223
B. Cress, R. Bost, K. Henke, G. Goodman

Asbestos Management in Buildings: FAA Southern Region Asbestos Control Program.....232
R. Nelson

Partnering for Sustainable Working Relationships.....282
J. Hobbs, C. Venuto

Hazardous Materials Elimination: A Management Perspective.....290
A. Brown

Session C2: Innovations in Propulsion Technology

Electrostatic Hazard Considerations for ODC Solvent Replacement Selection Testing.....295
B. Fairbourn

Chrysotile Asbestos Behavior During Burning of Waste Solid Rocket Propellant.....308
J. Dietz

Session C3: Advances in Aqueous Processes

High Pressure Water Stripping Using Multi-Orifice Nozzles.....314
D. Hoppe

ODC-Free Cleaning Experiences on Solid Rocket Motors.....323
N. Sagers, K. Evans, C. Saunders, B. Betenson, A. Rader

Replacement of a Hazardous Solvent Degreasing Operation with an Automated Aqueous Precision Clean Line.....330
M. Privett

Wash Solution Bath Life Extensions for Space Shuttle Solid Rocket Motor Aqueous Cleaning System.....336
C. Saunders, K. Evans, N. Sagers

Session D1: Engineering Evaluation of Materials for ODC Replacement - II

Advances in Environmentally Friendly Aerospace Electronic Cleaning Techniques.....360
J. Kennedy, L. Beeson, H. Klapper, W. Kinne, L. Vettraino, R. Fuchs

Evaluation of Solvent Alternatives for Cleaning of Oxygen Systems.....373
H. Beeson, P. Biesinger, R. Delgado, N. Antin

Evaluation of HCFC AK 225 Alternatives for Precision Cleaning and Verification.....378
D. Melton

Orbiter Program CFC-113 (Freon® 113) Replacements.....391
C. Nguyen, R. Newman

Elimination of Carbon Tetrachloride for Quantitative Hydrocarbon Analysis.....405
V. Douglas

Session D2: Developments in Coating Removal Processes

Flashjet® Coatings Removal Process.....414
T. Nied

Laser Coatings Removal.....444
T. Fuchser

An Interagency Depainting Study Status.....461
M. Clark-Ingram, B. Cook

Session D3: Advancements in Manufacturing Technologies

The Successful Transfer of Space Deprived Convergent Spray Technology(TM): An Application for Industrial Roof Coatings and Interstate Bridge Repair.....484
V. McMillan

Newer Cleaning Processes: Steam, CO_2, Plasma, and Maximal Solvent Containment.....495
B. Kanegsberg, D. Paquin

Alabama Rapid Prototyping and Manufacturing Alliance (ARPAMA).....501
J. Cranston

Chemical Fingerprinting of ODC Replacement Solvents for Acceptance Criteria.....508
W. McClennen, B. Weber

Session E1: Approaches to Environmental Management - II

Using Hazard Evaluation Techniques to Detect Potential Operational Risks Associated With Chemical Substitutions.....517
J. Mullen, R. Cardinal

Removal of Emulsified Oil and Aqueous Film-Forming Foam (AFFF) Using Air-Sparged Hydrocyclone Technology.....527
D. O'Sullivan, Y. Yi

Meeting the 50% Reduction Mandate: Progress at Marshall Space Flight Center.....532
S. Besler, J. P. Martin, N. Woods

Development of an Environmental and Health Risk Assessment Tool for Materials and Processes.....539
L. Weinberg, R. Doubt, D. Bourcier

Session E2: Analytical and Instrumentation Methods

Characterization of Environmentally Friendly Cleaning Processes with Surface Analysis.....550
M. Lesley

Near Real-Time Analysis of Hydrocarbon Contamination in RSRM Production.....562
M. Meltzer, H. Gregg, C. Koester, S. Ross

Refinement of Portable FTIR Spectroscopy to Characterize Metal Surface Contamination.....577
J. Blanks

Enhancing Infrared Reflectance Methods for Detection of Thin Organic Contamination Films on Bonding Surfaces.....590
L. Pearson

Session E3: Implementation of Current Technologies

Cleaning Solvents Based on n-Propyl Bromide Technology.....600
R. Shubkin, S. Chang

Semi-Aqueous and Vapor Degreasing Processes for Removing Waxes, Pitches and Fixturing Compounds from Precision Parts.....610
E. Bivins, S. Hayes, J. Last

Session Fl: Engineering Evaluation of Materials for ODC Replacement - III

Environmentally Acceptable Hydraulic Oil Flush Solvent Cleaning Program for the Replacement of Freon®, An Ozone-Depleting Chemical.....620
J. Weir, R. Doria, A. Sinowitz

Wiltech Component Cleaning & Refurbishment Facility CF Elimination Plan at NASA Kennedy Space Center.....635
O. Melendez, S. Williamson, B. Aman, A. Aurigema

Elimination of Methyl Ethyl Ketone for Removal of Tenacious Contaminants.....638
C. Clayton, M. Mason

Session F2: Pollution Prevention and Comprehensive Chemical Reduction

Contamination Control Changes to the Reusable Solid Rocket Motor Program- a Ten Year Review.....643
D. Bushman, R. Elliott

Development and Implementation of Environmentally Compatible Solid Film Lubricants.....651
H. Novak, P. Hall

Corrosion Evaluation of Aircraft Depainting Chemicals.....657
P. McGill, P. Torres

Phase II ODC Elimination: Hand Wipe Cleaning.....665
D. Danieu

Session F3: Emerging Technologies for Waste Management

What if We Could Purify and Reuse Waste Aircraft Hydraulic Fluid?.....681
D. O'Sullivan, E. Seaman, N. Werner

Anaerobic Treatment of Glycol Based Deicing Fluid Runoff.....683
R. Hickey, C. Weinert, S. Komisar, S. Veltman, M. Switzenbaum

Report of the Biodegradability and Toxicity Studies of Ethoxylated Aqueous Surfactants And Utilization of the Aqueous Surfactant Wastewater as a Carbon and Energy Source in Biological Industrial Wastewater Treatment Facilities.....690
K. Ball

Microtox Toxicity Test Compared with the Daphnid, Flathead Minnow Acute Lethality Tests Lethality Test for Use in Monitoring Wastewater Effluent at NASA, MSFC.....700
D. Obenhuber, T. Huff

Third Aerospace Environmental Technology Conference
Opening, Plenary and Closing Sessions
Summary

Opening Session

The 3rd Conference on Aerospace Environmental Technology was held June 1-3, 1998 at the Von Braun Center in Huntsville, AL. ***Robert Schwinghamer, Associate Director, Technical, of NASA/Marshall Space Flight Center (MSFC),*** opened the conference by stating that aerospace environmental technology is just as important today as it was at the first conference in 1994.

In the welcoming address, Mr. Schwinghamer stated that we are well past the planning stages in aerospace environmental technology activities with replacement and propulsion technologies. We are, as a matter of fact, well in to the implementation process and are realizing improved performance and reduced cost. "So far we've been picking the low hanging fruit and things will be tougher. The problems we have to attack now are more difficult," he warned.

In closing, he said that the conference is an excellent forum for engineers, scientist and managers to critically assess environmental issues and the evolving replacement and propulsion technologies.

The keynote address was given by ***Bruce Jordan, Director, Emission Standards Division, Environmental Protection Agency (EPA).*** Mr. Jordan reiterated the fact that we have picked the low hanging fruit and we have to think vastly different about how energy is used. He urged everyone attending the conference to take on the challenges to ensure a harmonious relationship between aerospace activities and the environment, so that we can then transfer our knowledge and technology to other areas. "The environment is the most challenging thing we face today," he stated.

He listed four goals that he hoped everyone in attendance would strive to achieve: First, to believe in the mission and that aerospace objectives can and should be accomplished in ways that are friendly to the environment; Second, to be a part of the solution; Third, to allow people the freedom to do things in an innovative way; and Lastly, to have a willingness to compromise. In reviewing the four goals, he stated that we need to be motivated and believe in what we are doing, but we must also look for ways to meet aerospace and environmental objectives. "Our environment is walking on very thin ice and we have to become part of the solution instead of waiting for someone else to solve the problem," he advised.

He then turned to his own organization, proposing that the EPA must realize that regulations should not hinder innovation. Mr. Jordan noted that technological advances are being jeopardized because there is currently no provision in the regulation for trial and error.

He recognized that the EPA has a responsibility for the rule to be environmentally feasible and a responsibility to ensure that innovation is not stifled. Mr. Jordan also stated, "We cannot afford to let the environmental technology we have be at status quo. We must let technology work for us." Mr. Jordan expressed a need for an enhanced cooperative working relationship between the EPA and industries that are truly trying to act as responsible environmental stewards. For the aforementioned relationship to be successful, compromise from both parties will be necessary.

In conclusion, Mr. Jordan challenged everyone to find ways to make contributions towards the solutions needed to remedy environmental problems. He felt that future generations will benefit greatly from our dedication to a cleaner environment.

Plenary Session

Session Chair --- Robert J. Schwinghamer, Associate Director, Technical – NASA/MSFC

Lt. Col. Jeffery Williams, NASA Astronaut, spoke during the Plenary Session. He provided his perspective of the space program regarding his personal experiences preparing for space flight.

He explained that the fundamental reason we send people to space is to explore the unknown. "But we also have the responsibility for being good stewards for the environment as we go about this exploration," he added.

Using actual photographs from space, he showed the impact that was made on our environment by smoke from oil fires in Kuwait near the end of the Gulf War and pollution to our oceans and rivers.

He then shared with us NASA's vision, which is to return to the moon and eventually send people to Mars. "We have to return to the moon because there is a high probability of resources for energy on the moon, but more importantly we must develop and validate the technology to send people to Mars and return them safely home again," explained Williams.

The current goal of everyone involved in the space program is to implement changes that will reduce environmental impact and costs while increasing safety, performance and efficiency. In conclusion, Lt. Col. Williams suggested that we all pause and step back from time to time and reflect on how our work fits into the big picture of exploration.

The final speaker of the plenary session was ***Luis Garcia-Baco, Joint Programs and Training, U. S. Army Material Command***. His comments resounded earlier statements made by Mr. Schwinghamer and Mr. Jordan.

He expanded on the need for compromise to include the Army, Navy, Air Force, and Marines along with the EPA, NASA and private industry during advanced technology developments and implementation. He concurred that the problems we now face will be much tougher to solve and that each area has to work together in harmony. Mr. Garcia-Baco recommended that representation is needed within the EPA from a branch of the military, NASA, and private industry.

Future Perspectives (Closing Session)

Session Chair --- Dr. Ann Whitaker, Director, Materials and Processes Laboratory – NASA/MSFC

Robert Schwinghamer opened the session by thanking the attendees, the exhibitors, and the sponsors. His closing message was of caution, warning us that we cannot let our guard down. He emphasized that we must continue to perform thorough analysis, and accountability is crucial to ensure safety. "We can't be too careful when safety is involved – our future depends on it," he concluded.

John R. Edwards, Chief, Environmental Management for the Air Force Space and Missile Systems Center expressed many of the same sentiments that were a common thread throughout the conference, by saying that "these are the times that try men's souls." He believes that it is time to let private industry be innovative – they can do it better, faster, and cheaper. He also pointed out that we need to maintain an awareness of what the public thinks.

Glynn Rountree, Director, Environment, Safety, and Health for Aerospace Industries Association was the closing speaker of the conference. He maintains that a cooperative team-oriented approach is necessary between NASA, DoD, FAA, aerospace manufacturers, subcontractors, airlines, suppliers and other stakeholders. He also noted that the EPA needs aerospace representation.

He predicts the following for the future: the pressure to reduce the use of toxic materials will continue; the record keeping burden will continue to increase; the use of the Internet will grow; and American aerospace products will become more recognizable.

Effect of Bearing Cleaning on Long Term Bearing Life

Tim Jett and Dr. R.L. Thom
Nondestructive Evaluation and Tribology Branch
National Aeronautics and Space Administration
George C. Marshall Space Flight Center
MSFC,Al 35812
(205)544-2514

For many years chlorofluorocarbon (CFC) based solvents, such as CFC113 and 1,1,1, trichloroethane (TCA), were used as bearing cleaning solvents for space mechanism bearings. The 1995 ban on the production of ozone depleting chemicals (ODC) such as CFCs caused a change requiring the use of ODC-free cleaners for precision bearing cleaning. With this change the question arises; what effect if any do these new cleaners have on long term bearing life? The purpose of this study was to evaluate this effect. A one year test using 60 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. Prior to testing the bearings were cleaned with one of four cleaners. These cleaners included two aqueous based cleaners, a CFC based cleaner and supercritical carbon dioxide. Three space compatible greases were tested. After testing, the mass of each lubricated bearing was measured both pre and post test. Along with mass loss measurements a profilometer trace of each bearing was taken to measure post test wear of the bearings. In addition, the bearings were visually examined and analyzed using an optical microscope.

Introduction

For many years chlorofluorocarbon (CFC) based solvents, such as CFC 113 and trichloroethane (TCA) were used as bearing cleaning solvents for space mechanisms. The 1995 ban on the production of ozone depleting chemicals (ODC) such as CFCs has resulted in a change to new ODC-free cleaners for the precision cleaning of bearings. With this change the question arises; what effect if any do these new cleaners have on bearing life and performance? Many space mechanisms require long life bearings and lubrication. These new ODC-free cleaners may have a negative effect on the long term life and performance of these space mechanisms. These ODC-free cleaners may modify bearing surfaces differently than CFC based cleaners. Performance anomalies may occur due to wetting differences or changes in surface reactivity resulting in shorter bearing life. There is evidence to suggest some new aqueous cleaners are detrimental to bearing operation. These cleaners may actually clean the bearing surface better that the CFC base cleaners. This could leave a reactive surface and contribute to lubricant degradation. It's also possible the detergent used for aqueous cleaners is not completely rinsed which might lead to a reduced bearing life. These new cleaners need to be carefully evaluated to determine the effects that they may have on long term bearing life.

A study was initiated to evaluate the effects, if any, these new ODC-free cleaners have on long term bearing life in a vacuum. For these tests sixty small electric motors (two R-4 angular contact bearings per motor) were tested. These tests were performed at elevated high temperature (90 C) and in a high vacuum (1E-6 torr) environment. Four cleaners and three space compatible greases were evaluated. These cleaners were CFC 113(Freon), Brulin 815 GD, Turco Vitro Clean and supercritical carbon dioxide. The three space compatible greases were Braycote 601EF grease(vacuum baked), Vackote 48822, and Rheolube 2000.

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 controlled aluminum mounting plate. Twenty electrical motors were installed on the plate. For this testing three bell jar work station were utilized. The bell jar workstations were maintained at identical environmental conditions.

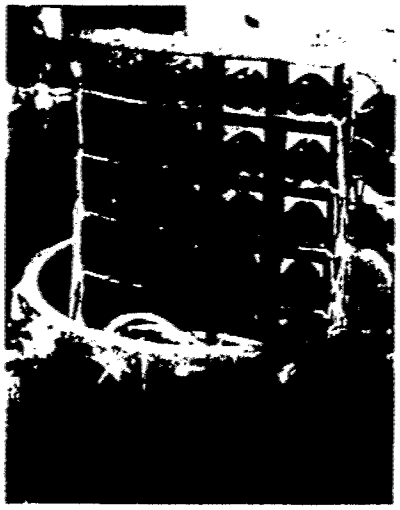


Figure 1. Test Motors in vacuum chamber with bell jar removed.

In this study a total of sixty electric motors, each containing two angular contact bearings, were used. The bearings 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. Motors were run continuously for one year at 90 ° C at approximately 10^{-6} torr pressure. The motors were loaded to maintain a 22.2 N thrust load with no radial load. The bearings operate at 3,600 rpm, and this results in a fully developed elastohydrodynamic film being formed. The motors used for the test have 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 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 re-circulating heated bath was used to circulate and control the fluid temperature and control the bearing operating temperatures.

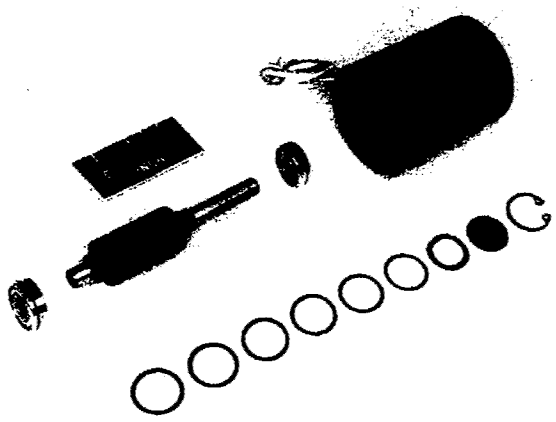


Figure 2. Disassembled ac motor with R-4 Bearing

Test Procedure

The purpose of this study was to determine the effect of cleaning on the long term bearing life. For this testing four cleaners and three space compatible greases were evaluated. These cleaners were CFC 113 (Freon), Brulin 815 GD, Turco Vitro Clean and supercritical carbon dioxide. CFC 113 is a chlorofluorocarbon solvent that historically has been used for precision cleaning of bearings. CFC113 is an ozone depleting chemical, and its production was banned in 1995. Turco Vitro Clean and Brulin 815GD are aqueous based cleaners. The final cleaning method utilized was a supercritical carbon dioxide cleaning method performed by Battelle. The three space compatible lubricants are Braycote 601EF grease, Vackote 48822, and Rheolube 2000. Braycote 601EF is a perfluoroalkylpolyether (PFPE) grease that is manufactured. In order to pass NASA's outgassing requirements (MSFC 1443) this grease was vacuum baked out. Vackote 48822 is a vacuum baked version of Vackote 44147EF. This grease is synthetic hydrocarbon grease that is manufactured by Ball Aerospace. Rheolube 2000 is a cyclic synthetic hydrocarbon grease which is produced by Nye Lubricants.

For this study sixty motors or 120 bearings were tested. Twenty motors were lubricated with Braycote 601EF (Vacuum Baked out). Twenty motors were lubricated with Vackote 48822 and the remaining twenty motors were lubricated with Rheolube 2000. A bell jar was dedicated to each type of grease.

Prior to lubrication, the bearings were contaminated by placing them in a solution of used grinding machine coolant for 1 hour. The bearings were cleaned with one of the four test cleaners. Twenty five percent of the bearings were cleaned with each cleaner.. All bearings were ultrasonically cleaned with Freon, Turco or Brulin according to one the procedures shown in Table 1; or they were cleaned by Battelle supercritical carbon dioxide method. After cleaning the bearings were lubricated with a 25 to 30 percent volume filled of the test lubricant. Next, the bearings were mounted on amartures and placed in the motors.

Cleaner	Step	Procedure	Bath	Temp C	Time(min)
Brulin 815 GD	**1**	**ultrasonic**	**Brulin GD(10:1)**	**60 max**	**10**
	2	rinse	distilled water	ambient	4
	3	rinse(ultrasonic)	distilled water	60 max	4
	4	dry	air	ambient	n/a
Turco	**1**	**ultrasonic**	**Turco vitro clean**	**60 max**	**10**
	2	rinse	distilled water	ambient	4
	3	rinse(ultrasonic)	distilled water	60 max	4
	4	ultrasonic	Turco 4215 additive(3.5%)	60 max	10
	5	rinse	distilled water	ambient	10
	6	rinse(ultrasonic)	distilled water	60 max	10
	7	dry	air	ambient	n/a
Freon	**1**	**ultrasonic**	**Freon**	**ambient**	**10**
	2	ultrasonic	Freon	ambient	4
	3	dry	air	ambient	n/a

Table 1. Cleaning Procedures

The motors were installed in the aluminum mounting plate which was held at a constant 90 ^{0} C temperature. The motors ran continuously for one year in the 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 N (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 operated continuously at 3,600 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 increased 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 in bell jars

3. Temperature of mounting plates

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.. A Rank Talyor Hobson Taly-Surf profilometer was used to measure wear depth of the inner race wear track inner race.

Test Results

In this study sixty motors were tested. Twenty motors were lubricated with Braycote 601EF and all of these motors were installed in Bell Jar 1. The results of this test are shown in Table 2. These results showed that eleven motors failed during the one year test period. All of these failures were verified to be bearing failures due to poor lubrication. It must be noted the results from Bell Jar 1 are questionable. At approximately 4,440 hours into the testing a problem with the re-circulating bath occurred. No coolant was supplied to the motors for a period of at least twelve hours. This caused a significant increase in operating temperature and a noticeable fogging of the bell jar glass due to grease outgassing. This temperature spike probably had an impact on the lubricant life. A large majority (nine) of the failures occurred either at the temperature spike or after it.

For this severe and off nominal test the type of cleaner didn't appeared to have an effect on bearing life. The failure rates for each cleaner were similar. CFC113, Brulin, and CO2 yielded a 60 percent failure rate while for Turco the rate was 40 percent. The lubricant weight loss results were all high. At MSFC there is a long history of testing Braycote 601 grease. In the past, under very similar test conditions, the average lubricant weight loss was approximately 15 %[1]. In this study the average lubricant weight loss was 41 percent. This higher weight loss is probably due to the temperature spike that occurred during the testing.

A profilometer was used to measure the depth of the inner race wear tracks. The results of the testing showed that the average wear depth of bearings lubricated with Braycote 601 grease was 6.04 microns. The bearings cleaned with CFC 113 exhibited the lowest wear, while the bearings cleaned with Turco had the highest wear as seen in Table 1. The results do not correlate well with the bearing life results.

Post test inspection of the bearings lubricated with Braycote 601 grease showed the lubricant to be significantly degraded. The used grease had turned black and was dried out. Originally, this grease was slightly tan in color. A typical post test bearing is shown in Figure 3. In most cases the bearings still had a small to moderate amount of grease, and the bearings still operated fairly smoothly. However, for several bearings the grease was dry with practically no visible lubricant. Dry, black powder was observed to come from the motors when the amartures were removed from the motor's housing. A typical example of a dry bearing is shown in Figure 4. The type of cleaner used appeared to have no influence on this lubricant degradation. Bearings with very little lubricant and black residue were observed for each type of cleaner. After lubricant inspection the bearings were cleaned and re-examined under an optical microscope. All bearings were in good condition with a visible wear track on both, the inner and outer raceways. No surface distress was noted on any raceways.

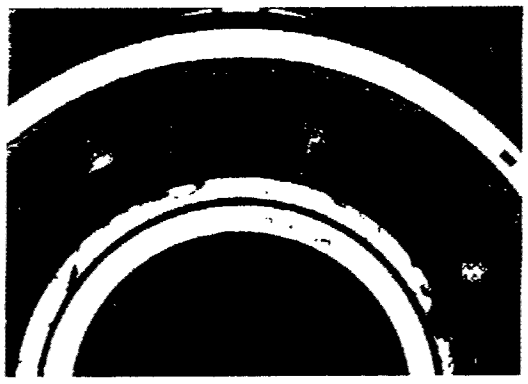


Figure 3. Bearing CB7, a typical post test bearing that was lubricated with Braycote 601EF

Figure 4. Bearing FB7, an example of dried out bearing(Braycote 601EF)

Motor #	Cleaner	Failure	Run Time (Hours)	Weight Loss (%)	Wear Depth (microns)
FB1	Freon	YES	4656	45.67	1.51
FB3	Freon	YES	4944	68.79	0.99
FB5	Freon	YES	4440	58.11	3.08
FB7	Freon	NO	8760	60.31	5.92
FB9	Freon	NO	8760	33.93	4.79
Average			**6312**	**53.36**	**3.26**
BB1	Brulin	YES	6624	53.44	9.21
BB3	Brulin	NO	8760	23.44	2.29
BB5	Brulin	YES	648	29.54	5.98
BB7	Brulin	YES	4680	62.10	3.67
BB9	Brulin	NO	8760	34.54	7.63
Average			**5894.4**	**40.61**	**5.76**
TB1	Turco	NO	8760	48.25	2.83
TB3	Turco	YES	3480	37.94	12.54
TB5	Turco	NO	8760	14.60	8.67
TB7	Turco	YES	576	60.72	11.57
TB9	Turco	NO	8760	0.73	6.69
Average			**6067.2**	**32.45**	**8.46**
CB1	CO2	YES	4440	100.00	3.83
CB3	CO2	YES	6024	54.62	3.80
CB5	CO2	NO	8760	14.64	7.25
CB7	CO2	YES	5280	9.20	12.84
CB9	CO2	NO	8760	7.65	5.78
Average			**6652.8**	**37.22**	**6.70**

Table 2. Summary of Bell Jar #1, Braycote 601EF

Twenty motors were lubricated with Rheolube 2000 and all of these motors were tested in Bell Jar 2. The results of this test are shown in Table 3. These results show that two motors failed in the one year time period. These failures were verified to be bearing failures. The type of cleaner didn't appear to have an effect on bearing failure rate or run time. The average lubricant loss for motors lubricated with Rheolube 2000 was 27.6 percent. This was the lowest of three lubricants tested. The highest weight loss was observed in motors cleaned with CO2 cleaning method. One motor in particular (CR3) had a very high weight loss (57.85 %). The motors cleaned with Turco had the lowest weight loss. The amount of wear observed from profilometer trace of the inner race was relatively mild (1.88 microns). Bearings lubricated with Rheolube 2000 exhibited the lowest amount of wear of the three lubricant tested.

Post test inspection of the bearings lubricated with Rheolube showed the lubricant to have turned to dark black color. Originally, the grease was tan in color. Most bearings had a significant amount of grease still in the bearing. The lubricant was still fairly moist and was still very lubricious. The bearings were still operating smoothly. Figure 5 shows a typical post test bearing. An exception was the bearings in motor CR3. The front bearing in this motor was very dry and rough operating. This motor was one of the two motors that failed. This motor exhibited the greatest amount of bearing wear. After visual observation of the lubricant the bearings were cleaned and inspected under a optical microscope. All bearings were in good condition with a visible wear track on both the inner and outer raceways. No surface distress was noted in any raceway.

Motor #	Cleaner	Failure	Run Time (Hours)	Weight Loss (%)	Wear Depth (microns)
FR1	Freon	NO	8760	26.76	0.41
FR3	Freon	YES	7752	28.57	1.80
FR5	Freon	NO	8760	19.79	2.07
FR7	Freon	NO	8760	25.15	0.74
FR9	Freon	NO	8760	33.41	0.44
Average			**8558.4**	**26.74**	**1.09**
BR1	Brulin	NO	8760	23.68	1.45
BR3	Brulin	NO	8760	28.83	2.85
BR5	Brulin	NO	8760	33.89	2.22
BR7	Brulin	NO	8760	21.95	0.52
BR9	Brulin	NO	8760	28.91	2.22
Average			**8760**	**27.45**	**1.85**
TR1	Turco	NO	8760	22.13	2.11
TR3	Turco	NO	8760	16.49	2.63
TR5	Turco	NO	8760	14.60	2.46
TR7	Turco	NO	8760	25.01	0.91
TR9	Turco	NO	8760	14.90	2.45
Average			**8760**	**18.63**	**2.11**
CR1	CO2	NO	8760	27.14	0.69
CR3	CO2	YES	6840	57.85	4.12
CR5	CO2	NO	8760	33.21	0.56
CR7	CO2	NO	8760	29.84	3.42
CR9	CO2	NO	8760	39.86	3.63
Average			**8376**	**37.58**	**2.48**

Table 3. Summary of Bell Jar, Rheolube 2000

Figure 5. Bearing BR10, a typical post test bearing with Rheolube 2000

Twenty motors were lubricated with Vackote 48822 and tested in Bell Jar 3. The results of this test are shown in Table 4. These results show that 19 of the twenty motors failed during the one year test period. This was the highest failure rate of the three lubricant tests. No correlation between bearing failures and cleaner used could be made. The average run time for the twenty motors lubricated with Vackote was 4,266 hours, which was the lowest average run time for the three lubricants tested. The average lubricant weight loss was 47 percent, which

was the highest of the three lubricants tested. The average inner race wear track depth was 2 microns, it was only slightly higher than the Rheolube 2000, and much lower than wear obtained using Braycote 601 grease.

Post test inspection of the bearings lubricated with Vackote showed the lubricant to be significantly degraded. All of the grease had turned black. Originally, the grease was white. In general, there was a small to moderate amount of dried grease remaining in the bearings, and the bearings were very rough running. A typical bearing is shown in Figure 6. In several bearings the grease had turn into a black powder and there was virtually no grease remaining. An example of this is shown in Figure 7. The type of cleaner appeared to have little influence on the lubricant life. After lubricant inspection the bearings were cleaned and examine under an optical microscope. The bearings were all in good condition with a visible wear track on both the inner and outer race. No surface distress was observed on any bearing raceways.

Figure 6. Typical post test bearing with Vackoke 48822

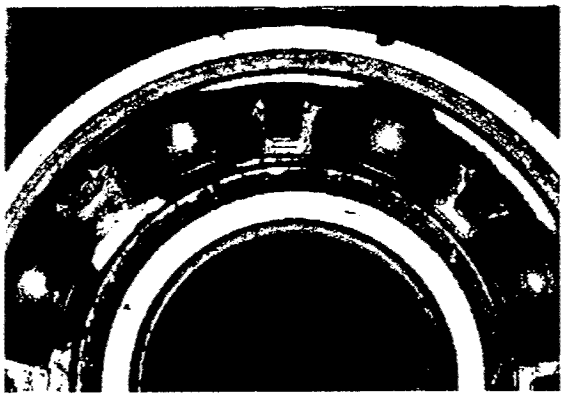


Figure 7. Bearing BV3, an example of a bearing with very little Vackote grease remaining

Motor #	Cleaner	Failure	Run Time (Hours)	Weight Loss (%)	Wear Depth (microns)
FV1	Freon	YES	1152	57.65	3.21
FV3	Freon	YES	1776	18.99	0.50
FV5	Freon	YES	3840	58.79	0.64
FV7	Freon	YES	5520	59.35	2.40
FV9	Freon	YES	2760	57.99	1.20
Average			**3009.6**	**50.55**	**1.59**
BV1	Brulin	NO	8760	25.09	2.33
BV3	Brulin	YES	8208	56.41	0.61
BV5	Brulin	YES	5592	53.20	0.20
BV7	Brulin	YES	2520	5.27	0.82
BV9	Brulin	YES	3792	56.91	0.31
Average			**5774.4**	**39.38**	**0.85**
TV1	Turco	YES	2496	43.90	3.94
TV3	Turco	YES	3360	59.07	0.44
TV5	Turco	YES	5592	52.01	1.99
TV7	Turco	YES	3840	59.96	3.01
TV9	Turco	YES	1224	54.22	5.43
Average			**3302.4**	**53.83**	**2.96**
CV1	CO2	YES	5952	45.27	1.82
CV3	CO2	YES	7872	39.10	1.77
CV5	CO2	YES	3360	42.97	1.25
CV7	CO2	YES	4512	46.72	4.02
CV9	CO2	YES	4200	57.24	3.97
Average			**5179.2**	**46.26**	**2.57**

Table 4. Results from Bell Jar 3, Vackote 48822

In this testing there were two test variables, lubricant used and cleaner used. In general the type of cleaner used did not have a significant effect on bearing life. The failure rate for all bearings cleaned with CFC 113 was 60% (9out 15). This compares to 47% failure rate for both, Turco and Brulin. These failure rates are relatively high. This rate is probably due to the temperature excursion that occurred in Bell Jar number 1 (Braycote 601EF). Prior to testing it was thought that aqueous based cleaners might be detrimental to bearing life. It was also thought that CFC113 might leave behind a protective film that helped delay or prevent the degradation of the PFPE based Braycote 601EF. The aqueous cleaner probably would not leave this film thus giving a cleaner and more reactive surface. This reactive surface could have higher tendency to cause the fluorinated lubricant to breakdown in service.

Unfortunately, due to the temperature excursion in Bell Jar 1, this testing neither proved nor disproved this theory. The results from Bell Jar 1 showed no significant difference in the bearing failure rate for the different cleaners. The overall bearing failure (11/20) was high, and this appears to be highly influence by the temperature spike that occurred during testing. Prior to this temperature spike only two motors had failed. Both of the motors had been cleaned with aqueous base cleaners (one Brulin and Turco).

The lubricant used, definitely had an impact on bearing life. Vackote 48822 had the highest bearing failure rate (19/20). Rheolube 2000 was the best performing grease with only two bearing failures. Braycote 601EF had 11 failures, but as noted previously these results are questionable. Figure 8 shows a comparison of bearing run time for the three lubricants tested. This chart shows that Rheolube is the best performing lubricant, and the Vackcote is the worst. No correlation between bearing run time and cleaner used could be made. Figure 9

shows a comparison of average lubricant weight loss for the three greases. These results show that Rheolube was the best while Vackote had the highest weight loss. No correlation between lubricant weight loss and cleaner used could be made. Figure 10 shows the inner race wear depth. This graph also shows that Rheolube gave the best performance.. This graph also shows that Brulin and Freon cleaned bearings tended to have lower wear.

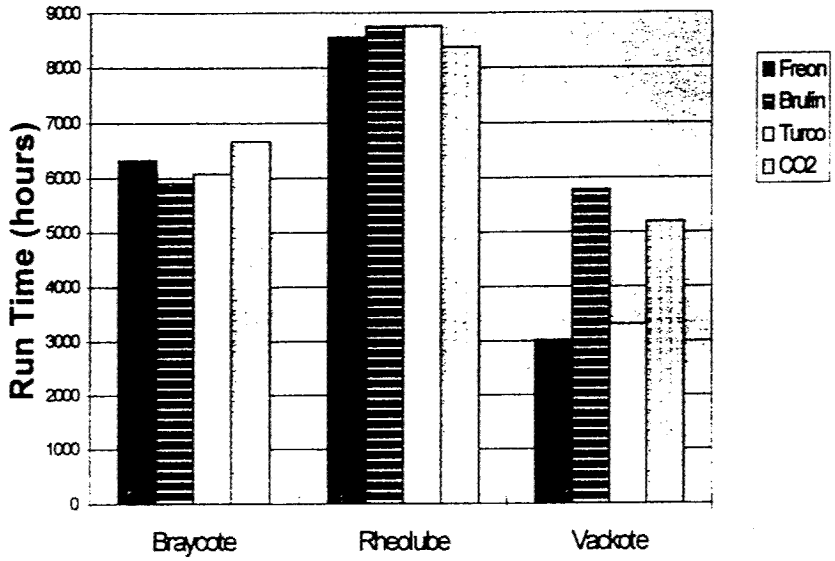


Figure 8. Comparison of average bearing run time

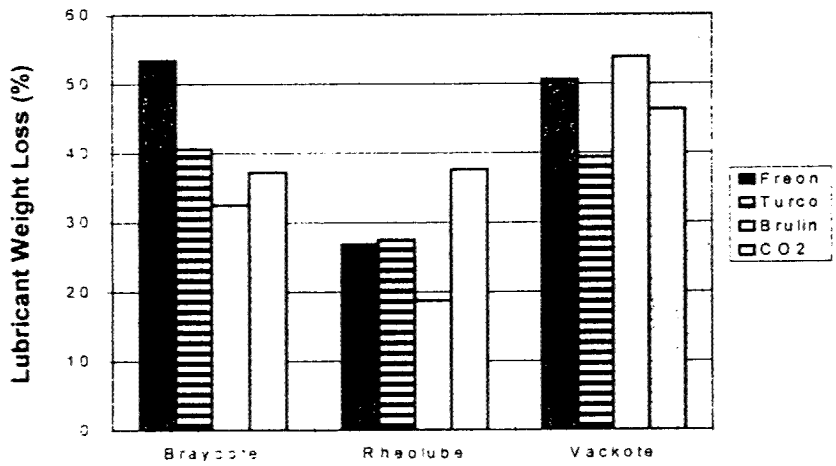


Figure 9. Comparison of average lubricant weight loss

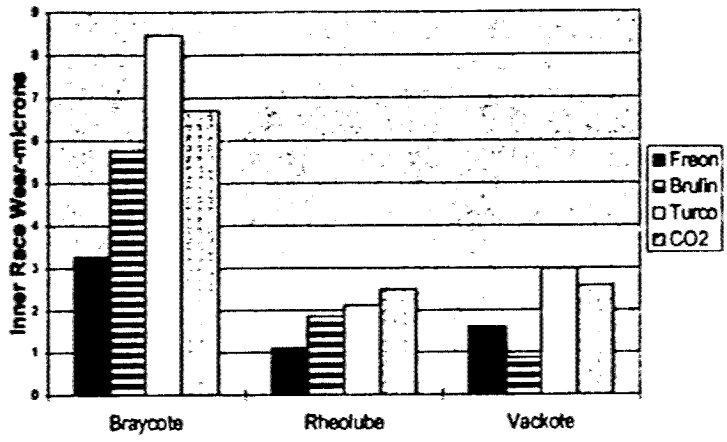


Figure 10. Comparison of average inner race wear

Conclusions

1) In a one year continuous high vacuum and high temperature bearing tests the type of cleaner didn't have a significant effect on bearing life.

2) Test Results from 3 different test grease provide useful design data.

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.

Implementation Update:
n-Propyl Bromide in Perspective

Barbara Kanegsberg
BFK Solutions
16924 Livorno Drive
Pacific Palisades, CA 90272
310-459-3614
email: bkanegsberg@compuserve.com

Introduction:

Components manufacturers face a dilemma. They must cope with increasing manufacturing requirements. With the increase in technology, comes increasingly stringent performance requirements. Tolerances decrease, the expectation of a long product lifetime is increasing. A one size fits all process approach is no longer appropriate. This is true for diverse industries including computer hardware inertial navigation systems, complex electronics, semi-conductors, and implantable biomedical devices. At the same time, world-wide competitive pressure is forcing strict cost containment. Strict, confusing, and often conflicting regulatory requirements, from global, national, and local agencies, may encourage use of cleaning and techniques which can be at cross-purposes to performance requirements

Because of this, components manufacturers work in a process and regulatory microclimate. They need a range of options, a range of process tools at their disposal. Process requirements are site-specific. The manufacturer must consider:

Substrate
Soils
Product mix
Product volume
Throughput
End use of product
Customer requirements, constraints
Regulatory requirements
Employee safety

Choices

While the phaseout of ozone depleting chemicals has resulted in a plethora of cleaning and process options (3), these options have not fulfilled all the requirements of components manufacturers. There is continued dependence on CFC 113, on 1,1,1-trichloroethane, and even on HCFC 141b, despite the usage ban for most applications. CFC 113 has proven relatively easy to replace. In some cases, CFC 113 was used as a final assurance or so-called "motherhood" cleaning; process engineers found that very often, it was not really needed. Many of the substitute solvents provided very mild cleaning. The hydrofluorocarbons (HFC's) and hydrofluoroethers (HFE's) can be combined with more active solvents to form mild to somewhat aggressive mixtures and azeotropes, or they can be used as rinsing agents for higher boiling solvents in co-solvent processes

Many of the newer solvents have provided manufacturers with very good options for the particular soils of interest. The KB number is a simple cloud point test, applicable to hydrocarbon-based cleaning agents. As such it provides only a rough guide to solvency. HFC's and HFE's, which have very low KB numbers, are very good solvents for Krytox and other fluorolubes. HCFC 225 can provide just the right balance of solvency and compatibility in cases where solvent-sensitive plastics or coatings are part of the build. The fact remains, however, that some manufacturers require aggressive solvency at reasonable costs

Some groups have successfully switched to aqueous or semi-aqueous processes. Aqueous processes can be environmentally preferred. However, maintaining water quality and process control can be difficult. High heat and

aggressive cleaning action are typically required, and the manufacturer may be faced with unexpected problems of materials compatibility, erosion, or galvanic interaction which compromise product appearance and/or performance. Managing the waste stream to avoid media transfer can be costly; and full-scale aqueous equipment has a large footprint. At the other end of the scale, classic chlorinated solvents provide good solvency, and can be used in airtight or airless systems. However, regulatory requirements (NESHAP, the California Toxic Hotspots program, etc.), company liability issues, and soil and groundwater contamination preclude their use in some cases. Some companies have been able to adopt the newer, more advanced cleaning systems such as CO2 or plasma cleaning. These processes, while useful, have tended to have specialized applicability.

Wetting Index, Kauri-Butanol Number (KB Number), and Boiling Point

Cleaning Agent	Wetting Index	KB Number	Boiling Point, Deg. C
CFC-113	121	32	48
1,1,1-trichloroethane	65	124	74
n-propyl bromide	105	125	71
HCFC 225	162	31	54
HFC 43-10	167	9	55
water	14	not applicable	100
water, with 6% saponifier	31	not applicable	100

The KB number is a cloud point test; it refers to the volume of solvent needed to produce a defined degree of turbidity when added to standard solutions of Kauri Resin in n-butyl alcohol. As a very rough rule of thumb, the higher the KB number, the more aggressive the solvency. The wetting index (5) is directly proportional to the density and inversely proportional to the surface tension and viscosity. As a general rule, the higher the wetting index, the better able is the solvent to penetrate closely-spaced components. CFC 113 was considered a very useful cleaning agent, in part, because of the wetting index. Having a reasonably high boiling point favors higher entropy, greater melting of soils, and therefore better cleaning. However, with very high boiling points, one runs into the problems of slow evaporation (slow drying), and solvent retainment.

N-propyl bromide (NPB) has become an attractive option for non-aqueous cleaning applications, because it provides aggressive solvency at moderate cost. Overall, it has a favorable regulatory profile. Typically if solvents are aggressive against soils of interest, workers must treat them with respect. NPB is no exception. However, NPB can be used safely with appropriate worker protection. It has an apparent at levels of 50 ppm and below. While odor or lack thereof is not a fool-proof method of solvent detection, the presence of an odor tends to be noticeable; it favors careful usage by employees. NPB can be used in modern, or upgraded (retrofitted) degreasing equipment. Since it is possible to analytically distinguish NPB from chlorinated solvents, companies who had problems with groundwater contamination through older, standard, but undesirable practices, could use NPB in newer equipment and with modern chemical handling practices. At the same time, they would be put on notice to keep these newer processes contained and to avoid inappropriate chemical handling.

Case studies, Implementation of NPB

NPB has been found useful and implemented in a wide range of applications including electronics assembly, precision metals cleaning and surface preparation, removal of pitch and wax from optics, cleaning and assembly of high precision inertial navigation system subassembly, final cleaning of convoluted tubing, and precision biomedical application including cleaning of implantable body parts and delicate surgical devices (1,8,and 9). A few case studies are highlighted in more detail below.

Galley Refrigeration Equipment

B/E Aerospace, Galley Products Group, produces 90% of aircraft galley refrigeration equipment. They must clean 5 to 6 feel long highly-coiled copper assemblies. Repair and recleaning must take place by the customer at remote locations, worldwide. Soils to be removed include mineral oil, polyolester oil, rosin flux, water soluble flux, small metal chips, large metal chips, particles, carbonized soils, undefined soils from subvendor processes, cleaning agent residue, and water. Water is a critical soil; moisture in refrigeration systems is fatal.

With Richard Petrulio, Engineer at B/E, a range of processes were evaluated. B/E has unique process requirements and suitable, economical compact flushing equipment was not available. Richard Petrulio therefore designed in-house compact flushing equipment. This was evaluated with aqueous systems. Repeated attempts were made to achieve adequate drying, including use of warm nitrogen and vacuum drying. However, while aqueous and steam cleaning were adopted for some applications, aqueous processing was judged difficult to control for cleaning copper assemblies; the dangerous potential of residue and moisture remained.

The decision was made to evaluate solvents. An extensive solvent evaluation program was undertaken; results have been reported. NPB was chosen because it cleaned effectively without damaging the components; and it was cost-competitive. NPB is specified for repairs by B/E and by B/E's customers. NPB was also adopted for cleaning certain components such as screens and stators. In addition, B/E was provided with good process support for ABZOL™ VG, including employee training, employee monitoring, and a solvent take-back program by the manufacturer, Albemarle Corporation (7,8).

Biomedical Devices

A company manufacturing biomedical devices needed to clean small, high-value devices to be used in critical and invasive surgery. The devices are exquisitely small, only a few mm long. The company wanted to replace 1,1,1-trichloroethane and CFC 113 for removal of rosin flux and a petrolatum-based solder paste from the devices without leaving interfering soils, cleaning agent residues, and without changing the surface properties of the device. A high level of cleanliness is necessary for surface preparation to assure acceptable adhesion in joining components as well as to avoid potential contamination issues in any surface which would be in contact with the body. The reference process had been developed pragmatically. It is very time-consuming, labor-intensive, and requires over fifteen steps in multiple solvents, including immersion cleaning at ambient temperature and ultrasonic cleaning. The company wished to streamline this established multi-step process.

Efficacy of cleaning was judged by experienced technicians by visual, microscopic inspection at 10x magnification. Several cleaning agent manufacturers of aqueous cleaners and of co-solvent designer blend processes had attempted to remove the flux. In some cases, flux was not completely removed. In other cases where sufficient force was applied to remove the flux, the surface finish of the device was modified. For example, with one aqueous formulation, visible flux residue was still present after two minutes of cleaning; after 5 minutes, the finish was dulled. A blend of HCFC 225 containing ethyl alcohol and stabilizers was evaluated; it removed some of the silver/tin plating. The company found it undesirable to use the classic, chlorinated solvents because of potential liability issues. In addition, the local air regulatory group puts restrictions on many air toxics, notably the chlorinated solvents.

Initial studies using fully-formulated NPB (ABZOL™ VG) were promising in that flux residue was removed while surfaces did not appear dulled. After some experimentation, the company evaluated a four-step process, cleaning the components at ambient temperature with NPB and alcohol. The soils appeared to be completely removed; and the surface finish appeared unchanged. The visual evaluation was confirmed by Auger analysis.

NPB has been introduced in other biomedical applications where high solvency with low residue is necessary, for example in cleaning ultra high molecular weight plastic implantable joints and in removal of rosin flux from electronics components for critical use in clinical equipment (1,9).

Gyroscopes, Accelerometers

Litton G&CS has implemented NPB (ABZOL™ VG) as part of the cleaning process for beryllium gyroscopes and accelerometers. Producing inertial navigation systems involves exacting, multi-step cleaning of complex subassemblies. Production throughput is typically low-volume. Each sub-assembly of the system may require skilled technicians to conduct hundreds of assembly and cleaning steps. An individual step might require only a miniscule amount of solvent. Over, the course of the build process, large amounts of solvent is employed. Classically, CFC 113, 1,1,1-trichloroethane, and isopropyl alcohol (IPA) were used. Because of the phaseout of ozone depleting chemicals (ODC's), starting in the late 1980's, Litton undertook an extensive ODC phaseout program (2). This program included Litton-wide teams, covering Litton facilities world-wide. Through analysis of then-current practices, solvent conservation and recycling, and extensive technology sharing, Litton significantly reduced dependence on ODC's. Aqueous processes were introduced in a number of facilities.

Replacing ODC's, particularly for the more high precision applications, proved to be easier said than done. Because of concerns with potential galvanic interactions and compatibility problems, aqueous cleaning was not judged acceptable for these applications. Significant detectable residue was considered to be unacceptable. During the early 1990's, the most viable option was to use the higher boiling solvent blends. Some of these blends provide good solvency for the rosin flux and other soils to be removed. However, the cleaning agents themselves need to be rinsed with more volatile solvents, such as IPA or perfluorinated materials.

With the permission of cleaning agent manufacturers, co-solvent cleaning studies were conducted at the Du Pont testing facilities. A number of promising options were found. Particularly given the complexity of components, very thorough rinsing was found necessary to assure that no solvent residue remained. Notably, highly purified d-limonene which might be used with little or no rinsing in many applications, was found to require thorough rinsing for these high precision applications. Refining and implementing these processes required the invaluable participation of both the Engineering and Operations groups.

Some of the co-solvent processes, were successfully implemented, with thorough solvent rinsing of the cleaning agent. When NPB became available, the advantages in terms of low residue and high solvency were apparent. The Materials & Processes Engineering group conducted preliminary evaluation. This was followed by testing and implementation by Operations.

NPB in Perspective to Other Solvents

There are certainly many cleaning and process options; many have been implemented. Other possibilities include eliminating redundant cleaning, designing for easier cleaning, aqueous, semi-aqueous, co-solvent, designer blends, low flashpoint systems, steam cleaning, CO2 (liquid, solid, supercritical), plasma cleaning (4), and laser systems.

Litton G&CS and B/E Aerospace have eliminated redundant and unproductive cleaning. A number of groups have re-designed products for easier assembly and cleaning. No-cleaning and aqueous fluxes are options in some, although not all, applications. HFC blends have been successful in some biomedical applications, providing effective cleaning of solvent-sensitive components. Low-flash point co-solvent systems have been adopted for a high volume lead frame application. This application involves removal of heavy oil and very high solids flux from millions of tiny, precision assemblies daily. Certainly, airtight and airless systems have been useful in utilizing classic chlorinated solvents and very costly designer solvents.

Why another solvent?

As a consultant I am often asked several questions, all of which add up to a similar answer. These questions tend to follow the following themes:

What solvent (or solvents) do you recommend?

Why do we need NPB? Aren't there plenty of solvents around already?

Why do we need any solvent or cleaning agent other than NPB?

If there were one magic solvent or magic cleaning process, or even a short list of solvents or processes, which would magically resolve everyone's cleaning and contamination problems, I would publish that list, then go on to solving problems in some other area.

Some other people have assumed that, because NPB has very good solvency, no other solvents are needed. Restricting cleaning to one solvent, NPB or some other solvent, would be like asking an artist to paint a landscape using only the color blue. A blue landscape might be appropriate once in awhile, but it would not realize the full potential of the medium. In this world of specialized materials of construction, high value products, and critical end-use requirements, restricting industry to one solvent would restrict technology.

Manufacturing processes are complex; processes are site-specific. Users must test each cleaning agent and each cleaning process in their own application, considering both solvency range and materials compatibility. For example, one manufacturer of print heads found that NPB was not as effective for removal of the particular mix of soils or as gentle to the particular non-metal components as was perchloroethylene. Another manufacturer found that for certain delicate precision stamped parts, trichloroethylene did not provide adequate cleaning; NPB was superior for that product line.

Cleaning processes may be multi-step, using multiple cleaning agents and processes. This has always been the case, to some extent. It is probably more true today. A range of solvents are needed.

The fact remains that while a number of new solvents have been introduced, they have not met all the needs of industry; they have not resolved all cleaning problems. Too many manufacturers are still dependent on CFC 113 and 1,1,1-trichloroethane. Some, in fact, have resorted to using smuggled solvent; and prosecutions for solvent smuggling has begun (6,8). Or, they are limping along using sub-optimal processes. Some in governmental regulatory agencies point to classes of cleaning agents, for example the large number of aqueous systems or the growing list of VOC-exempt solvents (solvents which are not volatile organic compounds). Too often, what is ignored in the regulatory shuffle are the requirements for:

Aggressive solvency

Efficient, effective cleaning

Moderate cost

NPB fills a niche. A number of components manufacturers have found NPB to be a useful weapon in their cleaning and contamination control efforts. No cleaning agent has universal applicability. However, in the relatively short time since its introduction as a cleaning agent, NPB has found widespread utility.

References:

(1) Kanegsberg, B., "Cleaning for Biomedical Applications," Precision Cleaning '97 Proceedings, April, 1997, 119 – 131.

(2) Kanegsberg, B.; Abbink, B.: Dishart, K,; Kenyon, W. G.; and Knapp, C. W., "Development and Implementation of Non-ozone Depleting, Non-aqueous High Precision Cleaning Protocols for Inertial Navigation Subassemblies," MICROCONTAMINATION 93 Proceedings, Canon Communications, Inc.

(3) Kanegsberg, B., "Precision Cleaning Without Ozone Depleting Chemicals," Chemistry & Industry, 21 October, 1996, 787 – 791.

(4) Kanegsberg, B., and Paquin, D., "Newer Cleaning Processes: Steam, CO2, Plasma, and Maximal Solvent Containment," 3rd Conference on Aerospace Environmental Technology, June, 1998, Huntsville, AL.

(5) Kenyon, W.G., personal communication.

(6) Morehouse, E.T., "A Decade of Progress," presentation and handouts, Eighth Annual International Workshop on Solvent Substitution, December, 1997, Scottsdale, AZ.

(7) Petrulio, R., and Kanegsberg, B., "Back to Basics: The Care and Feeding of a Vapor Degreaser with New Solvents," Nepcon West '98, March, 1998.

(8) Petrulio, R., and Kanegsberg, B., "Practical Solutions to Cleaning and Flushing Problems," CleanTech '98 Proceedings, May, 1998, 362 – 373.

(9) Shubkin, R. L., and Liimatta, E. W., "Developments in the Use of normal-Propyl Bromide as a Cleaning Solvent," CleanTech '98 Proceedings, May, 1998, 89 – 107.

AEROSPACE NESHAP COMPLIANCE: PLANNING AND LESSONS LEARNED AT DELTA AIR LINES, INC.

Ira G. Pearl
Manager, Environmental Compliance
Delta Air Lines, Inc.

Jack M. Burke, P.E.
Project Manager
Radian International LLC

Mitchell J. Hait, Ph.D., P.E.
Project Manager
Trinity Consultants

ABSTRACT

Delta Air Lines' began it's efforts to comply with the Aerospace NESHAP over two years before the effective date of the rule, with intensive efforts commencing upon issuance of the revised rule, approximately one year in advance of the scheduled compliance date. This paper discusses the processes used to develop, review, refine, and implement a Master Compliance Plan. In addition to outlining the planning and implementation processes used, this discussion will also focus on system requirements, such as material monitoring and recordkeeping, personnel training, and lessons learned during the implementation of the Master Plan.

INTRODUCTION

Delta Air Lines is one of the worlds largest air transportation companies. Delta operates a fleet of over six hundred jet aircraft, carrying passengers and cargo to over 184 destinations world-wide, completing over 3,000 flights each day. Delta is headquartered in Atlanta, Georgia, which is also home to Delta's major maintenance facility: Delta's Technical Operations Center (TOC).

Delta Air Lines performs the majority of the required maintenance for their aircraft fleet, as well as occasional in-sourcing of maintenance functions for other air carriers. This maintenance includes full aircraft and parts stripping and repainting, heavy maintenance visits (HMV), engine overhauls and testing, FAA required letter checks, and electroplating operations, among many other maintenance operations. While some maintenance is performed at Delta's other stations, the Atlanta TOC is the primary air rework facility. The TOC was built in three stages over the last 20 years and is staffed by over 4,000 mechanics, engineers, managers and other support personnel. There is no portion of aircraft rework on any of Delta's fleet that cannot be performed at the TOC. As a result of the breadth of operations and the size and variety of Delta's fleet, the TOC is one of the largest commercial aircraft rework facilities in the southeastern United States. The Atlanta TOC is currently Delta's only facility subject to the Aerospace NESHAP.

As mentioned earlier, aircraft maintenance operations are also performed at approximately 35 other maintenance facilities (outstations) located across the United States. Of these facilities, four are synthetic minor facilities for the purposes of applicability of Title V permitting regulations and the Aerospace NESHAP. Delta Air Lines has taken emissions limits on these facilities to reduce their potential emissions below the applicability thresholds of the Aerospace NESHAP (i.e., 10 tons per year of any individual HAP and 25 tons per year of total HAP) and the Title V operating permit rules. The remaining facilities are not subject to the Aerospace NESHAP because their "true" potential emissions are below the applicability threshold of this regulation.

Because the TOC is located in an ozone non-attainment area, it is also subject to the requirements of the Aerospace Control Techniques Guideline (CTG) document, in addition to the other Georgia State Implementation Plan (SIP) air quality requirements intended to reduce VOC emissions. Although the Aerospace CTG is only intended as guidance for State and Local Air Quality agencies, Delta and the Georgia Environmental Protection Division (EPD) have agreed to use the CTG to implement the requirements of a site-specific VOC RACT rule for all Delta maintenance facilities located in the Atlanta ozone non-attainment area. This use of the Aerospace CTG is a win-win proposition for both parties. It reduces VOC emissions in the non-attainment area, while having the appropriate allowances and exemptions for aerospace industry-specific operations.

The TOC is a full service facility, and as the name suggests, it is the center of Delta's maintenance operations. As a result this facility conducts most of the operations that are regulated by the Aerospace NESHAP. These operations include:

- Depainting (stripping);
- Surface coating (both aircraft parts and completed aircraft);
- Solvent Cleaning;
  - Hand-wipe cleaning;
  - Paint gun cleaning;
  - Flush cleaning; and
- Waste handling

The one main category of operations regulated by the Aerospace NESHAP that is not performed at this facility is the use of Type I and II chemical milling maskants, as defined in the regulation.

In addition to being subject to the Aerospace NESHAP, the TOC is subject to a variety of other air quality regulations. These regulations include New Source Performance Standards (NSPS), non-attainment permitting under new source review (NSR) regulations, VOC and NO_x RACT rules, and three other NESHAPs. Clearly complying with complex and involved regulations is not new to Delta. However, the Aerospace NESHAP and CTG are easily the most complex and wide-sweeping air quality requirements to ever affect Delta's operations

COMPLIANCE OVERVIEW

This section summarizes Delta's approach to bringing about compliance with the Aerospace NESHAP. This approach is based on completing a series of interrelated activities that drive the facility into compliance with this regulation. This section serves to introduce the plan that these steps comprise. The lessons that were learned in implementing these steps are discussed later in this paper.

Steps Used to Achieve Compliance with the Aerospace NESHAP

1. ***Understand the requirements as they apply to Delta's operations.***
2. ***Initiate capital improvement projects.***
3. ***Develop a master compliance plan and schedule.***
4. ***Collect shop level compliance data.***
5. ***Develop training program.***
6. ***Develop electronic information management system.***
7. ***Perform self audit.***
8. ***Correct deficiencies.***

The first step was to analyze the requirements of the Aerospace NESHAP and CTG with a clear emphasis on how the requirements apply to Delta's operations. Complicating this activity is

the breadth of the operations performed at the TOC. The TOC is almost a mile from end to end, has over 3 million indoor square feet, and contains almost 100 different departments that are potentially affected by the Aerospace NESHAP. This first analysis was performed on a big picture basis, taking into consideration which regulated activities are performed at the facility, but not yet identifying which shops performed which activity. This big picture emphasis allowed completion of this step without getting bogged down in the details.

During the first step, it became apparent that some equipment modifications would be required to meet the Aerospace NESHAP requirements. For example, the dry filtration systems for many of the existing paint booths would need to be upgraded. Because of the long lead time for capital intensive projects, these equipment modifications were started early in the process -- almost two years before the effective date of the regulation.

The next step was to develop a master compliance plan and schedule. This detailed plan listed the provisions of the Aerospace NESHAP that affected Delta's operations and the activities that needed to be performed to bring the facility into compliance with each applicable provision of the NESHAP. A schedule for completing these steps was also developed at the same time.

One of the challenges associated with complying with the Aerospace NESHAP is how to fulfill the myriad of recordkeeping and reporting requirements associated with this rule. Because of the complexity of these requirements and the site-specific approach that Delta chose for implementation of this regulation, it was decided to develop a customized Aerospace NESHAP module as part of a larger environmental information management system (EIMS) being designed for Delta. Since the EIMS was still under development, it simplified the process of including the needed tables, screens, queries, reports, and task management tools needed to demonstrate compliance with the NESHAP.

Many of the requirements associated with the Aerospace NESHAP involve implementing specific workpractices (e.g., handling solvent transfers in a manner that minimizes spills). Others require adhering to specific policies (e.g., only mixing paints according to established formulations). Thus, Delta feels that an essential step in achieving compliance requires that the over 4,000 affected workers be trained on the requirements of the Aerospace NESHAP. To deliver this training as efficiently and cost-effectively as possible, a multimedia computer based training (CBT) program is being developed. This training program ties Delta-specific compliance steps with the regulatory background and requirements to provide shop personnel with the understanding needed to do their jobs in compliance with the rule.

Once the procedures are put in place, and the training is performed (scheduled to begin in July 1998), Delta plans to perform a comprehensive self-audit to identify where the facility isin compliance, and where shortcomings exist. This audit will be performed before the compliance date of the Aerospace NESHAP to allow the opportunity to identify any deficiencies and take the appropriate corrective actions.

The EPA has projected that the Aerospace NESHAP will reduce HAP emissions by some 100,000 tons per year on a nation-wide basis. However, there is a considerable cost associated

with these reductions. At Delta, this cost is estimated to be over $2.8 million to effect initial compliance (including capital modifications), with additional operating expenses associated with continued compliance.

A variety of lessons were learned from preparing for compliance with this regulation. These lessons are discussed in a later section of this paper. The big picture lessons learned were:

- Get involved early,
- Do not underestimate the effort that compliance will take, and
- Obtain early support from the affected organizations and senior management at the facility.

RULE DEVELOPMENT

The Aerospace NESHAP and CTG are some of the first rules that were developed as part of the EPA's negotiated regulation approach to rule development. This approach involved the regulated community, equipment and product suppliers, citizen groups, and regulatory agencies in the rule development process. The goal of this approach was to develop a rule that has considerable environmental impact (i.e., reductions in emissions) in a manner that the regulated community can realistically implement. One of the consequences of this rule development process is the inclusion of specific exemptions for those activities that produce relatively low quantities of emissions and that alternate materials or processes are not readily available.

Delta was an active participant during development of this rule, both individually and through its industry association, the Air Transport Association (ATA). Delta's involvement included representation at virtually every public meeting and conference call held between EPA and the stakeholders This participation, both early in the process, and throughout public comments and subsequent revisions allowed Delta to work with the other parties to develop a rule that all can live with. This is not to say that the rule is easy to comply with. It most certainly is very complex and requires much preparation, planning, and hard work to attain and maintain compliance. However, without industry participation, this rule could have easily interfered with the industry's ability to build and maintain safe aircraft. Thus, the impact of having a "seat at the table" during the rulemaking process cannot be understated. Much credit goes to Mr. Bruce Jordan, Director of the Emission Standards Division at EPA for his forward-thinking, open, and honest approach to this process.

The aerospace industry that is regulated by this rule is quite diverse. It includes aircraft manufacturers, military installations, airlines, contract maintenance operations, and component manufacturers. Even within the specific examples listed, there is a great deal of variation. For example, the maintenance and overhaul of single engine aircraft is considerably different from that of commercial wide-body passenger aircraft. Thus, it is certainly a challenge to develop environmental regulations for such a diverse group. This difficulty is one reason that several changes were made to this rule, and additional changes were proposed in March 1998.

The Aerospace CTG was developed concurrently with the Aerospace NESHAP. Traditionally, a NESHAP will regulate HAP emissions, and a CTG will address VOC emissions. Because the Aerospace NESHAP regulates VOC emissions in addition to HAP emissions, there is considerable overlap between the two requirements. This overlap is an advantage to Delta and other industry members because it eliminated the potential for two separate regulations to impose conflicting requirements.

The VOC requirements of the Aerospace CTG tend to be more stringent than those of the Aerospace NESHAP. For example, the VOC content of specialty coatings is regulated by the Aerospace CTG, but not by the Aerospace NESHAP. However, HAP emissions are regulated by the Aerospace NESHAP, but only indirectly regulated by the Aerospace CTG in the event the HAP is also a VOC.

During the course of the rule development and subsequent revisions, Delta found it advantageous to remain involved in the rulemaking meetings. This involvement allowed Delta to voice their specific concerns, and to identify the implications of proposed changes. For example, Delta provided comments on exemptions to the hand wipe cleaning requirements and specialty coatings critical to safe aircraft operation and maintenance that were incorporated into the final rule.

Because of its involvement in this process, Delta had an early understanding of the requirements associated with the Aerospace CTG. Delta worked with the Georgia EPD to implement these requirements into permits in advance of the final Aerospace CTG.. This early implementation means that Delta is able to take significant steps towards reducing VOC emissions, which can help contribute to solving Atlanta's air quality problems.

EQUIPMENT MODIFICATIONS

A number of equipment modifications were identified that would have to be completed to comply with the Aerospace NESHAP. The lessons learned from implementing these modifications is discussed in this section.

First, the Aerospace NESHAP has specific requirements regarding surface coating application devices. To meet these requirements, Delta has primarily selected the options of using either high volume low pressure (HVLP) paint guns or electrostatic application equipment. Although neither of these options represents a major process change for Delta, there were some lessons that were learned from both changes.

Delta's experience indicated the combination of a high solids and low VOC content that met the Aerospace NESHAP requirements in combination with electrostatic spray equipment was an untried and unproven technology. Delta was involved in the development of this process along with some of the original equipment manufacturers (OEMs). The development process proved to be a trial and error process that spanned several years, costing both operators and OEMs several million dollars to complete. Some of the difficulties involved poor paint appearance, and in some

cases paint that came off in flight within weeks of initial application. Of particular concern in developing this process are the conditions that this coating must endure, including extreme temperatures, flexibility, and chemical resistance (e.g., skydrol resistance).

In contrast, the implementation of HVLP guns was found to generate considerable cost savings. The HVLP guns operate with a much higher transfer efficiency than do the conventional spray guns that they replaced. Because of the high cost of the aerospace coatings, the pay back period for the purchase of the HVLP guns was measured in days instead of in years. The lesson learned from this implementation is that environmental programs, especially those that reduce material usage, can actually generate cost savings. Thus, the common misperception that the environmental regulations only add cost to a process may not be entirely correct. However, even with this cost savings, the Aerospace NESHAP, as a whole, required a significant investment by Delta to achieve compliance.

Another equipment modification was the replacement of existing spray gun cleaners with enclosed spray gun cleaners. This implementation was so successful that Delta has adopted this equipment as the standard for all painting operations company-wide. In some cases, this equipment was supplemented with disassembled paint gun cleaners for some of the coating systems in use. However, these were the only two spray gun cleaning options in the rule that Delta needed to implement to achieve compliance and operational success.

Perhaps the largest single capital expense in meeting the requirements of the Aerospace NESHAP involves the upgrade of the paint booth filtration systems. Twenty-two paint booths were upgraded at a cost of approximately $1.5 million. These paint booths ranged from small, single painter booths to three large hangars used to paint entire aircraft. The process of converting the booth filtration systems began almost two years in advance of the September 1, 1998 compliance date with the investigation of potentially compliant filter technologies. In hindsight, this investigation was crucial, because the increased pressure drop of more efficient filters has vast implications on existing paint booth operations, particularly the aircraft paint hangars. An engineering study was commissioned to investigate the impacts of the new filters on fans and controllers, as well as exhaust plenum design.

It turned out that fans needed to be reshived, distributed control systems updated or installed to allow operation over a wider range of differential pressures, and fan housings needed to be fabricated to support the pressure drop associated with the two stage filters. In addition, filter differential pressure gauges were specified and installed along with data collection systems. The most time intensive steps included:

- Selection of a contractor to perform the initial engineering study on the booths and required modifications;
- Preparing an RFP and going through an engineering contractor proposal and bid selection process; and
- Completing the booth modifications, filter installation, and acceptance testing.

In addition to upgrading the equipment, the Aerospace NESHAP has considerable requirements for developing, implementing, and following a startup, shutdown and malfunction plan. Again, it is important to have these plans completed as far in advance as possible so that they can be implemented and debugged prior to the actual compliance date. There is a distinct advantage to keeping the plans short, and not directly including specific information that might change (e.g., a pressure range) as hard numbers. In this case, it is best to included pressure range selection as a procedure. For example, it is best to state the procedure for setting the clean filter differential pressure after a filter change, and including a calculation to determine the "change filter" setpoint, rather than plading hard numbers into the plan. This prevents having to revise and resubmit the plan each time the filters are changed.. Training of staff on revisions and document control is also critical. This training can be incorported into the overall NESHAP training.

MASTER COMPLIANCE PLAN

Perhaps the one single activity that has made this implementation process go smoothly for Delta is the development and implementation of a master compliance plan. In this section, we discuss the process for developing this plan and schedule, and how it is being implemented throughout the facility.

The first step in the plan development was preparation of a matrix of the rule requirements. As an example, this matrix is presented in Table 1 for the aircraft depainting activities. The concept behind this matrix is quite simple; to list in one place the requirements, compliance option selected, the current status of meeting these requirements, the gaps, plans for filling the gaps, and any additional comments that may apply. How this matrix was prepared is discussed in this section.

One of the first aspects of preparing this matrix was to identify which compliance options Delta elected to implement. For example, for surface coating operations, Delta has the option of using only materials that individually meet the requirements of the rule, or to use an averaging scheme. Delta elected to use an averaging scheme because it allows for the limited use of materials with VOC and HAP contents in excess of the Aerospace NESHAP limits and because Delta already had an information management system in place that could support the use of averaging. Another option was in the selection of the type of averaging scheme to use (i.e., per booth, per department, or for the entire facility). It was decided to use the per department approach because the authority over surface coating operations exists on a department-level basis at Delta. These options were selected during focus meetings with Delta's environmental staff, personnel from representative departments, and environmental consultants. As a result of these meetings, specific compliance approaches were selected, and later these selections were verified through meetings with representatives of all affected departments. The meetings with internal stakeholders also proved critical to success.

Table 1 – Aerospace NESHAP Compliance Analysis Matrix

Compliance Area	Subarea	Option Selected	Compliance Requirements	Current Status	Plans	Gap	Issues/ Comments
Aircraft Depainting	N/A	Use Non-HAP strippers and limit HAP stripper use to 190 lb of organic HAP per aircraft for spot stripping and decal removal.	Documentation for each type of aircraft model of the parts, subassemblies, and assemblies normally removed from the aircraft before depainting. This list of parts does not include wings and stabilizers.	Not performed at present	D. Hanson to prepare lists by 1/31/98	Institute a procedure for management of change (i.e., what to do when new models of aircraft are stripped)	Contract Aircraft 777s Need HMV and Paint Lists
			Track/record the volume or weight of HAP-containing stripper used for depainting	Track via Linden	Refine algorithms and data entry screens	Need to define and implement algorithms and data entry screens	
			Train staff responsible for depainting operations to input required data and remain below solvent usage limits.	Currently taught how to input data into database for TOC III emissions cap tracking	Perform as part of the CBT	Need to develop a CBT module to discuss	
			Documentation for each non-HAP stripper used (name, MSDS, or compositional data)	Use only Turco 6776, data in Linden	Gatekeeper is CRC and Linden	Ensure that proper information is maintained as part of Linden	Need to check on materials used by departments other than Dept 410C, can be done by Linden. M. Craig to generate first report.

Table 1 – Aerospace NESHAP Compliance Analysis Matrix

Compliance Area	Subarea	Option Selected	Compliance Requirements	Current Status	Plans	Gap	Issues/ Comments
			Track number and type of planes stripped each year (monthly is recommended).	Performed via hardcopy logs in Dept 410	Add to Linden	Need to define and implement algorithms and data entry screens	Track percentage of plane stripped on partial jobs
Aircraft Depainting (cont'd.)	N/A		Data management system upgrades to support preparation and submittal of annual and semi-annual reports	Not in place	Add to Linden	Need to define and implement algorithms and data entry screens	
			Annual HAP stripper calculations & related recordkeeping (note: monthly is recommended for consistency with other applicable requirements).	Not in place	Add to Linden	Need to define and implement algorithms and data entry screens	

Once the compliance options were selected, the focus group worked together to assess the current status. A detailed investigation was performed later; however; for the purposes of a global planning activity, a facility-wide snapshot was sufficient. This assessment allowed us to identify those areas where Delta was already meeting the requirements of this rule, and those areas where gaps existed. This group discussed possible ways to fill these gaps, and selected those options that made the most sense to Delta.

Once it was decided how to fill the gaps, a detailed implementation schedule was developed to allow for the tracking of several activities that were happening concurrently. Although this scheduling and project tracking appears simple, it was identified as one of the main shortcomings of the Aerospace NESHAP implementation process. However, it was one that was effectively addressed by the development of the master compliance plan. In short, the master plan defined the many activities needed to bring the facility into compliance with this regulation, and the responsible party was typically organized by the person's primary work function. This plan allowed for the environmental manager to have in one place a listing of what activities were being performed across the facility, the responsible party, and milestones for completion.

Although it is useful to have a global strategy, the Aerospace NESHAP needs to be implemented at the individual department level. Up to this point, Delta's focus was on the entire facility, not on the specific actions being taken by each department. To collect the appropriate information at the departmental level, meetings were held with representatives from each affected department. At these meetings, the requirements of the Aerospace NESHAP and CTG as they apply to Delta's operations were discussed. Also, a questionnaire was distributed to each shop to collect the information needed to ascertain the compliance status of the shop should the Aerospace NESHAP be determined to be applicable, and to collect the information required to document the department's compliance with this regulation.

Getting meaningful replies to this questionnaire was no trivial accomplishment. For many of the representatives from the affected shops, this was their first attempt at completing such a survey. To facilitate this process and to work the bugs out of the system, the questionnaire was piloted through two of the more complex departments at the TOC, and the results were provided to the other departments as an example. Additionally, material requisition data from a corporate purchasing database were supplied to each shop as a reference point. Even with early piloting and supplying shops with material use records and examples of how the forms should be filled out, many questions arose and many errors occurred during the completion of the questionnaires.

Also, the task of compiling the results from each individual shop was delegated to an engineering intern. The intern did an excellent job of compiling the information was supplied into a single spreadsheet, and later into a MS Access database. The only flaw, however, was that the intern did not have the appropriate level of expertise in the Aerospace NESHAP to identify problems with the information that was submitted by the individual departments. These data, once compiled into a single file, were reviewed by a professional that was well versed in the NESHAP requirements. A second set of meetings was held with the department representatives to enable refinement and completion of the data submitted.

The primary lesson learned from this experience is that a considerable amount of quality assurance and quality control needs to be built into the data collection process. Obtaining this data is a critical first step in identifying which materials are used, which exemptions or specialty coating categories apply, and where the need for material substitutions exists. Another lesson learned was that, at the initial meeting when the questionnaires were passed out, the specifics of how to complete the questionnaire should have been discussed in additional detail. Also, the responses should be reviewed for content as they were received, not after the results were compiled. Doing a "back-end" analysis wasted valuable time in the compliance planning process.

Once all the data collected from the questionnaires was compiled, Delta was able to identify those specific shops and departments that needed assistance in meeting the requirements of the Aerospace NESHAP. For example, sufficient data were collected to allow estimation of the average VOC content of surface coating materials for each department. These data are being analyzed to identify those departments needing the most attention to achieve compliance with the Aerospace NESHAP.

One important aspect of the results of the questionnaire is they allow Delta to clearly document what operations are exempt from the specific Aerospace NESHAP requirements. For example, if methyl ethyl ketone (MEK) is used for hand wipe cleaning, the exempt operations this solvent is used in are identified in this questionnaire.

Another activity of considerable effort is the identification of alternate materials, and gaining the associated approvals to assure the alternate materials meet the requirements of the original equipment manufacturers (OEM) and the Federal Aviation Administration (FAA). This process involves the assessment of a variety of potential alternate materials, selection of those that show the most promise, getting the appropriate approvals, and revising the appropriate technical manuals and work practices to allow for the use of the alternate material.

An important element in meeting the recordkeeping and reporting requirements of the Aerospace NESHAP is to have an appropriately designed electronic information management system (EIMS). While an EIMS is not strictly required in the regulations, the challenge of managing the required data without one is staggering. Delta elected to have a custom Aerospace NESHAP EIMS module designed as a part of a larger EIMS that is being developed to support a variety of environmental recordkeeping and reporting requirements at the TOC. This development of an EIMS is discussed in further detail later in this paper.

Other elements of the implementation of the Aerospace NESHAP requirements include the training of the affected workers and performing an internal audit to determine where the problems are with achieving compliance with this regulation. These topics are discussed in further detail below.

LINDEN ENVIRONMENTAL INFORMATION MANAGEMENT SYSTEM (EIMS)

One of the challenges of meeting the requirements of the Aerospace NESHAP is collecting, processing, and managing the quantities of data that are required to demonstrate compliance with this rule. Some of the complicating factors in selecting an EIMS is that there are several compliance options associated with this rule, and Delta has existing chemical use data management systems that this system must interface with. Therefore, Delta decided to build a custom EIMS module as part of their multimedia environmental EIMS. Discussed in this section are how this system is designed, the basic functionality of the system, and some of the features that Delta has incorporated into this system.

An essential element of the EIMS is the collection of material use data (e.g., coatings, solvents, strippers). For example, these data are required to demonstrate compliance with the VOC and organic HAP content limits for surface coating activities. Similarly, these data are required for solvent cleaning operations. Because the Aerospace NESHAP module is part of a more comprehensive EIMS, the material use data are either already available, or available with some minor changes to the system.

Also important is the control of distribution of the materials. For example, some solvents may only be used for exempt operations. Delta will use the EIMS to track on a department level, what materials are approved for use by each department, and, as appropriate, what exemptions apply to the operations in that department.

Having an EIMS is an important step in achieving compliance with this regulation. Another aspect is to establish a user interface that readily allows for the input of compliance-related data, while providing data integrity checks, and the appropriate level of security. Delta has achieved these constraints by developing a series of input screens that are used to allow for the entry of needed data. Product specific data for all VOC and HAP containing materials used in the affected aerospace operations will be entered into the EIMS by Delta's environmental compliance group. To control and assure the validity of these data, only Delta's Environmental Services Department will have authorization to change the data on these screens. Because of the different requirements associated with different materials, separate screens were developed for surface coating materials, solvents, and strippers.

Other input screens were developed for material use records and other operating parameter data required by the Aerospace NESHAP. Where appropriate (e.g., for solvents), material use information is accessed from the material distribution system. For surface coating materials, this option is not viable because there can be variations in how the materials may be mixed (i.e., different coating formulations using the same starting materials). Thus, for these materials, data regarding specific use of each individual formulation is entered in the system through a data entry screen. Similarly, for dry filters used in most paint booths, records of pressure drop are manually entered through a separate data entry system once per shift of operation. However, the large paint hangars are fully instrumented and the pressure drop data for these booths is archived electronically.

Once the appropriate data are entered into the EIMS, these data need to be processed to meet the recordkeeping and reporting requirements of the Aerospace NESHAP, and to assess compliance with its requirements. The algorithms that are used for processing the data are straightforward in nature, and for the most part are detailed in the Aerospace NESHAP. The biggest challenge to performing this task was to include appropriate error checking during the processing to avoid the "garbage in, garbage out" syndrome. For example, if a user accidentally enters an eight-digit part number in the field for number of gallons used, these algorithms will identify this value as being outside of the expected range, and will print an error warning to this effect. Wherever possible, pull down menus or pick-lists are used preferentially over direct data entry. Another challenge was to identify the appropriate ways to identify when materials are being used for exempt activities, and how this might affect the generation of other reports. For example, for surface coating operations, a facility is allowed to use up to 50 gallons of an individual coating formulation per year that does not meet the VOC and HAP content requirements of the Aerospace NESHAP. It is important that any use of such a material not be included in the calculation of the average VOC and HAP contents that are estimated monthly.

Developing these algorithms and reports required Delta's software supplier to understand the requirements of the Aerospace NESHAP as they apply to Delta's operations. To expedite this process, a team was established between Delta's environmental consultants and the software development company. The environmental consultants developed written specifications for each of the algorithms, and worked with the software development company to implement these specifications, and test the resulting system.

Once all the needed data are entered into the data management system and processed, it is useful to be able to generate reports for both internal use and as required for reporting to the Georgia EPD. The internal reports are developed to serve several purposes. For example, they provide warnings of potentially non-compliant situations, provide details on possible exceptions to the Aerospace NESHAP, provide the recordkeeping that is required by the regulation, and they provide documentation to support the responsible official in signing the required semi-annual certification of compliance. The majority of the reports that are submitted to the Georgia EPD focus on the semi-annual reporting requirements and the standard reports are developed for supporting reporting of full compliance with the regulation. Because any non-compliant situation is expected to happen occasionally, and have various root causes and fixes, it was decided to approach these situations on a case-by-case basis outside of the standard data management system.

TRAINING

Because of the comprehensive nature of the Aerospace NESHAP, it will directly affect over 4,000 people at the TOC, and the way they do their jobs on a day-to-day basis. Therefore, the challenge is how to train the affected workers on the requirements of this rule as implemented by Delta. This section addresses several elements of this training program.

First, it was decided to perform training of all affected staff members. This choice was selected over several other options, such as training a single representative from each shop, and relying upon this representative to then train the members of his department. Although training each affected worker is a more costly option, this approach provides the each worker with the information he or she needs to perform their operations in accordance with the requirements of this rule.

One important aspect of this training is that it was developed in a manner that addresses Delta's specific compliance requirements under this rule as influenced by Delta's choice of compliance options. The chosen media for delivering this training is a multimedia CD-ROM computer based training (CBT) -- a format that is used for a variety of other training programs at Delta. The advantages of selecting the CBT include the flexibility of scheduling (i.e., CBT can be done by an individual at their choice of times), and the ability to deliver only those parts of the training that the individual worker needs. For example, a person who does no painting does not need to take the surface coating module of the training program.

Delta's internal Training Department and Environmental Services Department worked with an outside training vendor to develop a multimedia CBT program. This vendor was teamed with internal and consultant process experts to facilitate the development of the program. An outside training developer was used because the workload on Delta's training department would not allow for timely development of this training. Also, the project was fast-tracked because the training materials were highly dependent on the information developed during the execution of the compliance plan.

INTERNAL AUDITING

Even with the amount of effort and planning that was part of the implementation program, there are expected to be areas that will need additional attention and assistance to fully meet the requirements of this rule. Therefore, Delta will perform a complete audit of the TOC for compliance with the Aerospace NESHAP. Delta's internal compliance date for the Aerospace NESHAP is June 1, 1998, three months in advance of the statutory compliance date of September 1, 1998. The internal compliance audit will begin in the first week of July, and proceed with review of processes, identification of issues, and implementation of corrective action plans through August 1998.

The internal audit team will be comprised of Delta's environmental staff, members of Delta's technical standards audit team, and outside consultants. The advantages to having a mix of audit personnel include having personnel with intimate knowledge of the facility and having several fresh perspectives on the audit team. Also, audit protocols will be developed that will serve as templates for future internal audits on the requirements of the Aerospace NESHAP. These audit protocols will include elements of EPA's Aerospace NESHAP guidance document suggested auditing guidelines.

As compliance or process issues are identified during this audit, solutions will be identified and implemented. Although the audit is being performed on individual departments, when systematic problems are identified, enterprise-wide solutions will be identified and implemented. Due to time constraints, these corrective actions will be identified and implemented "on-the-fly", as the audit team performs the facility-wide audit.

COMPLIANCE COSTS

At this time, Delta can only estimate the total cost of implementing the Aerospace NESHAP requirements, however, a large majority were capital costs, which are fairly well known. These costs are expected to exceed $2.8 million, and do not include the costs of maintaining compliance once it is achieved. A rough breakdown of the costs of achieving compliance is included in Table 2.

Table 2
Costs of Achieving Compliance with the Aerospace NESHAP

Item	Costs (estimated)	Comments
Equipment Modifications	$1,600,000	$1,500,000 for paint booth upgrades, remainder for assorted equipment including paint guns and paint gun cleaners
Consulting Services	$175,000	
Development of Training Program	$100,000	
Implementation of Training Program	$400,000	4,000 workers x loaded hourly rate x 3 hrs/worker
EIMS Development	$450,000	The Aerospace NESHAP module is only a portion of the cost, but was a key consideration in deciding to proceed with the entire system
Internal Labor Costs	$150,000	Over 2,000 man hours
Total Costs	$2,875,000	Does not account for cost of maintaining continued compliance

LESSONS LEARNED

Although Delta has not fully implemented all of the Aerospace requirements, it is still possible to discuss some of the lessons learned from pursuing this activity. These lessons are divided into what we did well, and those activities that we could have performed better. These lessons are presented to allow others facing Aerospace NESHAP compliance to gain from Delta's experiences.

What We Did Well

Get an early start on equipment modifications. Nothing is ever as easy as originally planned, especially when modifying equipment that needs to be taken out of service to perform the modifications. In particular, the time for the engineering study, the difficulty in locating old plans for the booths, and the extent of the modifications required to allow the use of the new filters were quite unexpected. Furthermore, it seems that all construction projects take longer than originally anticipated.

Get the affected departments involved early in the process. By having selected department managers and environmental coordinators involved in the rule development process, Delta was aware of how the regulation would affect the shop workers. This early involvement also enabled Delta to get "buy in" from the affected departments early, and fostered a cooperative relationship between the Environmental Services Department and the affected shops.

Developing a comprehensive EIMS is essential to achieving compliance with this regulation. Although the data could be collected with pens and clipboards, a comprehensive data management system allows for the selection of the appropriate compliance options, and makes the task of maintaining compliance with the regulation considerably easier.

Although Delta has yet to perform the internal "shakedown" audit, the initial feel by the environmental staff is this period will be essential. This time allows the environmental staff the opportunity to review and fine-tune the submittals from each department. Remember it is crucial to have your process experts take a lead role in identifying:

- Which exemptions apply to hand wipe solvent use in that department;
- Which processes are not subject to the NESHAP;
- The coating and applications that meet the specialty coating definitions; and
- How coatings are mixed for use.

There is no substitute for this type of direct process knowledge.

Training for user-level employees is critical. The comprehensive nature of this regulation makes training critical because each worker's cooperation is required to maintain compliance. How else would a mechanic know he can't use MEK for his task, when the mechanic at the next

bench is using it for an allowed, exempt activity. This situation is contrasted with other regulations that simply require the operation of a control device, which would affect a handful of workers instead of thousands of workers.

Activities That Could Have Been Better Performed

As much as Delta thought that they had an early start on achieving compliance with this regulation, there did not seem to be enough time or internal resources to complete the project according to schedule. The initial schedule developed as part of the Master Compliance Plan was useful in identifying schedule slip, and where to apply additional resources and attention.

Because of the nature of the Aerospace industry, the importance of resolving OEM and FAA considerations early can not be overstated. Delta has thousands of repair manuals that have specific product call-outs. Although good number of these conflicts were resolved, Delta determined that they would be unable to resolve all conflicts between repair manual procedures and Aerospace NESHAP requirements, and will enter into the compliance period of the rule with this conflict. Delta will resolve these conflicts on a case-by-case basis, when they are identified. The training program has specifically designed elements that exist to specifically tell the worker what to do in the event of a conflict between EPA and FAA guidance. The impact of this inability to resolve these conflicts early is that when a conflict is found, processing of the component or aircraft will be put on hold pending resolution of the conflict.

On a related subject, the identification and qualification of a substitute material takes considerable time to process. This process was started over a year ago, but again, with tens of thousands of manuals and procedures, some of the less common procedures may slip through the cracks. Again, training procedures will serve as a back-stop for these cases. In cases where procedures must be changed quickly, those mechanisms exist; however, they represent a severe time drain on resources.

The level of training and familiarity with the rule may cause one to underpredict the time, effort, and training requirement associated with collection of data from individual shops. Remember most of these people are not environmental professionals and don't know vapor pressure from HAP content. There is no substitute for taking the time to walk through the process with them and carefully reviewing the results of any data submitted.

SUMMARY

The Aerospace NESHAP is a complex rule that requires a complex set of responses to ensure compliance. Delta has aggressively worked to manage this challenge and is confident of its ability to attain and maintain compliance. The process used to achieve this goal, as outlined in this paper, can be used by others in the aerospace industry to achieve the same objective.

STORM WATER DISCHARGES FROM INDUSTRIAL FACILITIES: ACHIEVING COMPLIANCE AT KELLY AIR FORCE BASE

Paul Makowski,P.E.; Dewberry & Davis; 8401 Arlington Boulevard; Fairfax, VA 22031-4666
Gary Goodman; Universe Technologies, Inc.; 3203 Second Street, Building 538; Brooks AFB, TX 78235

ABSTRACT

Changes to the National Pollutant Discharge Elimination System (NPDES) program require that storm water discharges associated with industrial activity be regulated. How these NPDES regulations apply to Air Force installations and how these installations comply with the terms and conditions of the NPDES storm water permit is discussed. Central to permit compliance is the preparation of the Storm Water Pollution Prevention Plan emphasizing best management practices.

INTRODUCTION

The traditional approach in regulating water resources was to concentrate on point discharges from industrial wastewater and municipal sewage. However, Section 402(p) of the 1987 Amendments to the Clean Water Act established the requirement that storm water discharges associated with industrial activity and from municipal separate storm water sewer systems serving a population of 100,000 or more be regulated under the National Pollutant Discharge Elimination System (NPDES) program. Final NPDES storm water regulations were promulgated in the 16 November 1990 Federal Register (55 FR 48062-48091) and are contained in 40 CFR parts 122, 123, and 124. These regulations require that operators of industrial facilities that discharge storm water from a point source to the waters of the United States apply for a permit.

To be subject to the storm water permit regulations, an industrial facility (including industrial facilities that are Federally, State, or municipally owned or operated) must have activities that fall within one of 11 categories specified in 40 CFR 122.26(b)(14)(i)-(xi). The 11 categories of industrial activities subject to NPDES storm water regulations are summarized as follows:

(i) facilities subject to storm water effluent limitations guidelines, new source performance standards, or toxic pollutant effluent standards under 40 CFR Subchapter N;

(ii) facilities with Standard Industrial Classification (SIC) codes with initial digits of 24 (except 2434), 26 (except 265 and 267), 28 (except 283), 29, 31, 32, (except 323), 33, 344, or 373;

(iii) facilities with SIC codes with initial digits from 10 through 14;

(iv) hazardous waste treatment, storage, or disposal facilities operating under interim status or under the Resource Conservation and Recovery Act (RCRA) subtitle C;

(v) landfills receiving industrial waste;

(vi) recycling facilities with SIC codes of 5015 or 5093;

(vii) steam electric generating facilities;

(viii) transportation facilities with SIC codes with initial digits of 40, 41, 42 (except 4221-4225), 43, 44, 45, or 5171;

(ix) domestic sewage treatment works with design flow rates greater than one million gallons per day;

(x) construction activities disturbing five acres or more; and

(xi) facilities with SIC codes with initial digits of 20, 21, 22, 23, 2434, 25, 265, 267, 27, 283, 285, 30, 31

(except 311), 323, 34 (except 3441), 35, 36, 37 (except 373), 38, 39, and 4221 through 4225.

Five of these categories (ii, iii, vi, viii and xi) are defined relative to SIC codes and the six remaining categories (i, iv, v, vii, ix, and x) are defined descriptively. If no activities at a facility fall into one of the 11 categories, a storm water permit is not required.

The San Antonio Air Logistics Center (SA-ALC) at Kelly Air Force Base (AFB) is one of the major Air Force Materiel Command Organizations providing large-scale logistics support to the Air Force worldwide. SA-ALC manages aircraft engines, weapons systems, support equipment, and aerospace fuels. SA-ALC also provides depot-level maintenance of several types of aircraft. Kelly AFB acts as host to approximately 56 tenant organizations representing the Air Force, Army, Department of Defense (DOD), and other government agencies. The major tenants include the Air Intelligence Agency (AIA), Air Force News Center (AFNEWS), Civil Engineering Red Horse (RHCES), Texas Air National Guard (ANG) 149th Fighter Wing (FW), and Air Force Reserve (AFRES) 433rd Airlift Wing (AW).

Commercial industrial facilities are placed in the 11 categories based on the primary activity at the site. Under this approach, Kelly AFB, whose SIC code is 9711 (national security), would be exempt from the regulations, because 9711 does not fall in any of the five SIC-defined categories, and the primary activity of national security does not fit the definitions in the six descriptive categories. However, the U.S. Environmental Protection Agency (EPA) has ruled that military bases are subject to the storm water regulations based on the activities occurring at the shop level. This means that each individual shop must be evaluated against the 11 industrial categories as if it is a separate facility.

After reviewing the activities, it was determined that Kelly AFB was subject to the NPDES storm water program requirements. To comply with the NPDES storm water application requirements, a Notice of Intent (NOI) for coverage under the final General Permit for Storm Water Discharges Associated with Industrial Activity (General Permit) was filed for KellyAFB on 1 October 1992.

GENERAL PERMIT REQUIREMENTS

The primary emphasis of the General Permit is to require dischargers of storm water associated with industrial activity to prepare and implement a Storm Water Pollution Prevention Plan (SWPPP). There are three objectives of the SWPPP: (1) to identify potential sources of pollution that may reasonably be expected to affect the quality of storm water discharges associated with industrial activity from the facility; (2) to describe and ensure the implementation of practices that are used to reduce the pollutants in storm water discharges associated with industrial activity at the facility; and (3) to ensure compliance with the terms and conditions of the permit.

The General Permit also requires the permittee certify that the industrial storm water outfalls have been tested or evaluated for the presence of non-storm water discharges. Facilities with activities specifically identified in the General Permit are required to develop a storm water sampling program.

STORM WATER POLLUTION PREVENTION PLAN

The SWPPP prepared for Kelly AFB provides pertinent information regarding which activities and areas are subject to regulatory requirements and the actions that must be taken to ensure that pollution from storm water discharges emanating from these activities are minimized. The SWPPP was developed and organized as an information and implementation document. Organizational responsibilities for different elements of the SWPPP were also included so that the lines of responsibility and communication, which is necessary for SWPPP execution, are clearly established. Existing relevant operations management plans that outline management, contingency, emergency response, and environmental compliance measures as well as training plans that contribute to storm water pollution prevention were incorporated into the SWPPP. A summary of the industrial activities at Kelly AFB, by category, is included in the SWPPP as is the primary industrial activity by building or area. The SWPPP was

prepared to include all activities that affect storm water discharges associated with industrial activity, including those discharges covered in KellyAFB■s existing NPDES wastewater permit.

The major elements of the SWPPP include a description of potential pollutant sources and development of management practices to control pollutants. Exhibits, to be maintained in the appendixes of the SWPPPs, were prepared to: (1) record significant spills or leaks of toxic or hazardous pollutants that occur during the term of the permit; (2) record the results of all storm water sampling data collected subsequent to the preparation of the SWPPP; (3) record the preventive maintenance inspections; (4) record the areas or equipment that require any corrective action, the person who conducted the inspection, the inspection results, and the corrective action; (5) record the employee training activities; and (6) facilitate the comprehensive site evaluation.

Identification of Potential Pollutant Sources

Potential sources of pollution that may reasonably be expected to affect the quality of storm water discharges associated with industrial activity were identified. This information was used to target the most important sources for corrective and/or preventive action. For each building or area, potential pollutant sources and existing pollution control measures were identified.

A site map was developed to show the following information: all outfalls and storm water discharges; drainage areas of each storm water outfall; structural storm water pollution control measures such as flow diversion structures, retention/detention ponds, vegetative swales, and sediment traps; names of receiving waters; locations of significant materials; areas with significant erosion potential; locations of past spills and leaks; and locations of high-risk, waste generating areas and activities such as fueling stations, vehicle/equipment washing and maintenance areas, areas for unloading/loading materials, above-ground tanks for liquid storage, industrial waste management areas (landfills, waste piles, treatment plants, disposal areas), and outside storage areas.

An inventory of materials that have the potential to be exposed to precipitation was developed. The inventory included the materials that have been handled, treated, stored, or disposed in a manner to allow exposure to storm water since 1 October 1989, the method and location of on-site storage or disposal, a description of any existing structural or non-structural control management practices to reduce pollutants in storm water runoff, and a description of any treatment the storm water receives.

A list of significant spills or leaks of toxic or hazardous pollutants that have occurred in areas that are exposed to precipitation or that otherwise drain to a storm water conveyance was compiled. A significant spill is defined in the General Permit to include, but not be limited to, releases of oil or hazardous substances in excess of reportable quantities.

Summaries were developed for any existing discharge sampling data describing pollutants in storm water and potential pollutant sources associated with loading and unloading operations; outdoor storage activities; outdoor manufacturing or processing activities; significant dust or particulate generating processes; and on-site waste disposal practices.

Development of Management Practices

Management practices were developed based on the potential pollutant sources targeted for corrective and/or preventive action. The components of the storm water management controls include: good housekeeping, preventive maintenance, spill prevention and response procedures, inspections, employee training, sediment and erosion control, and management of runoff. For each building or area, site-specific control measures were identified.

Good housekeeping practices were designed to maintain a clean and orderly work environment. Elements of good housekeeping include material storage practices, material inventory controls, routine and regular cleanup schedules, well-organized work areas, and educational programs for employees.

Preventive maintenance is the regular inspection and maintenance of equipment, operational systems, and storm water management devices. The preventive maintenance program that was developed includes identification of

conditions that could cause breakdowns or failures that result in discharges of materials to storm drains and surface waters. Preventive maintenance inspections include the following: piping, pumps, storage tanks and bins, pressure vessels, pressure release valves, material handling equipment, and material bulk storage areas for leaks, corrosion, support or foundation failure, or other deterioration or non-containment. Storm water management devices (oil/water separators, catch basins, or other structural or treatment management practices) were also targeted for inspection.

Spill prevention and response procedures were developed to include identifying areas of the facility where spills can occur and their flow paths to the storm drainage system; specifying material handling procedures, storage requirements, and use of equipment such as diversion valves; identifying procedures used for cleaning up spills and informing personnel about these procedures; and providing appropriate spill cleanup equipment to personnel.

Regular inspections ensure that the elements of the SWPPP are in place and working properly. These routine inspections were not developed to be an all-encompassing examination of the entire storm water pollution prevention program--that is the function of the comprehensive site evaluation.

To meet the objectives of the SWPPP, the employee training program was developed to require that personnel be instructed as to their responsibilities relative to the SWPPP. The training program requires that new personnel are to be trained within six months and all personnel are to receive training every year to refresh and update them on the components and goals of the SWPPP. Topics include spill prevention and response, good housekeeping, and material management practices. With respect to spill prevention and response procedures, the training program was developed to target all personnel involved in industrial activities, not just those on the spill response teams. It is required that all maintenance facility personnel receive instruction in the prevention, control, containment, and cleanup of spills. The SWPPP requires that on-site contractors and temporary personnel also be informed of the facility operating procedures designed to help prevent accidental discharges or spills from occurring.

Areas having a high potential for significant soil erosion were identified and stabilization measures proposed. The SWPPP requires that any portion of a grassed channel that requires stabilization against erosion be reseeded using temporary stabilization measures such as straw with net; curled wood mat; jute, paper, or synthetic net; synthetic mat; or fiberglass roving. Areas of ongoing erosion are required to be stabilized with riprap. The SWPPP also requires that a sediment control plan be developed for any development activity that increases the potential for soil erosion. Additionally, construction activities greater than five acres must apply for and be in compliance with the NPDES general permit for storm water discharges from construction sites.

The SWPPP identifies any viable structural storm water management practices such as diversions, detention/retention/infiltration facilities, reuse, or treatment including oil/water separators. A cost study to determine the viability of implementation of the management practices was not included in the SWPPP. The SWPPPs require that, if and when a management practice is installed, it be added to the inspection program.

Evaluation

A comprehensive site compliance evaluation procedure was developed to provide a basis for evaluating the overall effectiveness of the SWPPPs and to verify of the accuracy of the SWPPP. The evaluation will focus on the areas contributing to a storm water discharge associated with industrial activity that will be inspected for evidence of, or potential for, pollutants entering the drainage system. The evaluation will include assessment of good housekeeping practices; areas identified for preventive maintenance; equipment needed to implement the SWPPP, such as spill response equipment; areas identified for routine inspection; evaluation of the effectiveness of measures to reduce pollutant loadings and whether additional measures are needed; and structural measures, sediment controls, and other storm water management practices ensuring proper operation. Following the comprehensive site compliance evaluation, a report summarizing inspection results, including the date of inspection and personnel who

conducted the inspection, will be prepared. The report will document any incidents of noncompliance and required follow-up actions or certify that the facility is in compliance with the SWPPP.

NON-STORM WATER DISCHARGES

Non-storm water discharges to the waters of the United States, which are not authorized by an NPDES permit, are unlawful and must be terminated or appropriate NPDES permit application forms must be submitted. All discharges covered by the General Permit are to be composed entirely of storm water; however, the following non-storm water discharges may be authorized by the General Permit: fire fighting activities; fire hydrant flushings; potable water sources including waterline flushings; irrigation drainage; lawn watering; routine external building washdown that does not use detergents or other compounds; pavement washwaters where spills or leaks of toxic or hazardous materials have not occurred (unless all spilled material has been removed) and where detergents are not used; air-conditioning condensate; springs; uncontaminated ground water; and foundations or footing drains where flow is not contaminated with process materials such as solvents.

The General Permit requires that the SWPPP include a certification that the discharge has been tested or evaluated for the presence of non-storm water discharges. The certification must include the identification of potential significant sources of non-storm water at the site, a description of the results of any test and/or evaluation for the presence of non-storm water discharges, the evaluation criteria or testing method used, the date of any testing and/or evaluation, and the on-site drainage points that were directly observed during the test. Except for flows from fire fighting activities, sources of non-storm water that combine with storm water discharges associated with industrial activity must be identified in the SWPPP.

STORM WATER SAMPLING PROGRAM

For those storm water outfalls covered by the General Permit, only those storm water discharges associated with 16 types of industrial activity categories are required to be monitored. Kelly AFB is <u>not</u> subject to the monitoring requirements for airports because the facility operates below the regulatory threshold of 50,000 flights per year. However, because Kelly AFB is subject to reporting under Superfund Amendments and Reauthorization Act (SARA) Title III, Section 313, the following information must be provided for outfalls where storm water discharges containing industrial activity come in contact with a Section 313 water priority chemical: analytical results of sampling parameters (which are dependent on the industrial activity category); date and duration (in hours) of the storm event(s) sampled; rainfall measurements or estimates (in inches) of the storm event that generated the sampled runoff; the duration between the storm event sampled and the end of the previous rainfall greater than 0.1 in.; and an estimate of the total volume (in gallons) of the discharge sampled. When a facility has two or more outfalls that discharge substantially identical effluents, the General Permit allows that the effluent from one of these outfalls be tested and the quantitative data applied to substantially identical outfalls. If adverse climatic conditions preclude sampling, a sampling waiver can be requested.

SUMMARY

Kelly AFB is subject to the permitting requirements resulting from changes to the NPDES program. To comply with the NPDES permits, Storm Water Pollution Prevention Plan emphasizing best management practices was prepared.

X-33 Environmental Impact Statement: A Fast Track Approach

Dr. Rebecca McCaleb
Donna L. Holland

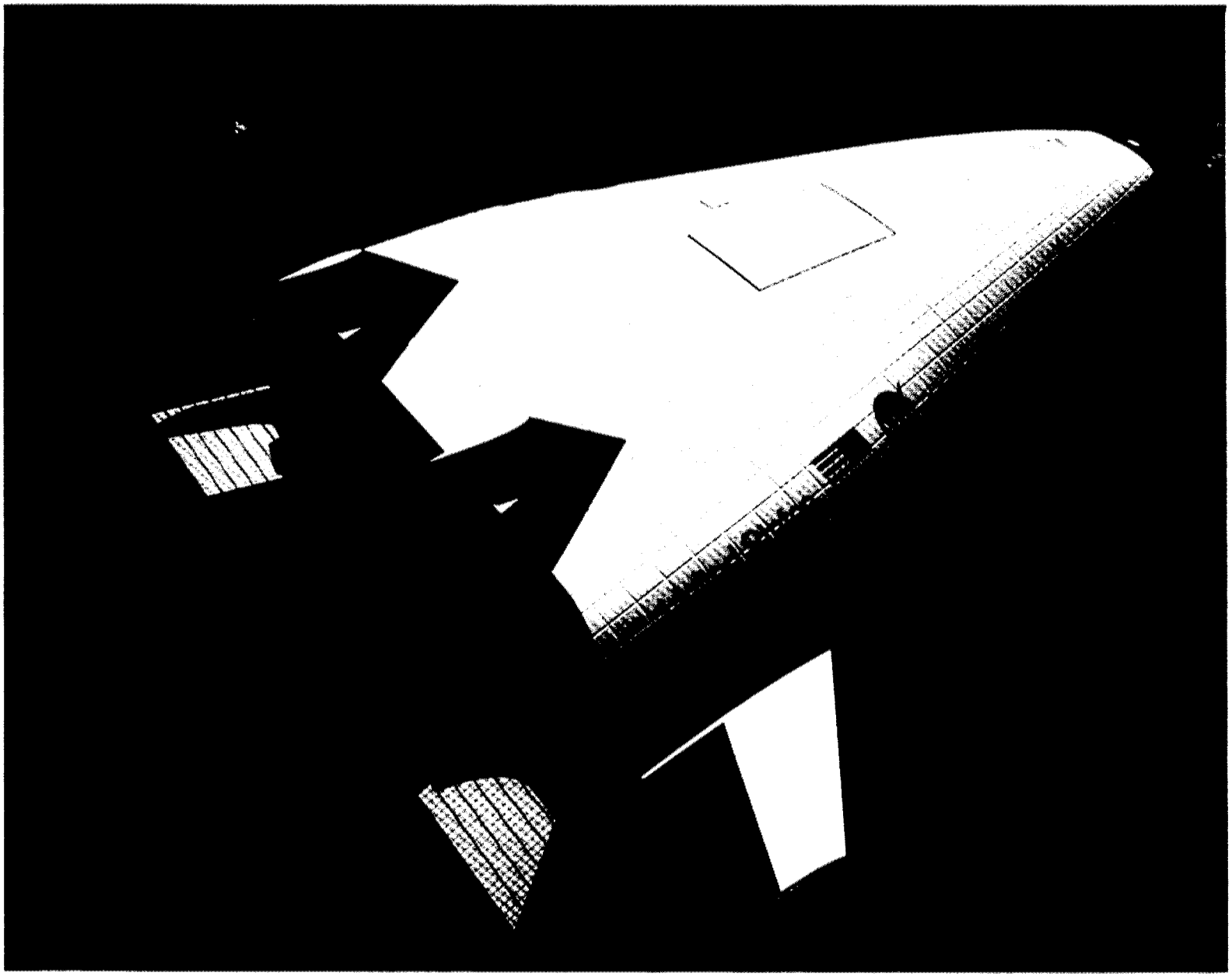
Environmental Engineering and Management Office
National Aeronautics and Space Administration
Marshall Space Flight Center, AL 35812

Presented At:
3rd Conference on Aerospace Environmental Technology
Huntsville, Alabama

June 2, 1998

National Aeronautics and
Space Administration

X-33 Advanced Technology Demonstrator



X-33 Program Schedule

- Cooperative Agreement Notice CAN 8-1
  - RFP: January, 1995
  - 3 Cooperative Agreements for Phase I issued March, 1995 for 15 months:
    - Lockheed Martin Skunk Works
    - McDonnell-Douglas Aerospace
    - Rockwell International Corp.
- CAN 8-1 Final Reports issued June, 1996
- Cooperative Agreement Notice CAN 8-3
  - RFP: April, 1996
  - 1 Cooperative Agreement for Phase II issued to Lockheed Martin Skunk Works: July, 1996
  - Construction Startup: September 15, 1997

Phase I

Final X-33 Programmatic Environmental Assessment:
– Vehicle and Technology Demonstration Concepts, June 1996

- Proposed Launch Sites: KSC, Edwards AFB, White Sands Missile Range
- Landing Sites: Generic
- Special considerations: Global impact (stratospheric) of theoretical full size vehicle based on X-33 technology
- Decision: Proceed with Phase II and prepare EIS to support final development, selection of launch and landing sites, construction, and flight testing

Background (Cont'd)

Phase II
Preparation of EIS

- **Notice of Intent: October 7, 1996**
- **Scoping of issues: October 1996 through January 1997**
  - 12 Public meetings: 528 total attendance
  - 80 Comment letters, e-mails, faxes, and voice messages ("800" number)
- **Issues**
  - Public safety/risk
  - Avalanche (sonic boom)
  - Disruption of airport services
  - Noise/sonic booms
  - Reliability
  - Benefits
  - Hazardous materials
  - Wildlife impacts (sonic boom)
  - Threatened and endangered species impacts
  - Accessibility to launch/landing
  - Avoidance of sensitive facilities
  - Schedule
  - Flight path(s)
  - Spectator impacts
  - Diminishment of National Airspace
  - Wilderness Area impact
  - Aborts/emergencies
- **Program endorsements from public and political leaders**

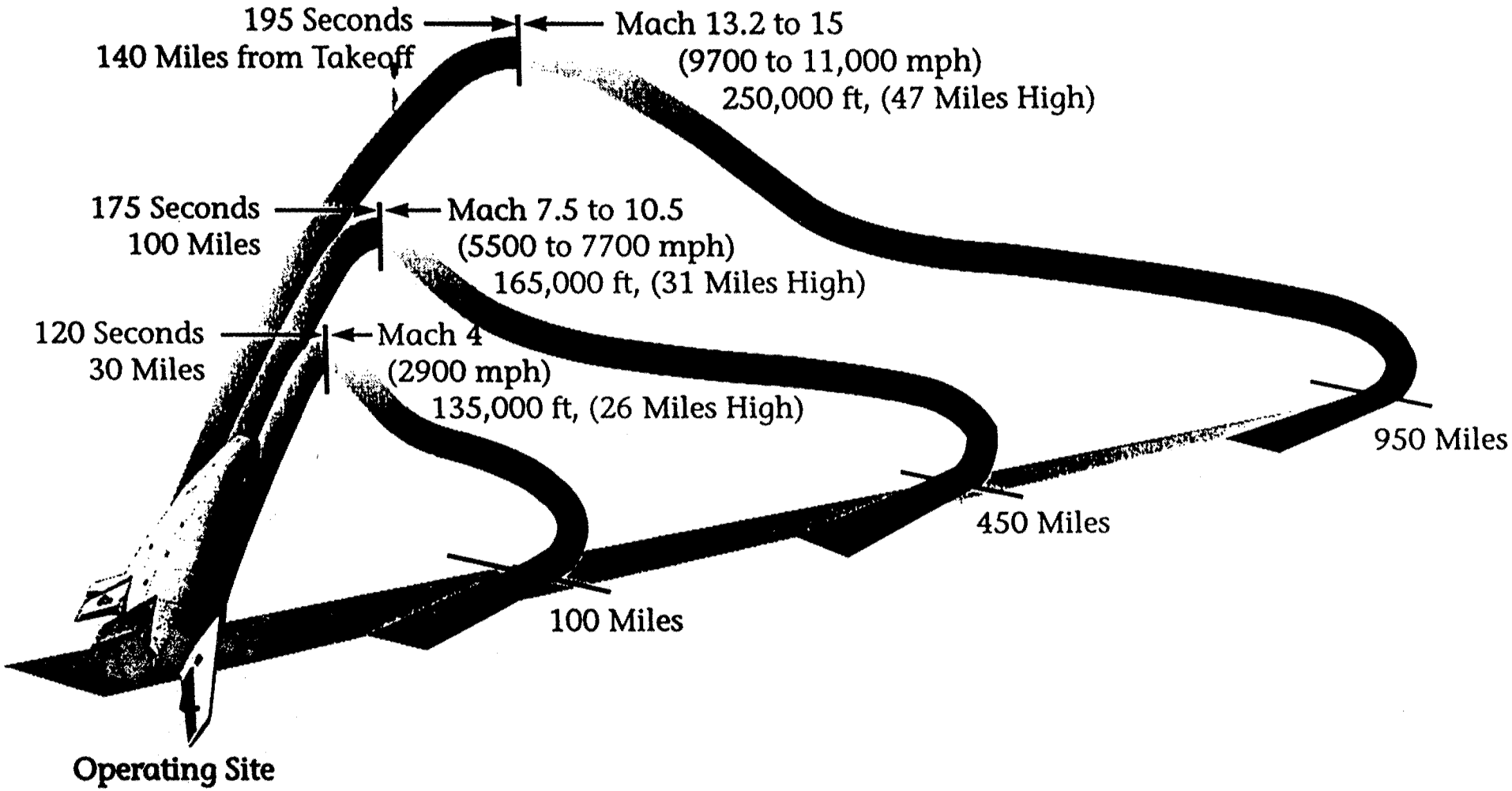
Background (Cont'd)

- **Draft EIS: July 3, 1997**
  - 750 DEIS and 500 Executive Summaries mailed
  - 11 public meetings
  - Total attendance: 298
  - Advertisements of availability in 7 states
  - Issues/concerns/questions: essentially same as scoping
  - 53 letters, e-mails; 8 voice messages

- **Final EIS: October 3, 1997**
  - 650 FEIS and 500 Executive Summaries mailed
  - Advertisements of availability in 7 states
  - 1 comment letter received to date; 1 more expected from JSC
  - 30 day regulatory wait period expires November 3, 1997

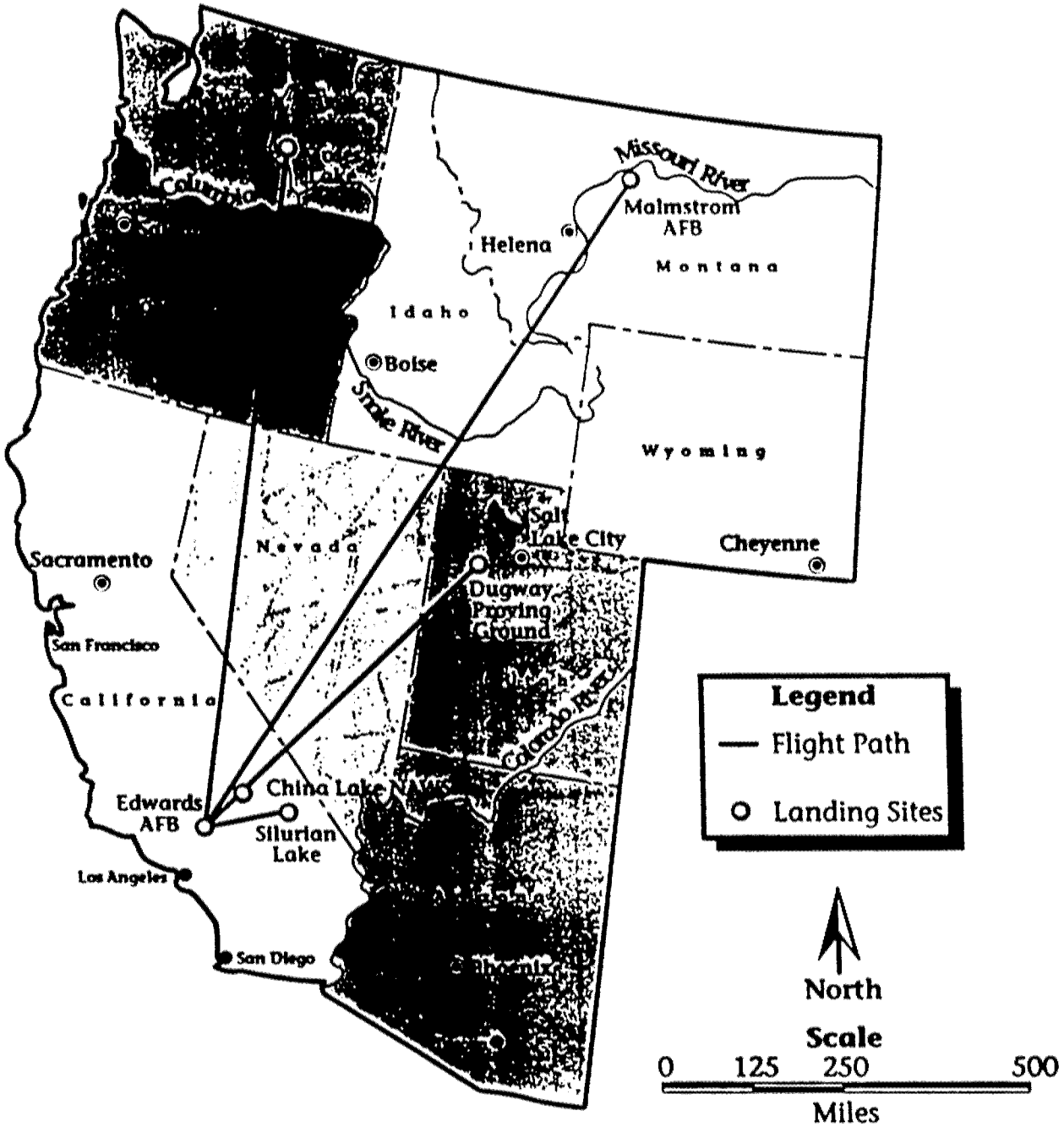
X-33 Baseline Flight Envelope Expansion Test Plan

Higher—Faster—Farther



3 Landing Sites

X33 Alternative Flight Operations and Landing Sites



EIS-3885

X-33 Cooperating Agencies, Sub-Elements, and Sites

Cooperating Agency	Sub-Element	Site	Purpose
Department of Defense	U.S. Air Force	Edwards AFB	Flight operations/launch site
		Utah Test and Training Range	Trajectory(ies) to Dugway Proving Ground
		Malmstrom AFB	Long-range landing site
	U.S. Army	Dugway Proving Ground	Mid-range landing site
		Ft. Irwin[1] (Silurian Lake)	Short-range landing site
	U.S. Navy	China Lake Naval Air Weapons Station	Short-range landing site
Department of the Interior, Bureau of Land Management	California Desert District, Barstow Resource Area	Silurian Lake	Short-range landing site
Department of Transportation	Federal Aviation Administration	National Air Space	Trajectories, or portions thereof, under 18,000 m (60,000 ft) and not within established controlled air space

[1]Potential future federal manager of Silurian Lake

X-33 Techniques Contributing to Success of Fast Track EIS

- EIS team began work early with CAN 8-1 and brought team up to speed on X-33 Program requirements and issues early

- Cooperating Agencies agreed to review EIS products on NASA schedule, and NASA did not extend invitation to sign concurrence of release of EIS major documents or the Record of Decision (ROD)

- Cooperating Agencies subsequently issued their own RODs and adopted NASA EIS

- EIS team maintained intact from EA through EIS

- EIS team prepared majority of documents in-house with limited outside contracting; therefore, no time was required for a competitive procurement process

- Detailed project scheduling

X33 Techniques Contributing to Success of Fast Track EIS

continued

- **EIS team personally briefed key reviewers on draft documents and conducted resolution of cooperating agency comments quickly in face-to-face meetings in Washington, D.C.**

- **Used the following services extensively: Videoteleconferencing, e-mail, fax, Fed Ex, credit cards**

- **Compressed public meeting schedules**

- **Used rapid turn around GSA printers (premium cost)**

- **COMMITMENT TO SCHEDULE BY ALL INVOLVED PARTIES INCLUDING THE COOPERATING AGENCIES: THE MOST IMPORTANT FACTOR!**

Title V Application Preparation at MSFC: Lessons Learned

Author: J.P. Martin, P.E.
CH2M HILL ■ Montgomery, Alabama

Introduction:

The purpose of this paper is to present a summary of the Title V application development process at Marshall Space Flight Center (Marshall or the Center), and to describe the major challenges involved in developing an effective Title V regulatory compliance strategy for this unique NASA facility. As lead environmental contractor at Marshall, CH2M HILL has worked closely with the Center's environmental and management staff to integrate an air emissions compliance plan into their overall environmental program.

Body:

What is Title V?

Title V began as one of the major permitting initiatives under the landmark Clean Air Act of 1990. Its main purpose was to consolidate the many existing air permitting and compliance regulatory requirements into one overall permitting process – in theory making it easier for both the regulatory agency and the permit applicant to achieve and maintain full air permitting compliance. Whether Title V has actually served to clarify or simplify the air permitting process seems to depend on which State is administering the program. But there is general consensus that, in Alabama, Title V will achieve its primary goal of simplifying the air permitting process.

Title V

- Began in 1990 under Clean Air Act
- Consolidates air permitting regulations into one permitting process.
- Targeted primarily at major air emissions sources; but covers all sources.
- Managed in Alabama by ADEM since 1995.

Regulations that now fall under the Title V umbrella include:

- Maximum Achievable Control Technology (MACT)
- National Emission Standards for HAPs (NESHAPS)
- New Source Performance Standards (NSPS)
- Ozone Depleting Compounds (ODCs)
- Accidental Release Prevention
- Prevention of Significant Deterioration (PSD)
- Various State Regulations

The Alabama Department of Environmental Management (ADEM) sought and was issued EPA approval to manage the Title V process, and in 1995 began receiving Title V applications. Although Title V is intended to apply to primarily ***major source*** emissions, exactly what constitutes a major source and what combination of ***minor sources*** might trigger major source permit requirements is not always apparent. Also, an approved Title V permit certifies compliance for an applicant for at least five years; yet significant changes in facility operations and capacities usually may require an update or revision to the Title V permit. Both of these issues, emission source designation and changing facility operations were key considerations in planning and managing the Marshall Title V permitting process.

What is Marshall Space Flight Center?

Briefly, the Marshall Center is NASA's principal U.S. propulsion development facility where a team of hundreds of scientists, engineers, and technical support personnel manage the design and production of the Space Shuttle's main engines, solid rocket boosters, and external tanks. Marshall is also emerging as a leading player in the development of new NASA programs including the reusable "space plane", new cutting-edge propulsion systems, planetary

Marshall Center

- NASA's main propulsion development facility.
- Multiple missions; multiple operations/processes.
- Ever-changing programs/activities; a dynamic mission; flexible Title V permit a must.

observations, and basic scientific/space research. Because of this evolving and dynamic mission, and the corresponding changes in facility operations, achieving maximum flexibility for Marshall's Title V permit was critical.

Marshall is a large complex (more than 3,820,000 square feet under roof) with a wide variety of processes and activities. Major and minor air emissions sources number well over 100, and are related to precision cleaning operations, solvent replacement, maintenance/restoration of high-tech rocket components, rocket test stands, numerous on-site laboratories, and other similar activities. Processes range from spray-on foam insulation (SOFI), metal surface preparation, metal plating, degreasing, painting, engine testing, and paint stripping to high-tech cleaning and preparation of oxygen tubing used to fuel rocket engines.

CH2M HILL & Marshall

- CH2M HILL has been at work at Marshall continuously since 1987.
- Past projects include air, water, hazwaste, and other projects.
- Key role in strategic long-term planning for Marshall. Tradition of a strong CH2M HILL / Marshall partnering relationship.

What is CH2M HILL 's involvement at Marshall?

CH2M HILL has been at work for Marshall since 1987 and has provided of multi-media environmental services in the areas of environmental restoration, compliance, process evaluation, pollution prevention, and strategic planning. Projects have included a wide range of major air, water, and hazardous wastes initiatives – all conducted in close partnership with Marshall/NASA environmental and facility management. CH2M HILL is Alabama's most experienced air permitting compliance consultant with more Title V projects completed and ongoing than any other environmental consultant. Marshall's Title V project was awarded to CH2M HILL in 1995.

What are the major Title V issues/activities at Marshall?

Typical Title V Permit Preparation Procedure: CH2M HILL's general approach to Title V permitting has typically consisted of the following tasks:

Task 1 *Scoping*
Task 2 *Preparation of Emissions Inventories*
Task 3 *Regulatory Review*
Task 4 *Compliance Assessment*
Task 5 *Strategic Planning*
Task 6 *Permit Preparation*

Although all of these tasks were a part of the Title V process for Marshall, there were major challenges peculiar to the facility that required significant flexibility in developing an effective Title V action plan. Special problems/challenges included:

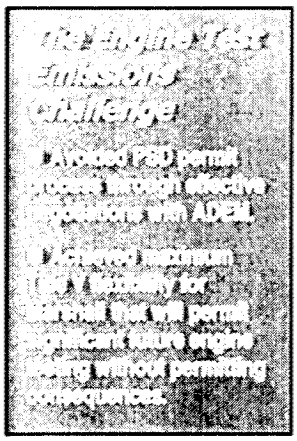
- ***Emission Inventory Preparation:*** Upon initiating the Title V process, it was immediately apparent to CH2M HILL that there would be difficulty in establishing a basis for identifying and assessing air emissions sources. There were scores of potential sources to be investigated, with non-existent or incomplete emissions inventory data available. There was existing data from a previous contractor (Ebasco), but its accuracy and currency required validation. Moreover, most of the Ebasco information regarding quantities was based on Marshall's own annual self-survey wherein each activity area would report on their use of hazardous materials – a process that on the whole provided inconsistent data.

CH2M HILL did finally establish a complete emissions inventory basis from which to proceed with the Title V process, but only after a major field and investigative effort. CH2M HILL also developed a customized Excel-based database system to manage and control emissions inventory data.

The Emission Inventory Challenge

- Scores of separate sources to be investigated.
- Began with limited or nonexistent source data.
- Major field effort was required to finalize EI.

■ *Engine Testing Requirements:* As noted, part of Marshall's NASA mission is to test the propulsion systems that it designs and develops. Although this activity represented a potentially significant source of air emissions, testing had been, and continues to be episodic and at widely varying levels depending on the current status of the various propulsion system development programs and the ever evolving Marshall mission. The CH2M HILL challenge: How to accurately inform ADEM of this emission activity yet still provide for the maximum flexibility required from the Title V permit to cover future testing programs that were as yet largely undefined?



At stake was the possibility that Marshall's engine testing emissions would trigger the requirement for a Prevention of Significant Deterioration (PSD) permit – another 1990 Clean Air Act permitting process that typically demands a very significant commitment in time and dollars to achieve compliance. Adding PSD to Marshall's Title V project could easily have doubled the air permitting scope, and was to be avoided if at all possible.

CH2M HILL was successful in negotiating with ADEM to escape the PSD process. ADEM was persuaded to follow the examples of their sister regulators in Florida and Mississippi – both states with a major NASA presence – and classify Marshall as an "area" source (difficult to control and predict emissions of a special nature) as opposed to a "point" source. PSD applies only to point sources and thus Marshall became exempt from PSD provisions. It was only for CH2M HILL to further demonstrate an historical pattern of major "area" emissions, thereby grandfathering the Marshall facility as a special case. Thereafter, ADEM issued their final ruling excusing Marshall from PSD liability. Thus, Marshall was spared very significant amounts of permitting time and money, and the Title V process continued forward.

■ *Aerospace MACT Requirements*: Although early in the process, it was CH2M HILL 's judgement that Aerospace Maximum Achievable Control Technology (MACT) regulations probably would not apply to Marshall's processes, ADEM and EPA did not rule definitively on this issue until late in the Title V process. Therefore, CH2M HILL proceeded with the assumption that Marshall was covered by MACT until there was official confirmation of Marshall's exclusion from the MACT provisions.

The Aerospace MACT Challenge

■ Avoided aerospace MACT permitting provisions through special loophole designating space-related activities as a special case.

■ Included the aerospace MACT liabilities into Marshall's Title V process until exclusion was finalized.

Although Marshall does perform all of the activities regulated in the Aerospace MACT, these activities are in total support of the facility's mission to manage the Space Shuttle's main engines, solid rocket boosters, and external tank and thereby fall under a special exemption as stated in 40 CFR 63.741(h):

"Regulated activities associated with space vehicles designed to travel beyond the limit of the earth's atmosphere, including but not limited to satellites, space stations, and the Space Shuttle System (including orbiter, external tanks, and solid rocket boosters) are exempt from the requirements of this subpart,...."

Marshall's aerospace activities also support the development of the Space Station Freedom, as well as many other major NASA programs. Therefore, the facility's cleaning operations, primer and topcoat applications, chemical milling maskant applications, and waste storage and handling operations are all exempt.

■ *EPA Degreaser MACT:* Maintaining an extraordinarily clean production and testing process for the types of high-tech equipment and systems being developed at Marshall is crucial. Contamination in even the minutest quantities can spell failure for multi-million dollar design/production/testing initiatives. The use of solvents for degreasing and verification is an essential part of Marshall's activities, and among the best substances for these purposes are certain perchloroethylenes, trichloroethanes, and Freon 113 (trichlorotrifluorethane). On the other

The EPA Degreaser MACT Challenge:

■ Marshall has maintained the integrity of its stringent cleaning requirements while meeting all Degreaser MACT guidelines.

■ Compliance approach combined use of alternative chemicals with elimination of waste/inefficiency, and implementing minor process modifications.

hand, EPA is determined to eliminate or severely limit the use of these chemicals, which have been proven to adversely affect earth's protective ozone layer. The challenge of CH2M HILL and Marshall was to obtain compliance within the EPA Degreaser MACT guidelines without compromising the quality, safety, and integrity of Marshall's highly specialized program.

It was clear that Marshall did indeed produce large quantities of vapor emissions covered by EPA Degreaser MACT. Most of the larger-scale cleaning/degreasing operations employed a batch system, which is typically a prime source of vapor emissions. The solution for many facilities is to change from a batch to a continuous cleaning process, thus eliminating large quantities of chemicals occurring in one place. This was not an option for Marshall -- batch cleaning was the only way to ensure the cleanroom standards that their processes demanded. The alternative, was to do all that was possible to reduce emissions of these chemicals facility-wide to bring Marshall below the Degreaser MACT threshold, and then submit rolling three-month averages from emissions testing to ensure steady maintenance of below-the-threshold operations.

Wherever possible, alternative chemicals were substituted and waste or inefficient use of cleaning/verification solvents was eliminated. The solution for reducing air emissions from the large batch cleaning processes was relatively simple and inexpensive. The height or "freeboard" area of the cleaning vats was increased so that vapors tended to remain in the vats longer and could be more effectively condensed by a system of condenser coils. This approach combining use of alternative chemicals, eliminating waste, and implementing minor process changes proved highly cost-efficient in achieving Degreaser MACT compliance for Marshall. Thus far, the three-month average emissions rate has remained below the EPA threshold.

■ ***EPA Stratospheric Ozone Rule:*** This EPA rule is similar to the Degreaser MACT guidelines in that it pertains to protection of the ozone layer from air emissions from certain chemicals. But the emphasis under stratospheric ozone is on refrigerants involved in air conditioning for buildings and motor vehicles. Once again, Freon 113 was the focus of EPA concern under this rule

The EPA Stratospheric Ozone Rule Challenge:

- Marshall obtained agency permission to exhaust current inventories of ozone-depleting substances, provided strict recordkeeping accompanies this process
- CH2M HILL is working closely with Marshall to facilitate smooth transition to alternative chemicals that ensure compliance without compromising Marshall's mission. ADEM approval is pending.
- Identified alternatives that met cleanliness standards, environmental compatibility standards, and material compatibility standards.

Although Marshall is currently using ozone-depleting chemicals as covered under the EPA Stratospheric Ozone Rule, both for air conditioning and for cleaning, the Center will be allowed to continue use of these substances until its inventories are exhausted – provided that exacting inventory and usage records are maintained and frequently updated. Also, it was necessary that Marshall demonstrate that personnel handling these chemicals had received the proper training and that this training regimen would continue.

Compliance with this rule, at least for the near term, was not difficult to achieve. Marshall simply agreed to find substitutes for ozone-depleting chemicals as current inventories are used up. Marshall cannot afford any compromise in most of its temperature control and cleaning operations, and the challenge for the long-term will be to develop alternatives that achieve the same level of effectiveness as the substances being phased out. CH2M HILL is currently working closely with Marshall to ensure a smooth transition to those alternatives.

Conclusion / Lessons Learned:

Generally, Title V compliance for Marshall was accomplished in an expeditious and efficient process, certainly in view of the complexity of the facility's operations and some of the unique challenges involved in these highly specialized production and testing processes. Emissions inventories were investigated and compiled with no disruption to the critical ongoing operations at Marshall, and ADEM/EPA requirements were satisfied at each stage of the process. But, as always, a look back can provide valuable insight on how to best handle these types of air emissions regulatory questions in the future. Pearls gleaned from Marshall's Title V experience include:

Summary of TITLE V Challenges at Marshall:

A key element of success for the project was to ensure that a Title V permit application was prepared which was realistic, yet will allow flexibility of future Marshall operations. To accomplish this goal, challenges encountered in the preparation of the Title V application were numerous and included the following:

- The Title V process began with limited information on chemical use operations, their locations, and the organizations responsible for the operations.
- Once chemicals were identified, clarifying the quantities used, composition, and expected future variability of those chemicals was a major hurdle.
- Identifying expected future usage of chemicals was essential yet problematic considering Marshall's continually evolving mission.
- Predicting the future engine testing and infrastructure-related emissions sources was difficult because these activities were episodic and occurred in cycles that were hard to predict.
- A major effort was required to effectively manage and consolidate the large amount of information prepared as part of the emission inventory preparation.
- Correlation of the emissions estimates with other programmatic estimation, particularly the Form R and NPDES estimates, required extensive investigation and verification.

Start from scratch on the emissions inventory. As renovating and remodeling an old house can often be more complicated and expensive than building a new one; perhaps simply throwing out the existing emissions inventory data at Marshall and starting from ground zero would have expedited the EI process.

Try to resolve the issue of emissions from Marshall's engine testing activities sooner in the process. Hindsight reveals that ADEM might have been further assisted and prompted in providing a faster decision as to the regulatory status of the engine test emissions. Although the ultimate judgement was highly favorable to Marshall, the uncertainty that preceded the final decision created some minor inefficiencies and planning difficulties for the Title V process, and the specter of a requirement for the PSD permit was troubling and distracting.

Craft a better approach to ADEM that will result in more timely and favorable feedback regarding the Aerospace MACT issue. Although it was evident for some time that Marshall's activities would be exempt from the Aerospace MACT provision, no firm interim commitment from ADEM could be obtained, and the Title V process was forced to proceed on the assumption that the Aerospace MACT liabilities were in force. Resolving this issue sooner would have eliminated the need for factoring in this compliance issue.

Title: **Life Under The NESHAP: Experiences of the Regulators, Industry and Users**
Author: **John B. Durkee II, Ph.D., PE**
Affiliation: **Creative EnterpriZes**
Address: 105 Anyway Suite 209
Lake Jackson, Texas 77566

ABSTRACT

This paper describes the history, methodology, and impact of the NESHAP for chlorinated solvents past through the compliance date. This rule "broke the mold" because it: spoke against "political correctness" and validated use of solvents; was "user friendly" because the EPA gave users so many ways to comply; and yet was not a complete break from the past because enforcement was based on an old-style punitive approach.

Was this rule a success? Were users happy about the "user friendly" rule? Did the enforcement approach have an effect? The answers are revealed in this paper.

Many users have complied with it's provisions; yet evidence suggests that success hadn't happened through 1997. Users were presented with a smorgasbord of choices for compliance, yet they are seen as being as confused as a kid with a $5 bill in a candy store. The EPA wanted to make it simple and easy for users to make the choices which most reduced emissions, yet the vast majority have chosen other approaches because of the enforcement basis in the rule.

BACKGROUND

This standard was one of the enabling events that spawned what many have described as the "renaissance of solvents". The EPA spent several years in development of this NESHAP, and it was their method of validating use of solvents as cleaning agents.

Simply, the NESHAP for chlorinated solvents said that it was OK to use solvents about which there are environmental or health concerns -- if emissions from cleaning operations were controlled in certain ways. The NESHAP didn't speak about solvent concentrations being below certain limits -- that's OSHA's (and your....) responsibility.

In addition to the normal problems associated with complying with environmental regulation, this NESHAP brought one more problem -- it wasn't simple.

- The EPA had to allow US industry the opportunity to have a great deal of flexibility in choice about compliance. US industry made it plain they demanded that choice in their comments about the initial draft of the NESHAP they provided to the EPA. The EPA met their aim. Unfortunately, the breadth of choices lead to confusion -- similar to Congress after a tax increase.

- The EPA had to make enforcement simple and low-cost. They met that aim -- because compliance

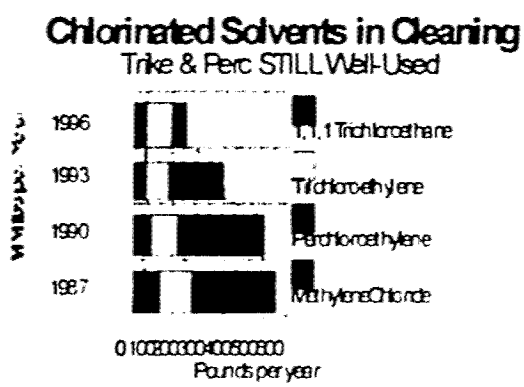
involves self-monitoring and reporting.

- The EPA had to make it easy for US industry to make the "right" choices -- those which allowed less emissions of HAPs. Again, they met that aim by creating the idling and total emission methods. Unfortunately, very few users have chosen those methods because the self-reporting process requires a report if emissions exceed limits, and the other compliance method does not require an exceedance report.

This paper is divided into three sections: (1) what others have done and how their choices fared, (2) what else could have been done by the EPA (with hindsight); and (3) what are your choices and what you should do to get in compliance.

What Others Have Done and How Their Choices Fared

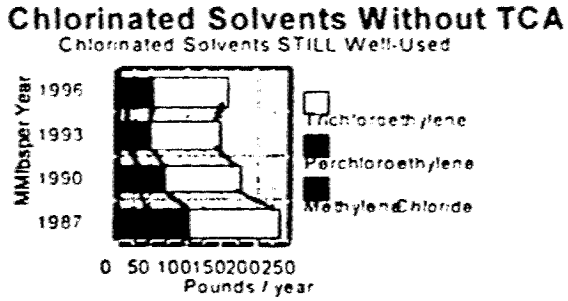
Research for these articles included lengthy telephone interviews in the summer - fall of 1997. Those interviewed included roughly two dozen end users and a dozen state EPAs or state-based technology transfer organizations, the US EPA, and six major equipment suppliers. Also observed were the actions and results of many more users in the past three years. First of all, through 1996 there has been negligible effect on solvent use except as expected for 1,1,1 TCA. Please see Figures 1 and 2 at right[1].



While it may be too soon to see an effect of the NESHAP, plainly little effect has been seen through 1996--except for methylene chloride, whose use is affected by an additional NESHAP for aerospace operations.

Secondly, the only generalization about US compliance with the chlorinated NESHAP is that it has been controlled by state and local entities.

One state EPA has a list of permitted vapor degreasers that dates from 1972. They have achieved around 85% compliance with the NESHAP.



Another state EPA reports they only received 5 (five) initial notification reports through late-1997.

Three national firms who produce solvent vapor cleaning equipment report that practically nobody has chosen the idling or total emissions approaches to

---

1 Data Source: SRI International & Center for Emission Control

compliance.

Yet, one regional equipment firm reports that around 80% of their customers for the past 3 - 4 years have chosen among those two compliance options.

One Pollution Prevention group reports that those in their area have converted from cleaning with NESHAP solvents to use of aqueous cleaning technology. They claim to know nothing about those still using solvents on the NESHAP list. In another state, a technology transfer association reports good conversion to the NESHAP because small users could see how it would save them money in solvent costs.

Illinois and Rhode Island appear to have put this situation behind them. Nationally, estimates of overall compliance (including switching to aqueous, no-clean, etc.) range from 25% to more than 50%. A consensus is that at least half of the vapor cleaning machines in the US which are covered by this rule will not have complied with it by the compliance date (December 2, 1997).

Fourthly, the bulk of available data supports the statement that compliance with the NESHAP means compliance with OSHA's exposure limits for workers. Don't turn down serendipity when you find it -- EPA and OSHA had little coordination when this NESHAP was developed.

Don't take OSHA limits for granted. You are likely to overexpose your workers to solvent fumes if you were: to implement EPA choice #6, use MeCl, don't install a working mode cover or practice control of dwell, and locate your machine in a small poorly-ventilated area.

Finally, it is interesting that our responses covered both sides of the question about whether it was large or small firms who had achieved the highest percentage of compliance.

User attitudes about this NESHAP were found to vary from ignorance to confusion to various levels of satisfaction. Despite many local and national communication efforts, confusion was the dominant attitude because of the complexity of the rule. Some users were pleased that the NESHAP validated solvent cleaning; others were pleased because the NESHAP would provide them with appropriate motivation to move on to aqueous cleaning. Is this a philosophical view and not a technical or business view?

At some places a psychological view was found -- users choosing the engineering controls approach because they could comply with the NESHAP with a purchase order (and lots of record keeping and reporting). These users felt the total emissions method was a gamble, and they had no wish to take a gamble when losing the gamble meant writing an exceedance report to someone who works for Carol Browner (and maybe the local newspaper).

EPA's attempt to provide flexibility appears to have only created confusion, and their insistence on traditional reporting schemes to ensure compliance has created a significant disincentive to the non-traditional compliance methods it offered.

What company wants to select the total emissions limit as its compliance option, if it can't be sure it can

meet the limit month to month? More specifically, what plant manager wants to go to his management to tell them that the company has to file an exceedance report with the EPA because production was up last month?

Something else significant has happened regarding the degreasing NESHAP. Much like companies have come to look to the SNAP program to determine what solvents they can use, some firms appear to look at the degreasing NESHAP to determine how to use these solvents. A number of companies are specifying NESHAP-compliant equipment for use with other solvents. Although they are not required to install NESHAP-level controls, these companies have decided that, for economic, occupational, or environmental reasons, it makes good sense to do so.

What The EPA Could Have Been Done
[with hindsight]

The depth of the requirements for compliance, compared to the breadth of options in, demonstrate both the "user friendly" and punitive sides to this NESHAP. On one hand, many options were provided. But if you chose the options which produce the most emissions (the engineering controls method), you have the greatest burden of monitoring and record-keeping

The EPA developed a cunning plan -- offer the carrot of simplified monitoring and record-keeping to gain reduced emissions But, in general, it didn't work

The vast majority of compliant vapor cleaning machines have become so via the engineering control method -- the one which produces the most emissions!

The main reason is the exceedance report In general, it has been the "death warrant" for the engineering controls method

No plant manager wants to file an exceedance report -- which could be ultimately forwarded to Carol Browner (EPA Administrator), or their local newspapers (through the Freedom Of Information Act). Few plant managers want to wait until the end of a reporting period to find out if they are in compliance Most plant managers want to the minimum necessary as soon as possible to get in compliance, and then get on with profit-making issues

What else could have been done? Several things

1 **Require Only Total Emissions or Idling Choices** This requirement for compliance minimizes emissions, and maximizes user flexibility

2 **Kill the exceedance report** Or, at worst, make it annual, or biannual, while continuing to require monthly monitoring This should reduce the pressure the plant manager feels

3 **Enforce tough auditing** via state or local EPAs There is no reason to let users flaunt the law --

as many are now doing.

4. **Extend to all regulated solvents** (chlorinated, halogenated, VOC). This step would make choices simple for users (today ≅ 5 years after the NESHAP was crafted). Users could switch from HAP to VOC solvents and use the same tight equipment

5. **Cooperate with OSHA** --users have to do so! Structure the NESHAP so that the likelihood of compliance with OSHA exposure limits is almost a certainty. With a tight machine, that will meet the total emissions requirement for compliance, only an extremely low air flow would produce non-compliance.

6. **Publicize** the existence of successful applications of the total emissions methods. Many believe it can't be done.

The point to remember about complexity is that users demanded flexibility in their public comments to the initial draft of the NESHAP. In this case, we users got for what we wished.

Another approach would have been to combine the above change in reporting of an exceedance, and eliminate all methods but the total emissions method. Users and suppliers would be provided with the EPA's basic data from which to make choices. This change would cut to the heart of the matter -- the EPA wants emissions reduced and under control, users want maximum flexibility and minimum complexity. This change would have been sure to have increased the percentage of users under compliance.

A third aspect is breadth of coverage. Basically, this NESHAP applies to two solvent: Trike and Perc -- which are HAPs. It should have been applied to all solvents about which there is some degree of regulation: HAP VOC, exposure limit less than 100 ppm, That would made it simple for users, effective for regulators, and profitable for manufacturers. In this way, all solvents would have been treated the same. Users would not save money by switching from solvent which is highly regulated because a lot about it's hazards is known to a new solvent about which little is known.

On the other hand, this rule is plainly better than what might have been expected from the EPA of 10 years ago -- one method for all, monthly exceedance reports, and quarterly inspections....

What You Should Do to Get in Compliance

DOES THIS APPLY TO ME?

This rule applies to you if you are the owner of a solvent cleaning machine and the solvent in your machine

contains more than five weight percent of the 6 solvents listed in this NESHAP[2]. The reader is directed to reference 3 for complete coverage[3] of the above in more detail, in-line cleaning machines of various sizes, cold cleaning, enclosed machines, and very large solvent cleaning machines.

VAPOR CLEANING MACHINES (open-top)

There are three options for open machines (vs enclosed). They apply to new or retrofitted, large or small, and batch or in-line units. They are described below.

1. You can buy a new unit or retrofit your existing unit so that your degreaser has **certain engineering controls** which restrict emissions. You are in compliance when you choose among ten combinations of features, and implement one, and your machine meets a few base design requirements. You prove compliance on a continuing basis by monitoring that each engineering feature is performing properly. You must also train your employees and teach them certain work practices.

2. You can prove that your new or retrofitted unit passes a test where it's **emissions are measured when it is idling** (hot, but not cleaning parts), and with the cover on. You can choose any group of engineering controls, though your machine meets a few base design requirements. You prove compliance on a continuing basis by annually measuring the solvent loss when idling. You must also train your employees and teach them certain work practices.

3. You can "simply" **measure your unit's monthly performance**, and compare it to a norm. This choice is also called the "alternate" method. You prove compliance on a continuing basis by monitoring solvent purchase and disposal amounts and reporting a net rolling average consumption vs a norm. There are no requirements about training or work practices.

Note that the method of using engineering controls does not directly controls emissions. It manages the control technologies used to restrict emissions. The idling and total emissions methods are based on measurements of actual emissions. Consequently, the EPA expects higher emissions if the engineering controls method is chosen, because the method of control is only indirect.

---

2 Methylene chloride (MeCl), perchloroethylene (Perc or perk or perky), trichloroethylene (trike), 1,1,1 Trichloroethane (tri, 1,1,1), and two less common solvents: carbon tetrachloride and chloroform. They aren't used to a significant degree in cleaning operations.

3 Durkee, J. B., "The NESHAP For Chlorinated Solvents — What You Need to Know and Others Have Learned," *Precision Cleaning*, Vol 5, No. 10, 1997.

	Table 1 -- Comparison of Choices for Compliance		
	Engineering Controls	**Idling Emissions**	**Total Emissions**
Pro	Compliance continuously known	Compliance only known after testing, Can be out-sourced,	Compliance only known after billing & calculation, Lowest emissions, Least effect on employees
Con	Most monitoring & reporting burden	Requires tight machine	Requires tight machine

RECOMMENDATIONS

In 1995, we wrote[4] that you should choose the total emissions method for compliance. We still believe that's the right choice, for most firms, because it consumes the least amount of your staff's time in non-productive record keeping.

Recently, top supplier firms have developed some good applications and performance data, for vapor cleaning machines no more than ~ 8 ft on a side. This appears to be the current limit of effect for sidewall-based heat-transfer (cooling or heating) devices. Beyond that limit, it will be very difficult to meet the total emissions method. Here, the engineering control approach should be used.

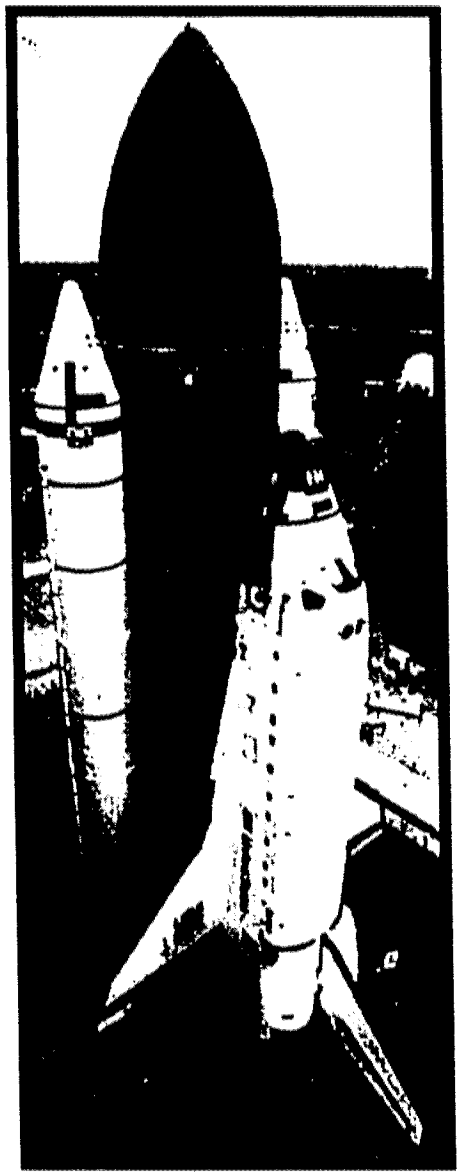
SUMMARY

In 1994, the EPA caused a significant resurgence of interest in use of solvents, vs. aqueous cleaning technology, through creation of the NESHAP for chlorinated solvents. Because the regulation was complex and not well understood, only about half of the affected users are thought to have complied (though December 2, 1997).

Research for this paper showed that users have mainly chosen the approach which has the greatest level of emissions -- because compliance using this approach involved less risk to them. We believe the EPA could have reduced emissions by increasing the level of compliance and fostering low-emission choices by: not requiring users to file an exceedance report, allowing only the total emissions method of compliance, and letting users choose any method of emission control.

---

4 Durkee, J. B. Precision Cleaning, Vol 3, (4), 1995, page 39 - 48.

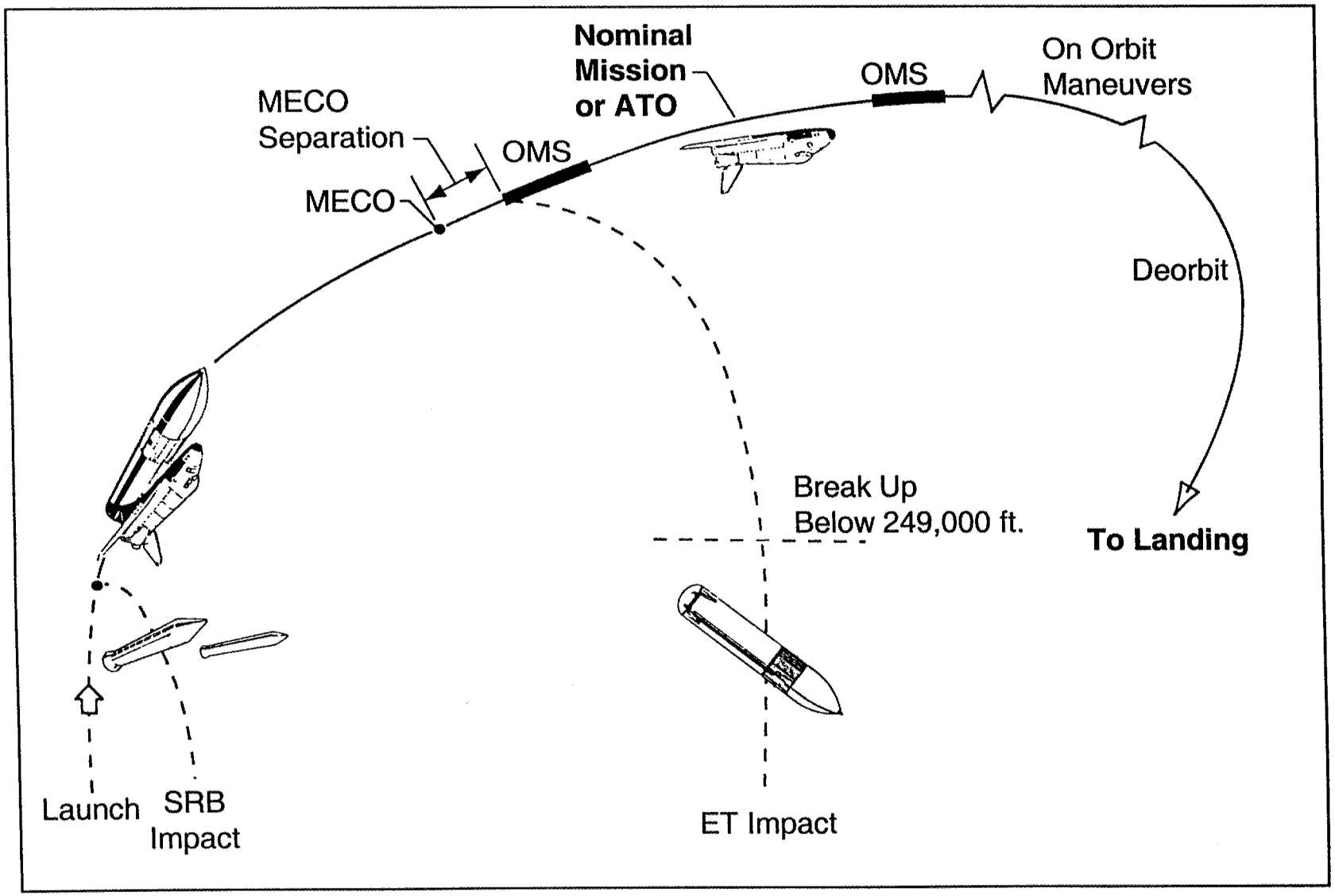


Cryogenic Bonding Primer Replacement for the External Tank

Larry A. Groves

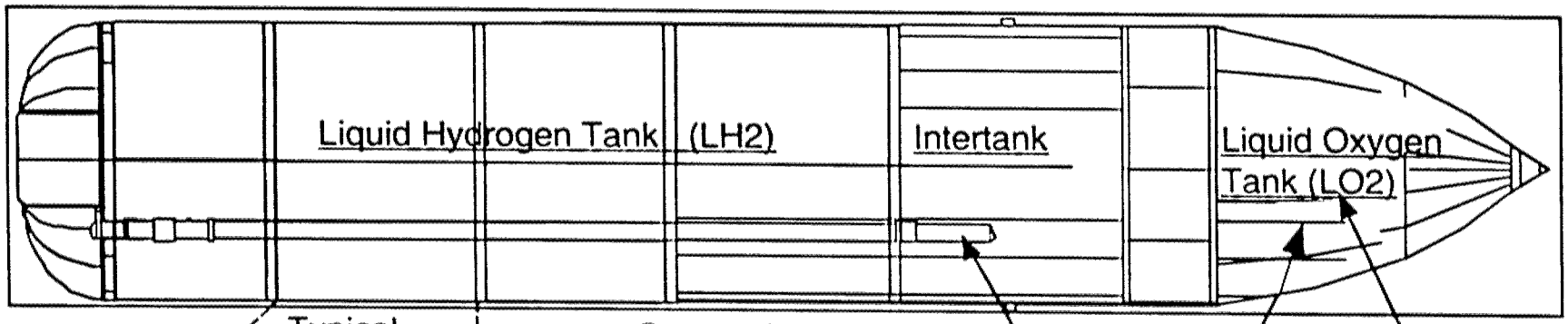
LOCKHEED MARTIN

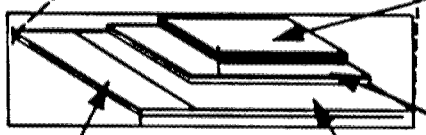
Mission Profile



Environmental Program Scope: ET Pollution Sources

- **Pollution Sources Primarily Originate from Various ET Production Operations**





Sprayed-on Foam Insulation (SOFI)
- Non-chlorinated solvents
- Unreacted Components
- Cured SOFI
- Waste SOFI

LO_2 Tank Proof Test
- Non-chlorinated solvents
- Chromium
- Wastewater

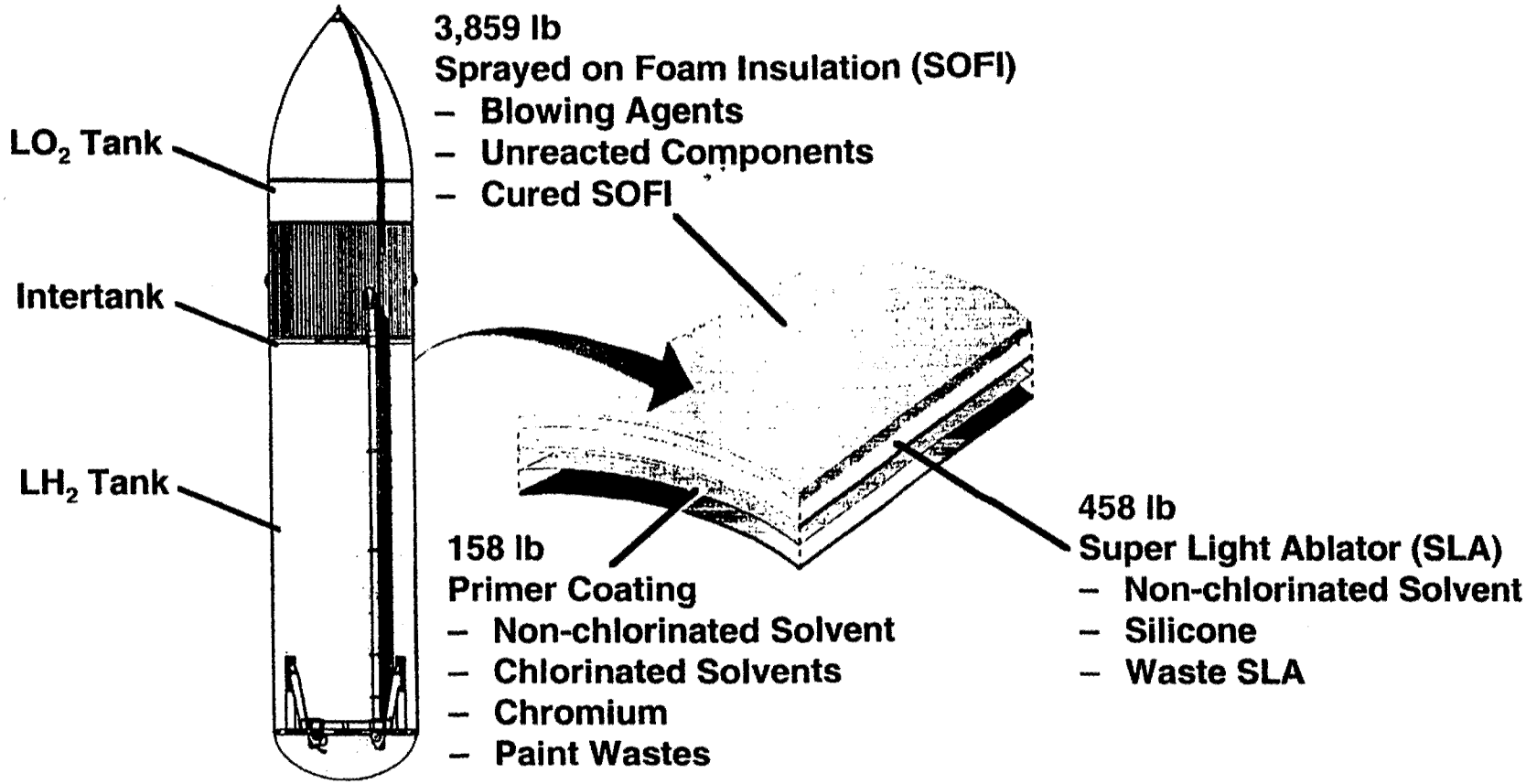
Aluminum Barrel Panel & LO2/LH2 Tank Cleaning
- Non-chlorinated solvents
- Corrosives
- Phosphates
- Chromium
- Wastewater

Super Light Ablator (SLA)
- Non-chlorinated solvents
- Silicone
- Waste SLA

LO2 Cleanliness Verification
- Trichloroethylene
- HCFC 225

Primer Coating
- Non-chlorinated solvents
- Chromium
- Paint Wastes

Environmental Program Scope



- Recognized small volume user
- Very stringent technical requirements

Why Prime the ET?

- Aluminum (Unprotected) Oxidizes Rapidly to Form a Dense Coherent Layer of Aluminum Oxide
- Aluminum Alloy Contains Copper in the Metal Matrix and is Exposed at Surface Allowing Formation of Electrolytic Cell (AL as Anode and Copper as Cathode) Subject to Corrosion
- Aluminum Corrodes Rapidly in Presence of Salt Water (CL - Ions Also Present Due to TPS Raw Material/Precursors and Blowing Agents)
- Primer Protects Aluminum

Why Change Primer???

- Material Availability to Support Space Shuttle
- Environmental Regulation Impacts
- Support Technology
- Cost Savings
- Lockheed Martin Manned Space Systems
  100% Mission Success™
- Current Primer (Increase in Non-Conformance)

Key Qualification Constraints

- 1,000 hours Salt Fog Resistance (FTM Std.41A, MTD.5061)
- No Corrosion Under 1" TPS (7 Wks. @ 95% RH & 120°F)
- TPS Foam Adhesion (Pass, Cohesive @ R.T. & -320°F)
- Cryogenic Flexibility and Adhesion (-423°F, 4.13" Radius)
- Flexibility (Pass, 0.5 "RAD; FTM 141a, MTD. 6221)
- Adhesion (Pass, FTM 141a, MTD. 6301.1)
- Drying Time (Tack free - 2 hours, Hard - 16 hours, FTM 141a, MTD. 4061.1) Desired Cured Film = 0.4 To 1.5 Mil
- One Year Shelf-life Stored at R.T.
- General Compatibility with Other Materials in Use

Which Primer Technology Fits?

- Powder Coatings
- Electrostatic Coatings
- Waterborne Coatings
- High-Solids Coatings

Can We Find a Primer Replacement?

- **Yes,**

  If we take advantage of the synergistic benefits below:

  – Avoid paradigms, and

  – Re-evaluate our qualification criteria!!!

    — New TPS foam formulations with new blowing agent (significantly reduced chloride ion at primer bondline interface)

    — Ongoing replacement of high density ablator (significant reduction in use of ablator via composite use and USBI Convergent Spray Technology™)

    — Vastly improved touch labor performance

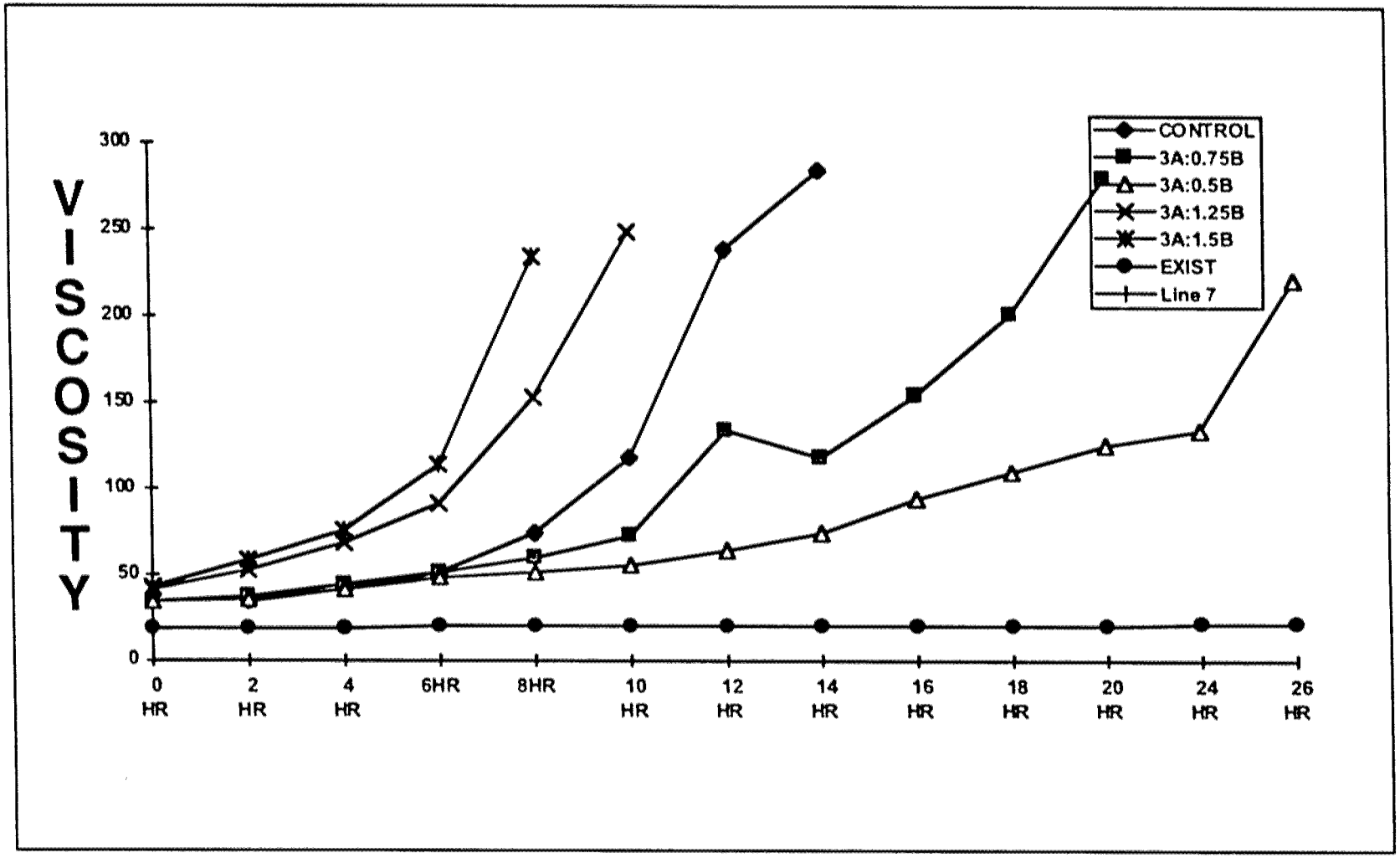
    — Significant improvements to MAF process technology

Spraylat Corrosion Testing (Patti-Jr) 2219/2195

C/O Foam (psi)	Spray Foam	Spray Foam	Ablator
C - (7 wk) 2252 psi	2720	2720	3270
S - (7 wk) 1315 psi	1965	1824	1519
C - (26 wk) 1763 psi	2801	2475	2230
S - (26 wk) 847 psi	1926	847	760

C - (7 wk) 2190 psi	1905	2007	1967
S - (7 wk) 2252 psi	1254	1173	1417
C - (26 wk) psi	1743	1498	1050
S - (26 wk) psi	888	643	650

Spraylat (Pot Life)



Test Results: Spraylat Primer

- ASTM B117 Salt Spray, Scribed Panels Pass 2,000 Hours
- No Corrosion Under 1" TPS Foam, 26 Weeks Exposure
- Cryogenic Adhesion and Flexibility at -423°F, Pass
- Cryoflex Testing at -423°F, Pass (3 TPS Foams)
- Bond Adhesion Tests at -423°F to +400°F, Pass
- Dry Tape Test and Solvent Rub Pass at 6 Hours Cure
- Ongoing Wet Chemistry Shelf-Life Test, 8 Months
- No Need for Induction Time, Confirmed
- Pot-life of 4 Hours, Confirmed

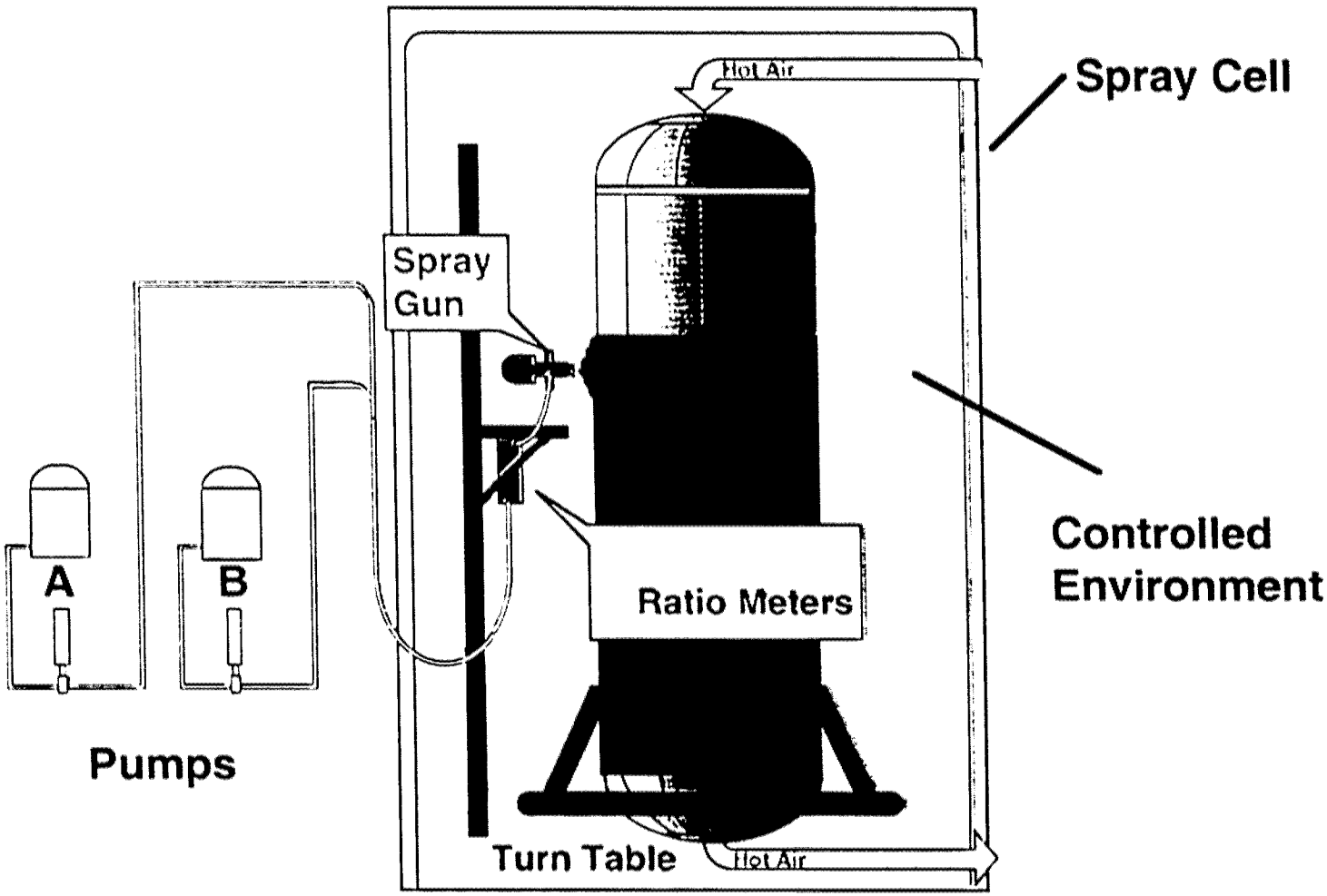
Today's Primer versus New Primer System

Today's Primer	*New Primer System*
• Requires Long Pot-Life	• No Pot-life Issue
• Mix Ratio Variable (Manual)	• Automatic Ratio Control
• Sweat-in/Induction Time	• No Induction Time
• Shake/Prep/Mix Labor	• Auto Mix on Demand
• Pre-measured Small Kits	• Bulk 2K Purchase
• Labor QC Inspection	• Automated Optics
• Touch-up Labor	• Auto Dispense
• Manual Reporting	• ISO/SPC Electronic
• High V.O.C, Toxic, Carcinogenic	• EPA/LDEQ Compliant

Does Primer Impact Process?

- VAB Process Serial Time too Long for 4 Hour Potlife
- New Primer Requires Enhanced Ratio Control for Large Structure Duration Spray Applications
- Process Need to Minimize Waste and Cleaning
- New Primer From Spraylat Permits the Resolution of Above Process Concerns Via Elimination of Induction Time and Use of Plural Component Mixing at or Near the Spray Gun With Auto Ratio Control!!
- Mix on Demand Minimizes Mixed Material Waste
- Using Water-based Flush Minimizes and/or Eliminates Solvent Flush

Spray Process



LOCKHEED MARTIN

On Versus Off-site Primer Process Requirements

- Must Qualify Primer with Both Conventional and New Processes
- Must Establish the Qualification Test Plan that Includes Buy-in of all Cognizant Disciplines at LMMSS, KSC as well as with Customer, NASA/MSFC
- Cognizant Community Must Recognize and Accept the Need for the Interim Low VOC Primer and Process Technology Change Today Which is a Necessary Step to Achieve the Ultimate Goal of a Non-Chromate Water-Borne Primer

How do we gain support?

- Initiate a "Development Tool Order" Which Allows all Disciplines to Respond to a Contractual, Funded, and Scheduled Work Effort to Design, Install, and Test the Full-scale Large Structure Spray Application Process Concurrent with Primer Material Qualification to Resolve any Potential Issues Prior to Formal Implementation

Chromium Electroplating Alternatives Reference
Executive Summary

Southern Technology Application Center
One Progress Blvd.
Box 24
Alachua, FL 32615

The ***Chromium Electroplating Alternatives Reference*** is designed for professionals who work in the metal finishing or related industries. It is intended to review many of the elements and issues relating to chromium electroplating as well as provide current information on state-of-the-art technologies being used and developed in the industry. Originally the focus of this reference was on identifying and categorizing alternative processes to chromium electroplating. However, through extensive research with companies and several key industry associations, it became apparent that this was only half the story. In fact, many companies are vitally interested in achieving and maintaining compliance with increasingly stringent environmental regulations while continuing to use chromium in electroplating and finishing processes.

Consequently, this reference is organized into two distinct parts. Part I focuses on the regulatory environment, specifically air and water regulations, and the strategies currently use d by firms in the industry to comply with the regulatory environment. Part II turns to an examination of alternative processes and materials being developed and used by firms that have opted to discontinue the use of chromium in electroplating and metal finishing processes for some or all of their applications.

Much of the data provided in this reference are drawn from responses to an extensive industry survey conducted by the Southern Technology Applications Center (STAC) in 1997. More than 500 firms in the metal finishing and related industries were contacted by telephone and by letter to elicit information on environmental compliance strategies, replacement alternatives for chromium, and electroplating and finishing processes. The resulting data were combined with information derived from extensive literature reviews and assembled into a matrix format for ease in reference and comparison by the reader. Wherever appropriate, responding companies are identified so that the reader may contact them directly for more information.

The findings of this research effort yield insight into the current state of the industry and company perspectives on the future use of chromium in the metal finishing industry. Thus, in Part I not only are current and proposed future regulations reviewed and highlighted, but current financial and legal liability issues and their relations with the regulatory pressures being exerted on the industry are also explored. Key questions, including costs associated with waste generation, handling, disposal, and liability are addressed, and various solution strategies developed by industry firms are described. Checklists are provided to assist the reader in assessing whether or not processes used in his/her firm are compliant with current regulatory standards.

An assessment of the available alternatives to traditional chromium electroplating processes and a review of advantages and limitations of each alternative are contained in Part II of this reference. Summary information for areas where pollution prevention can play a significant role in improving the economics of the metal finishing business are also addressed. Metal plating and finishing operations represent some of the best and most classic applications of pollution prevention approaches, and numerous opportunities exist for source reduction ranging from complex technological advances to relatively simple and inexpensive operational changes. Research results indicate that innovative industry members have made significant progress in developing and implementing pollution prevention and control methods. These methods and their impacts along with a look at projections on where the industry is headed are detailed.

The alternatives identified are categorized and compared on the matrices. Categories include wet tank alternative processes, thermal spray alternative processes, vacuum deposition alternative processes, and other alternative processes which have the potential to replace some chromium applications.

Matrices include the operating and performance characteristics for the alternative coating processes as a comparison to standard chromium electroplating. The matrices employ a common set of elements to present a standard basis for evaluation, including the alternative's process, physical properties, quality control, hazardous materials, and costs. The matrices provide a format that allows the reader to see at a glance which alternative(s) could be considered as a replacement technology for specific chromium electroplating applications.

More detailed information on both the regulatory environment and identified alternative processes are provided in Part III, Appendices, along with a listing of the company respondents to the STAC survey.

It is our hope that this reference will be a useful guide to management and technical professionals employed by firms in the metal finishing and related industries. While we make no claims as to the validity of information provided to us by industry respondents, we believe that the information contained in this reference is an accurate and true representation of the technology development and environmental compliance trends in the industry. The reader is advised to use caution in drawing conclusions based solely on information contained in this publication, and STAC will not be held responsible for outcomes of decisions made based solely on the information contained herein.

Introduction

Purpose

The Chromium Electroplating Alternatives Reference was developed by the Southern Technology Applications Center (STAC) to provide a useful comparison of chromium electroplating with other processes and to address the most important concerns of the metal finishing industry as reported in the Industry Overview included in Part I, Chapter 1. Specifically, these concerns relate to compliance with increasing environmental regulations, pollution prevention, use and properties of coating substitutes, cleaning and preparation needs, and economic criteria, all of which are addressed in this reference.

This reference has been compiled without bias toward a specific company, organization, or group. The information included in this reference is based on the assumption that the object of metal finishing is to coat a surface with a material(s) that possesses a specifically chosen set of properties, and that the cost-effective satisfaction of this object can only be achieved if process performance is evaluated independently of the business history.

The chromium electroplating process is one of the largest sources of chromium emissions in the United States. Because of chromium's toxicity, environmental concerns and regulations have changed the chromium electroplating industry dramatically over the past several years. Additional regulations are anticipated in the next five to ten years.

These regulations affect approximately 10,000 metal finishing companies and more than 500,000 workers in the industry. For those companies that plan to continue to use chromium, this reference provides a detailed look at regulatory compliance. For organizations considering alternative processes, this reference provides an in-depth look at alternative processes and the advantages and disadvantages of these processes.

The Chromium Electroplating Alternatives Reference is intended to help organizations find answers and solutions to the many questions and concerns relating to the chromium electroplating industry. This useful tool will help decision makers save time and money by consolidating much of the relevant information about the industry in one complete source.

The reference addresses in detail the impact of current and future regulatory requirements and the cost of non-compliance. It also provides insights on industry trends and alternative processes which have been adopted, including a comparative matrix of alternative processes for new developments and emerging technologies that will soon be commercially available.

Report Scope and Format

This reference covers the current and forecasted regulatory and business climate in the metal finishing industry regarding the use of traditional chromium electroplating. In addition, the available alternatives that can realistically be considered for numerous applications are also addressed and displayed in easy to read matrix tables, which allow for fast comparisons between various alternative technologies.

There are no recommendations that chromium electroplating facilities must switch to another coating process; however, these coating processes should be evaluated for use based on the nature of the coating they provide. There is no fundamental conflict in an electroplating shop installing a thermal spray process or some other alternative if it makes economic sense. Alternative processes and not mutually exclusive. It is common for some electroplating facilities to add other processes to their operations for certain applications and continue to perform electroplating activities as well.

The Chromium Electroplating Alternatives Reference provides the following information:

General Industry Description - This reference provides a general industry description of chromium electroplating and the impending changes to the industry which may impact your company.

Environmental Regulations - A review of major federal environmental regulations is included to provide a reference so you can determine whether your organization is in compliance.

OSHA and Worker Safety - A review of OSHA and worker safety requirements and guidelines for meeting these requirements is included.

Legal Liability - Legal liability considerations are addressed to provide insights into the costs associated with non-compliance to environmental and OSHA regulations.

Process and Materials Comparison - A process and materials comparison matrix table is provided for each alternative which includes a comparison of coatings and processes, physical properties, hazardous materials and waste, suppliers, and relative costs. Having all this information in one place and being able to compare the advantage of each process is invaluable in making decisions.

Conversion Costs - Financial considerations relating to the costs of conversion are provided in the matrix table for each alternative to assist in strategic planning.

Survey of Industry Trends - Survey results from hundreds of leading companies provide valuable insights on current and projected industry trends, including new developments and emerging techniques that will soon be commercially available.

Part I includes the current regulations and business trends that are expected to continue in the industry. Each applicable regulation is summarized and then highlighted in a format for quick reference and easy use. Other industry concerns, such as financial and legal liability issues, insurance considerations, and worker safety issues, are also analyzed and assessed. Surveys of key industry leaders were also conducted. Their perspectives have been compiled to provide insight on industry trends relating to the future use of chromium in the metal finishing industry.

Part II of the reference provides a comprehensive assessment of the available alternatives to traditional chromium electroplating processes. Chapter 5 of Part II addresses the following common metal finishing operations:

Coating;
Cleaning and Preparation; and
Grinding, Buffing, and Polishing.

Following the common metal finishing operations description, the alternatives are broken down into four main groups:

Wet Tank Alternative Processes,
Thermal Processes Alternative Processes,
Vacuum Deposition Alternative Processes, and
Other Alternative Processes.

Within these categories, specific subprocess alternative technologies are thoroughly assessed and then summarized in comparison matrices. These matrices provide specific data regarding the alternative's process, physical properties, quality control, hazardous materials, and costs. This format allows the user to make quick decisions regarding which alternative(s) would be the most likely candidate as a replacement technology for specific chromium electroplating applications.

Part III contains appendices of valuable information such as other selected matrix data, additional regulatory agency information, company profiles and vendor lists, and references.

Methodology and Information Sources

Extensive information research was performed to obtain the most current, pertinent information available on chromium electroplating alternatives and the regulations affecting the metal finishing industry. The data were then organized in a logical, easy to follow format. The reference was reviewed by numerous industry experts to ensure comprehensiveness and accuracy of the information contained within it.

Information sources used to compile this reference include current information on regulations using the Federal Register, Code of Federal Regulations, U.S. Environmental Protection Agency (EPA) Home Page, and the Metal Finishing Guidance Manual. For current information on the status of the industry and alternative technologies, information was obtained through surveys of the metal finishing industry, metal finishing conference proceedings, text books, journal articles, white papers, and websites. Throughout the reference information sources are cited by author and date. A complete listing of sources is included in the Reference section (under Part III).

The matrices describing suppliers and alternative processes were compiled through telephone surveys and questionnaires completed by the suppliers about their process(es). Each matrix presents a comprehensive overview of an alternative technology available to chromium electroplating, the manufacturer and/or supplier of the technology, and other pertinent information necessary for decision making.

Glossary of Key Terms

Definitions of key terms used throughout this reference are included so that users of this reference will be aware of the context in which these terms are used, and understand how they should be interpreted to gain the maximum value from this reference.

Alternative: a process or coating which could be a potential replacement for chromium electroplating.
Captive shops: provides metal finishing services within a manufacturing company.
Chromium electroplating: wet process used to deposit hexavalent chromium onto a substrate.
Decorative chromium: thin deposit of chromium applied to substrate, providing a durable finish.
Dry processes: processes that are non-aqueous in nature, such as thermal or vacuum oriented processes.
Hard chromium: also referred to as industrial or engineering chromium; deposition of a thick coating of chromium directly over the substrate.
Hexavalent chromium: traditional formulation of Chromium VI (Cr6) used in most chromium electroplating processes.
Job shops: provides metal finishing services as a contractor for a fee.
Metal finishers: comprised of all companies engaged in coating and finishing metals after they have been fabricated.
Metals industry: includes all companies working with metals (*e.g.*, finishers, fabricators, etc.).
Platers: companies engaged in electroplating or electroless plating of coating material on a variety of substrates.
Pollution prevention: techniques used to minimize or eliminate pollution generating activities.
Wet processes: metal finishing processes that involve aqueous solutions, typically electroplating or electroless plating processes.

Pratt & Whitney's Joint Group Acquisition Pollution Prevention Program (P&W - JG-APP)

Zinc-Chromate Primer Alternatives For Aircraft Engine Inserts & Fasteners

Samir Patel (561-796-2536)
Pratt & Whitney
P. O. Box 109600
West Palm Beach, FL 33410

Zinc-Chromate Alternatives JG-APP

Overview

Objective:

Qualify Alternate To Zinc Chromate Primer (TT-P-1757 or AMS 3110) **used in assembly of fasteners & inserts for galvanic corrosion protection (~1500 lb/yr usage)** under JG-APP* program.

Systems Involved:

- o Air Force - F100 and F119
- o Navy - TF30 and J52
- o NASA - ATD/SSME

Key Parts Involved:

- o Gear Box & Pump
- o Oil Tank
- o Fan Case

(Over 800 Parts)

Project Timeline:

P&W Participation Agreement - Late 1994
PM/Technical Meetings & Material Selection - 1995
JTP Finalization/Approval & Contract Award - 1996
JTP Testing & Implementation - 1997 - 1998

* JLC chartered JG-APP in 1994 to jointly reduce/eliminate HazMat from weapon systems in co-ordination with OEMs.

Zinc Chromate Alternatives JG-APP

Project Team and Acknowledgments

JPPAB
Luis Garcia-Baco
Ken Siler
Dick Myers

P&W
Mike Gehron
Mal Privett
Terry Hollis
Samir Patel

P&W DCMC
Janice Wilson

PMs
Jay Tiley (Air Force)
Linda Fry (Air Force)
Brian Townsend (Air Force)
Larry Noah (Navy)
Jack Benfer (Navy)
Beth Cook (NASA)
Paul Goosh (NASA)

Terry Albach (SA-ALC)

CTC/NDCEE
John Tanzola
Mark Cleary

Air Force

Navy

NASA

Zinc Chromate Alternatives JG-APP

Joint Test Protocol (JTP)

JTP Outlined Following Qualification Tests For Alternatives

-Material Compatibility (Stress & Hot Corrosion Cracking)

-Durability (Fluids Resistance)

-Corrosion Resistance (Salt Quench, Salt Spray, Electrochemical)

Key Substrates Tested (over 350 test samples Required)

-Aluminum 6061-0 (F100, TF30, J52, SSME Components)

-Aluminum C355-T6P (F100, TF30, J52, SSME Components)

-Magnesium WE43A-T6 (F119 Engine Components)

Zinc Chromate Alternatives JG-APP

Candidates Selection

Identified Several Candidates After Extensive Vendor Search

Four Candidates Selected:

- -Zinc Phosphate (TT-P-664D)
- -Zinc Molybdate (TT-P-645B)
- -Alumazite ZDA
- -ZRC Cold Galvanizing Compound

Selection Based On:

- -EHS Analysis (Cr IV & Carcinogen free, Low VOC)
- -One Component System (No Pot life Constrain)
- -Room Temperature Cure Capability (No Need For Oven)
- -Brush Application
- -Corrosion Resistance Information
- -Flexible Binder System
- -Long Term Availability

Zinc Chromate Alternatives JG-APP

Candidates Screening Study

Laboratory Screening Tests Conducted to Down Select Most Viable Candidates

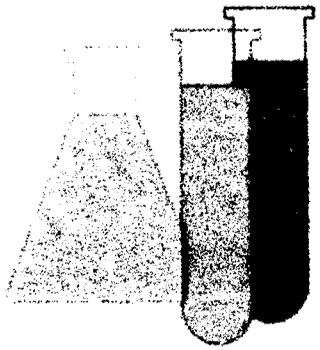
-Substrate Coverage (Uniformity, No Cracking/Delamination)

-Substrate Adhesion (Tape Test)

-Limited Hot Corrosion (On Aluminum & Magnesium Alloys)

-Fuel & Oil Resistance

-Galvanic Corrosion Salt Spray Test (On Magnesium alloy)



ZRC Primer failed hot & galvanic corrosion tests

Inexpensive Screening Study Identified The Three Most Viable Candidates For JTP Testing

Zinc Chromate Alternatives JG-APP

Summary

JTP Conclusions

Two Out of Three Candidates Met JTP Requirements

Zinc phosphate & Zinc Molybdate Recommended Substitute For Zinc Chromate For Aluminum Alloys (F100, TF30, J52, SSME)

Zinc phosphate Recommended Substitute For Zinc Chromate For Magnesium Alloy (F119)

Key Lessons Learned

- -Include Laboratory Screening Tests in JTP
- -Include Only Qualification/Performance Tests in JTP
- -Allow Flexibility to Modify Approved JTP
- -Keep Communication flowing

Zinc Chromate Alternatives JG-APP

Summary

Implementation

P&W Submitted SPI Concept Paper in February 1998 to Implement ZnCr Substitutes via Single Block Change

SPI Approved on 5-28-98

Block change in Process For Alternates Implementation

Benefits

-500 lbs VOC Reduction (37% from ZnCr VOC)
-NESHAP VOC Compliance, <350 g/l (ZnCr VOC = 500 g/l)
-$350,000/10 yrs cost avoidance (Lower environmental liability)
-Other OEMs Can Use Substitutes (Save time & $$$)

Over-all

Successful Completion of P&W - JG-APP Program

Zinc Chromate Alternatives JG-APP

JTP Results

JTP Testing Initiated in March 1997 on Zinc Phosphate, Zinc Molybdate, Alumazite ZDA, & Zinc Chromate baseline (ZnCr) Primers

Stress Corrosion - On Ti-8-1-1 & Al 7075-T6 Alloys @ 50-60 Ksi Stress
Al Samples heated @ 425 F for 250 hrs & Ti samples
@ 900 F For 100 hours
Acceptance Criteria: No Cracks/Breaks In Alloy

-All Primers Passed

Hot Corrosion - On 9 Alloys (Al 2024-T3, C355-T6P, 6061-0; Mg AZ31B-0; 4340 Steel, Greek Ascoloy; Hastelloy X, Waspaloy; Haynes 188)
Test Samples Heated in 450 -1600 F for 8-10 hours
Acceptance Criteria: NO Intergranular Attack (IGA) > 0.2 mil

-All, except ZnCr passed. ZnCr Failed hot corrosion on Hastelloy X alloy with IGA of 0.7 mil
-Test Temp. changed from 750 to 450 F for Aluminum & Magnesium alloys (lesson learned)

Zinc Chromate Alternatives JG-APP

JTP Results

Fluids Resistance - On Al 6061-0, Al C355-T6P, & Mg WE43A-T6 Alloys
Samples Immersed In DI Water For 4 Days @ 120 F &
In 7808 Oil, JP-8 Fuel For 4 hours @ RT.
Acceptance Criteria: No Peel Away From Alloy or Comparable to baseline ZnCr **(lesson learned)**

-Baseline ZnCr had most peel away after water immersion
-No Peel away after oil/fuel immersion on Al alloys. On Mg alloy Candidates comparable to baseline ZnCr

Salt Quench - On Al 6061-0, Al C355-T6P, & Mg WE43A-T6 Alloys
Heat Samples to 300 F, Spray Artificial Sea Water, Store For week, Heat to 400 F for 20 hrs, Cool to RT., Re-heat to 300 F, Spray Sea Water, & Store for a week
Acceptance Criteria: White Corrosion < ZnCr Primer

-All passed, except Alumazite ZDA
-Test Temp. changed from 450 to 380 F due to severe oxidation of baseline ZnCr at 450 F (lesson learned)

Zinc Chromate Alternatives JG-APP

JTP Results

Salt Spray - On Al 6061-0, Al C355-T6P, & Mg WE43A-T6 Alloys (Adjacent Protection, Repair Panels & Fitted blocks) 250 hours exposure in Salt Spray Chamber

Acceptance Criteria: No White Corrosion for Al alloys. Candidates should be comparable to baseline ZnCr for Mg alloy (lesson learned)

-All Primers Passed for Al alloys (No corrosion up to 500 hrs)
-Zn Mo & ZDA Corroded Mg alloy within 30 hrs
-Zn Po Comparable to Zn Cr on Mg alloy
- **No corrosion noted on inserts & fasteners after 250 hrs**
- **No galvanic corrosion noted on fitted blocks**

Electrochemical - Test In Progress With High Impedance Potentiostat
Acceptance Criteria: None (Outcome will not impact over-all conclusion)

Jack L. Weeks
President
Vacuum Arc Technologies Inc.
847 Pine Island Point
Scottsboro, Al. 35769

INTRODUCTION:

The Vacuum Arc Vapor Deposition process, VAVD, is a new process with several unique processing capabilities. The VAVD process was developed in 1993, at Marshall Space Flight Center/NASA, and patented in 1995, ref. Patent # 5,380,415.

The key feature of the VAVD process is the ability to utilize a high-energy, stable ionizing arc as a heat source in a vacuum environment. This feature provides a focused high-energy heat source that can melt a wide range of target materials. The stability of the arc eliminates the production of macro particles from the melted pool on the target material surface.

The VAVD process, using the prototype system, can apply 3.5 microns of material per minute. This deposition rate will vary depending on the target material. With this system the pool size is limited to 0.5" diameter and a process time of 10 minutes. The thermal loads on the crucible dictate these process limits.

The actively cooled prototype crucible is being installed in the VAVD system. This new design will allow the pool size to be increased to 2" and the process duration to be increased to 1 hour. This will allow deposition of coatings with thickness greater than 0.001".

BODY:

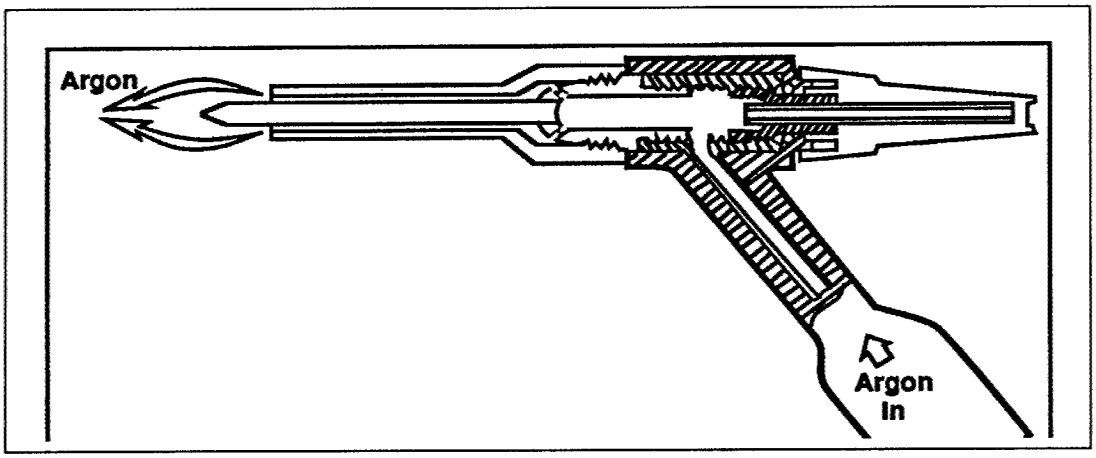
The Vacuum Arc Vapor Deposition process, (VAVD), was developed during the performance of work under NASA contract at Marshall Space Center.

The VAVD process is a method for vapor deposition of thin metallic and ceramic films utilizing an ionized gas arc in a vacuum environment.

The prototype VAVD system is unique because of the ability to establish and maintain a stable, focused ionizing arc in a reduced pressure environment, operating range-$5x10^{-5}$ torr to 25 microns.

Using a conventional Gas Tungsten Arc Welding system, as an example, the ionization medium is ported to the arc region and confined to a localized area with a ceramic cup, (Ref. Figure. 1).

Figure 1



This allows a stable ionizing arc to be established in an inert environment. This method of gas delivery can not be used in a vacuum environment because at reduced pressures the gas medium escapes into the vacuum so rapidly that there is not enough to sustain the ionization process and the arc is extinguished.

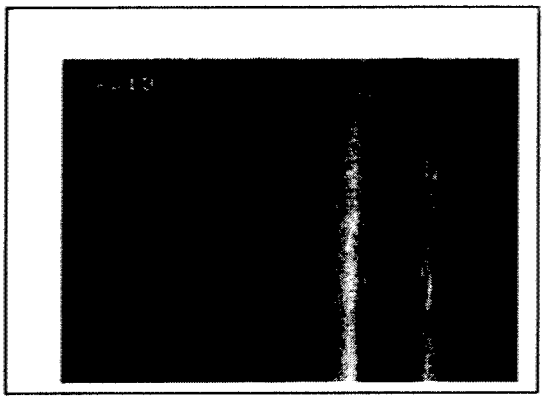
The VAVD process incorporates a unique gas porting design that delivers the gas to the arc region through a co-axial hole in the tungsten cathode. This approach restricts the gas medium to the arc region and allows a stable ionizing arc to be established in a reduced pressure environment.

Another advantage to this porting design is that the arc column is restricted to the path of the ionization medium. This arc column geometry can be modified in process by changing the gas flow to the arc region. This change in the arc column changes the energy transfer point on the target material. Using a low gas flow, i.e. 10 ccm, the target material can be rapidly heated to the melting point. Once the target material has reached the melting point the gas flow can be increased to increase the energy transfer point and increase the pool size.

When the arc is initiated the gas is entrained into the plasma column is does not escape until it is at the surface of the target material. This creates a pressure differential at the source of the vapor and accelerates the vapor into the vacuum at sonic velocities.

Because of these unique process characteristics the VAVD process can produce amorphous/continous films. The VAVD TiN samples were examined using the Scanning Electron Microscope, (SEM), at 10,000 magnification, (Ref. Figure 2).

Figure 2



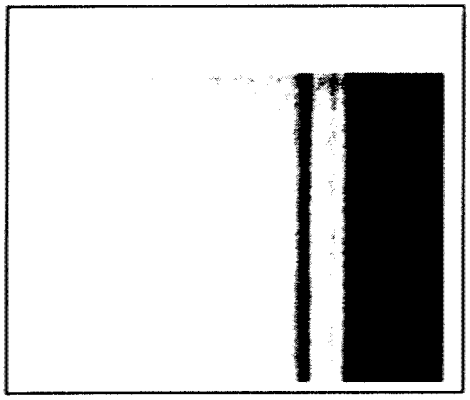
The samples were prepared by cutting through the film and substrate material and polishing the surface. The rough area on one side of the film is were the substrate material has pulled away during processing. The removal of the parent material from the substrate indicates a good bond of the film to the substrate.

The SEM results show no porosity or grain structure this would suggest that the VAVD coating would provide an excellent corrosion resistant coating.

In an effort to verify the absence of grain structure the samples were etched and reexamined using the SEM, (Ref. Figure 3). This image shows the edge of the coating has been etched away and has a depression in the center.

The initial effort focused on depositing VAVD pure chrome coatings as a replacement process for electroplated chrome coatings.

Figure 3



During these initial tests efforts were made to produce a film using a reactive gas as part of the ionization medium.

As an extension of the basic VAVD process involves the exploitation of the chemical reactions among the constituent materials. In the basic VAVD deposition, there are no such reactions: A substrate to be coated is placed in the vacuum chamber near the target, the material to be deposited. The arc and a ionized gas, argon, is directed onto the target, causing a liquid pool to form. This pool is the source of the vaporized material. The gradient of pressure in the chamber is arranged so the vapor is accelerated toward

the substrate.

The reactive VAVD process is similar, except that the deposition conditions and constituent materials, (target material and arc gas), are chosen to exploit chemical reactions between the two materials.

The reactive process has been demonstrated using titanium target material and nitrogen, argon mixed gas to produce TiN coatings. Similar tests have been conducted using chrome as the target material and nitrogen gas to apply CrN coatings.

It was found that during the reactive gas process it is necessary to maintain a percentage of argon gas for two reasons:

- The ionization potential of argon is greater than nitrogen, an arc can established more easily in an argon/nitrogen mixture than in pure nitrogen.
- A pure nitrogen environment causes a nitride layer to form on the titanium target. This is undesirable because it prevents the flow of titanium vapor from the target material. Trail and error established that with the proper mixture of argon and nitrogen this nitrite layer formation could be inhibited.

Bond Test:

The bond tests were conducted on five polished nickel sample with a 0.75 nm surface finish. Each of the five samples was then coated with a VAVD coating. These samples were removed from the container and placed into the VAVD chamber with no additional cleaning. There was no in process cleaning performed. The surface finish was than scanned to determine the change, (Ref. Table 1).

Test Set 9 Group 1									
Coupon Number	Adhesive Product	Bonding Method	Cure (Hour)	Area (sqin)	Stress (psi)	Mean Stress (psi)	Test Date	% Debond Estimate	Remarks
9b	Dexter EPK 608 A/B Clear Epoxy 2 PartRatio 1:1 Volume	Applied adhesive to Tensile Fixture (TF) surface. Bonded the Plating Coupon to TF surface after 2 minutes. Adhesive was still tacky.	24	0.196 0.238	957 788	882	02.27.98	100	Tensile Test PATTI. 100% Au debond from the Vacuum Arc Technogy Mo coated surface Note: The gage pressure at failure using the F4 fixture was recorded at 47 psig
10b	Dexter EPK 608 A/B Clear Epoxy 2 PartRatio 1:1 Volume	Applied adhesive to Tensile Fixture (TF) surface. Bonded the Plating Coupon to TF surface after 2 minutes. Adhesive was still tacky.	24	0.196 0.209	1263 1184	1224	02.27.98	100	Tensile Test PATTI. 100% Au debond from the Vacuum Arc Technogy Cr coated surface Note: The gage pressure at failure using the F4 fixture was recorded at 62 psig
21a	Dexter EPK 608 A/B Clear Epoxy 2 PartRatio 1:1 Volume	Applied adhesive to Tensile Fixture (TF) surface. Bonded the Plating Coupon to TF surface after 2 minutes. Adhesive was still tacky.	24	0.196 0.252	2648 2060	2354	02.27.98	100	Tensile Test PATTI. 100% Au debond from the Vacuum Arc Technogy Nb coated surface Note: The gage pressure at failure using the F8 fixture was recorded at 65 psig
24a	Dexter EPK 608 A/B Clear Epoxy 2 PartRatio 1:1 Volume	Applied adhesive to Tensile Fixture (TF) surface. Bonded the Plating Coupon to TF surface after 2 minutes. Adhesive was still tacky.	24	0.196 0.220	1977 1761	1869	02.27.98	100	Tensile Test PATTI. 100% Au debond from the Vacuum Arc Technogy Ta coated surface Note: The gage pressure at failure using the F4 fixture was recorded at 97 psig
25b	Dexter EPK 608 A/B Clear Epoxy 2 PartRatio 1:1 Volume	Applied adhesive to Tensile Fixture (TF) surface. Bonded the Plating Coupon to TF surface after 2 minutes. Adhesive was still tacky.	24	0.196 0.242	1793 1452	1623	02.27.98	100	Tensile Test PATTI. 100% Au debond from the Vacuum Arc Technogy Ti coated surface Note: The gage pressure at failure using the F4 fixture was recorded at 88 psig

Table 1

The samples were then coated with an Electron Beam generated Au coating. The actual test was to establish the bond strength of the Electron Beam Au coating to the VAVD coating. Of the five materials, (Ref. Table 4), the failure always occurred at the Electron Beam Au interface with the VAVD coating. This failure consistently removed 100% of the Au coating from the test area and did not remove the VAVD material.

The next set of tests will be to determine the bond strength between the VAVD coating and the nickel substrate.

Surface Replication:

The surface test was conducted using polished electroplated nickel samples. The initial surface finish was 0.75nm RA. The VAVD coatings were applied to the samples as received without additional cleaning. The results of the test showed a minimum of surface change after the VAVD coating was applied. (Ref. Table 2).

The right hand column in Table 5 represents the surface condition after the Electron Beam Au coating was applied over the VAVD coatings.

Table 1

Test results for Optical Surface Coatings; Mo, Cr, Nb, Ta & Ti
Base Material Electroplated Ni Polished (.75nm RA)

				VAVD Coating		EB Au Coating	
Sample#	Material	Area	Objective	RMS	RA	RMS	RA
9	Mo	#1	20x	1.010nm	0.7601nm	3.020nm	1.650nm
"	"	#2	20x			2.140nm	1.420nm
10	Cr	#1	20x	1.000nm	0.778nm	6.210nm	3.300nm
"	"	#2	"	1.900nm	0.979nm	6.170nm	3.250nm
21	Nb	#1	20x	1.520nm	1.210nm		
"	"	#2	"	1.420nm	1.180nm		
24	Ta	#1	20x	1.140nm	0.927nm		
"	"	#2	20x	1.450nm	1.170nm		
25	Ti.	#1	20x	1.210nm	0.888nm	3.020nm	2.600nm
"	"	#2	20x	3.060nm	4.130nm	2.730nm	2.220nm

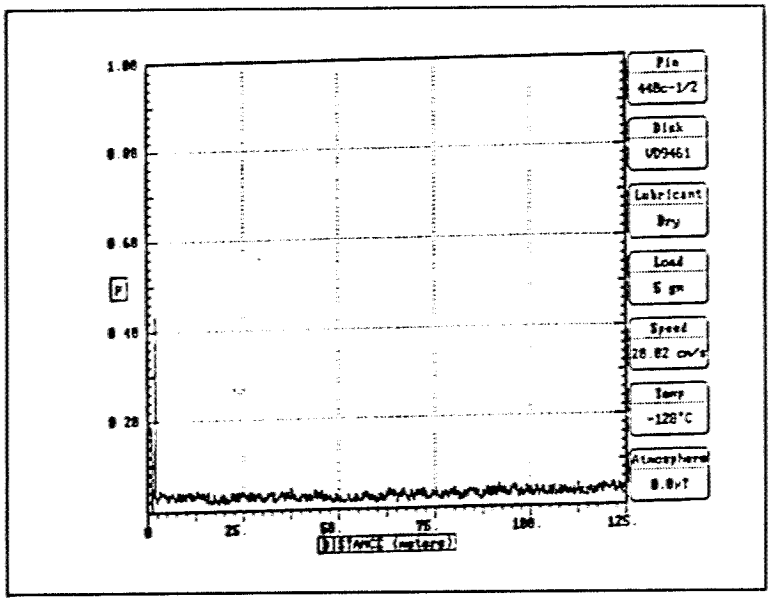
Wear Data:

The wear data tests were conducted using the static ball on disk wear apparatus. Implant Sciences Corporation. Tribometer ISC-500.

The tests were conducted on 440-C disks with 440-C ball material. All disk surface preparations were duplicated.

First test set were polished surface on un-coated 440-C disk. The test results showed the 440-C surface failure occurred consistently at duration of 24 to 26 meters.

Table 3



The second sets of test were conducted on the VAVD TiN coatings. The VAVD TiN coatings were 0.0005" thick and were deposited using the VAVD reactive gas process. The test duration was set for a maximum of 125 meters. The VAVD TiN coatings did not fail during the test duration, (Ref. Table 3)

The third sets of test were conducted on the electroplated chrome samples. The chrome coatings were 0.001" thick. The test results were difficult to interpret because of the rough surface condition of the chrome sample. The surface failure occurred at approximately 110 meters.

The overall test results demonstrated that the VAVD TiN coatings consistently outperformed the electroplated chrome and the 440-C disk.

Conclusions:

The VAVD coatings produced using the prototype system have demonstrated acceptable properties for wear and bond strength. The preprocess cleaning of the substrate samples has been minimal, hand wipe with acetone and placed in chamber.

Improvements in preprocess cleaning and vapor acceleration parameters will further improve the material properties of the coating applied.

The actively cooled crucible will improve material deposition rates and process duration. This will allow thicker coatings to be applied to substrate material.

Because of the process characteristics these coatings can be applied to very low temperature materials, i.e. plastics, paper and paraffin and others. With the low processing temperatures the substrate material is not heated during the processing. The low temperature application lends it's self to a variety of low stress coating applications.

Health and Safety Issues of Compliant Aluminum Metallic –Ceramic Coating

K. Eddinger and A. Piacentino
Sermatech International
115 S. Limerick Road
Limerick, PA 19468

Abstract

Aluminum pigmented metallic-ceramic coatings have been used to provide corrosion and oxidation resistance to steel turbine and aerospace components for thirty years. The metallic-ceramic coatings are spray applied overlay coatings which require a heat cure at temperatures from 176-371°C (350-700°F). They consist of aluminum metal dispersed in an aqueous solution of chromate and phosphate salts and generally meet the requirements of MIL-C-81751B, type 1.

More recently these aluminum metallic-ceramic coatings have been used to replace cadmium and nickel cadmium plating in applications where sacrificial corrosion behavior is required. There is an environmental incentive to restrict the usage of cadmium since federally regulated exposure limits demand that a worker be exposed to no more than 5 $\mu g/m^3$. While the exposure limits for the hexavalent chromium found in metallic-ceramic coatings are currently less stringent than cadmium, there are initiatives underway that recommend reducing exposure limits to levels similar to cadmium.

This paper will discuss the environmental and health and safety issues related to the use of these chromate containing inorganic coatings. In addition, a review of the environmental and health and safety issues for new aluminum metallic-ceramic coatings that can replace the chromium containing coatings will be given. These new coatings contain no carcinogenic or toxic materials. They can be applied by conventional paint spraying equipment. Residues of the coatings are not considered hazardous waste and do not require hazardous or toxic solvents for clean up. The coatings do offer corrosion resistance and performance characteristics similar to the more conventional chromium containing coatings. Application process controls and waste disposal issues for the coatings including aluminum residues will also be discussed.

Background

Cadmium plating has been used and continues to be used in aerospace applications that require a thin, uniform coating with good corrosion resistance properties. High strength steel parts and fasteners are typical examples. Since the early 1990's, however, industry has been investigating alternate materials to replace cadmium plating. The reason for this is the well-documented concern over the use of cadmium, both from a hazardous waste and a worker safety standpoint. Along with the reduction of the exposure level for cadmium to 5µg/m3, associated regulations requiring the monitoring of workers and implementation of process controls have made it difficult to use cadmium plating economically. For example, the removal of very small amounts of cadmium plating by grit blasting can create a large amount of hazardous waste since the contaminated grit is considered hazardous at such low levels of cadmium concentration. Environmental impact notwithstanding, there is still a need for a coating product that has the performance properties of cadmium. A list of the desired properties for a Cadmium replacement coating process is given in Table 1.

TABLE 1: List of Desired Properties for a Cadmium Replacement Coating

1. Sacrificial and resistant to corrosion-capable of withstanding 500 hours exposure to salt fog per ASTM B117 in a "X" scribed condition.
2. High use temperature-greater than 350°C (662°F)
3. Compatible with aerospace oils, fuels, greases, hydraulic fluid.
4. No embrittlement of high strength steels.
5. Process cure temperature of 232°C (450°F) or less (preferable 190°C (375°F) or less).
6. User friendly process-capable of coating large parts and inside diameters.
7. Compatible with other paint systems.
8. Durable, damage resistant film.
9. Easily repairable.
10. Cost competitive.
11. Environmentally acceptable.

Metallic-Ceramic Coating as a Replacement

One choice for a replacement for cadmium plating is the family of metallic-ceramic coatings. Such coatings have been used for many years in aerospace applications. SermeTel®W, SermeTel 962, and SermeTel 984 are examples of these coatings. SermeTel coatings are manufactured by Sermatech International Inc. Limerick, PA (SermeTel is a registered trademark of Sermatech International). These coatings are typically characterized by a dispersion of finely divided aluminum powder in an aqueous, acidic solution of phosphate and chromate salts. The resulting slurry is spray applied to the steel part and cured to yield a tightly adherent coating with good mechanical properties and good sacrificial corrosion properties. A metallic-ceramic coating such as SermeTel 984, for example, will have the desirable properties listed in Table 1.

Environmental Concerns with Metallic Ceramic Coatings

Worker Safety

While the metallic-ceramic coatings mentioned above could be considered environmentally acceptable alternative to cadmium plating, they do present other environmental issues that must be dealt with. Most notable is the presence of hexavalent chromium in the liquid coating material. Hexavalent chromium compounds are considered to be carcinogenic by NTP and IARC. While overexposure to hexavalent chromium can occur from ingestion, skin contact, and inhalation of atomized coating mists, by far the most significant of these when dealing

with coating processes is inhalation of atomized coating mists. ACGIH calls out a TLV of 0.05 mg/m^3 based on an 8 hour time weighted average. Worker exposure must be controlled below that value. As low as the level is, suitable controls can be put into place to safely and economically control worker exposure to hexavalent chromium compounds during the spraying of metallic-ceramic coatings. Table 2 gives some actual data obtained from a production area in which SermeTel 962 was being applied to aerospace components. The air was monitored under conditions to which a worker would be exposed during normal spray application of the coating. These values are well below the ACGIH TLV. In addition to proper ventilation of the spray booth, the sprayer can wear a positive pressure air supplied respirator. This will reduce actual exposure levels introduced in the spray booth essentially to zero. The variation seen in Operators 1 and 2 can be explained by differences in the configuration of the parts being sprayed. Large parts can create more turbulent air flow and alter the efficiency of the exhaust. Table 2 shows, however, that exposure levels can be maintained at quite low levels.

Table 2: Spray Booth Data

- Air samples were collected using MSA and Gilian battery operated personal sampling pumps which were attached to the operators.
- Chromium was collected on 37mm mixed cellulose ester membrane filters.
- Flow rates were set at 2.5 liters/minute and were calibrated before and after sampling.
- Two operators were monitored. Spray activity lasted a total of three hours in the spray booth. This was deemed to be the amount of time an operator actually spends in the booth for an eight hour workday.
- Results: OPERATOR 1 -- 0.008 mg/m^3 hexavalent chromium (3 hrs total)
  OPERATOR 1 -- 0.001 mg/m^3 hexavalent chromium (3.5 hrs total)

Another area of environmental concern is the dusts and residues generated from machining and blasting operations performed on parts that have been coated with the metallic-ceramic coatings. When the metallic-ceramic coatings cure they are converted into a water insoluble matrix of aluminum metal and chromate-phosphate ceramic. During that process most of the hexavalent chromium is converted to an insoluble trivalent chromium form. In either form there is no water solubility, unlike chromate pigments such as zinc or strontium chromate.

Theoretical calculations based on the formula for SermeTel 984 give a value for the amount of hexavalent chromium available in a one square foot surface coated to a thickness of one mil (0.001 inch or 25.4μm) to be less than 50 mg. Given these levels in the cured coating it is difficult to imagine how a worker might be exposed to chromium levels in excess of the TLV.

While grit blasting to remove a metallic-ceramic coating is possible, a much more efficient and economical way to strip the coating is to chemically remove the coating by immersing in caustic solution. In the process of that caustic treatment the hexavalent chromium in the coating would be converted to trivalent chromium. The used stripping solution would contain aluminum and phosphate in solution and trivalent chromium either in solution or as a residue. There would be no hexavalent chromium. While the material would be considered a hazardous waste, there would be no risk of carcinogenic exposure.

Waste Disposal Issues

Discarded liquid coatings and liquid or dried coating residues will contain hexavalent chromium and would be considered hazardous waste. Liquid wastes can be treated to reduce hexavalent chromium to the trivalent state and then precipitating the chromium to create a less hazardous solid waste. When solid waste residues of cured coatings were tested per the appropriate TCLP procedure (EPA200.7), the wastes were found to be nonhazardous. This includes residues from machining or blasting cured coating.

Summary of Environmental Issues

The metallic-ceramic coatings can be considered an environmentally responsible solution for cadmium plating. All of the environmental issues discussed above can be reasonably dealt with. Exposure to atomized coating can be safely and economically controlled below the TLV during application of the coating. Residues generated from machining and blasting cured coating are not considered hazardous waste per current EPA standards. Chemical methods exist to strip the coatings without generating large amounts of toxic material or hazardous waste. Cured coating residues are not considered hazardous waste.

Effect of more stringent Regulations

The information presented above shows that metallic-ceramic coatings that contain hexavalent chromium can be considered environmentally acceptable alternatives to cadmium plating. Recent information from OSHA indicates that a proposed new occupational exposure limit for hexavalent chromium may be introduced as early as the 4th quarter of 1999. If a new PEL is established at the 5 μg/m3 currently called out for cadmium, then it may become economically impractical to use coatings containing hexavalent chromium safely. The same discussion of worker safety and hazardous waste issues used for cadmium above would become appropriate for hexavalent chromium.

Chromium Free Metallic-Ceramic Coatings

Work on an aluminum filled metallic-ceramic coating that contains no heavy metals or carcinogenic materials has been reported previously [1]. Basic properties of the new chromium free coating, designated SermeTel 1408, are listed in Table 3. This coating can offer the good performance properties associated with metallic-ceramic coatings without the growing environmental and health concerns found with current metallic-ceramic coatings. Since the coating contains no heavy metals or carcinogenic ingredients, the primary concern during coating application is inhalation of the acidic atomized mist. Control measures need only consist of the good industrial practices for a paint spray operation (i.e. good ventilation and respirators to control exposure to nuisance atomized mists). Airborne residues obtained during blasting operations are no more hazardous than the airborne blasting media that is used. Stripping of the chromium free coating can be accomplished with the same chemical treatment as the chromium containing coating. Liquid wastes would be hazardous only by virtue of the corrosivity of the caustic solution and could be easily treated to be made nonhazardous. Cured coating residues are not considered hazardous waste.

Table 3: Basic Properties of a Chromium Free Metallic-Ceramic Coating

- Water based, solvent free, not toxic or carcinogenic, waste residues from cured coating nonhazardous
- Can be made sacrificial to ferrous alloys
- Temperature resistant, up to 871°C (1600°F)
- Thermal shock resistant- 635°C (1175°F) to water quench without coating loss
- Heat cycle/salt spray resistant – 16 hours at 538°C (1000°F) followed by 32 hours salt spray; the cycle repeated six times
- Resistant to water, oils, greases, hydraulic fluids and most other organic solvents
- Resistant to particulate erosion
- Meets the performance properties of MIL-C-81751B

Conclusions

1. Metallic-ceramic coatings have been used to solve corrosion, erosion, and oxidation problems for over thirty years. More recently certain of these coatings have been used as environmentally acceptable replacements for cadmium and nickel-cadmium plating.
2. Environmental issues about coating application and handling resulting from hexavalent chromium in the coating can be controlled using readily available control processes.
3. Cured coating residues are not considered hazardous waste.
4. Metallic-ceramic coatings that are chromium free have been developed that eliminate the most serious worker safety and handling problems associated with the hexavalent chromium containing coatings.
5. The chromium free coatings provide similar performance properties to the chromium containing coatings in many applications.

References

1. Mosser, Mark F. and Eddinger, Kevin B., "Environmentally Compliant Coatings for Turbine Compressor Applications"; Presented at AESF 31st Annual Aerospace/Airline Plating and Metal Finishing Forum , April 1995.

Fire Protection Considerations for Critical Electronic Equipment Facilities

Gary Taylor - 1

Risk Factors

Begin by considering the following factors :

(a) Life safety aspects of the function (e.g., process controls, air traffic controls);

(b) Fire threat of the installation to occupants or exposed property;

(c) Economic loss from loss of function or loss of records; and

(d) Economic loss from value of equipment.

Location within the Building

To reduce the risk of water damage from firefighting operations or other sources of water, the area should be located above grade.

The area should not be located above, below, or adjacent to areas or other structures where hazardous processes are located.

Control rooms that must be located in proximity to industrial processes should be provided with adequate additional protective features, such as pressurization, emergency fire shutters, etc.

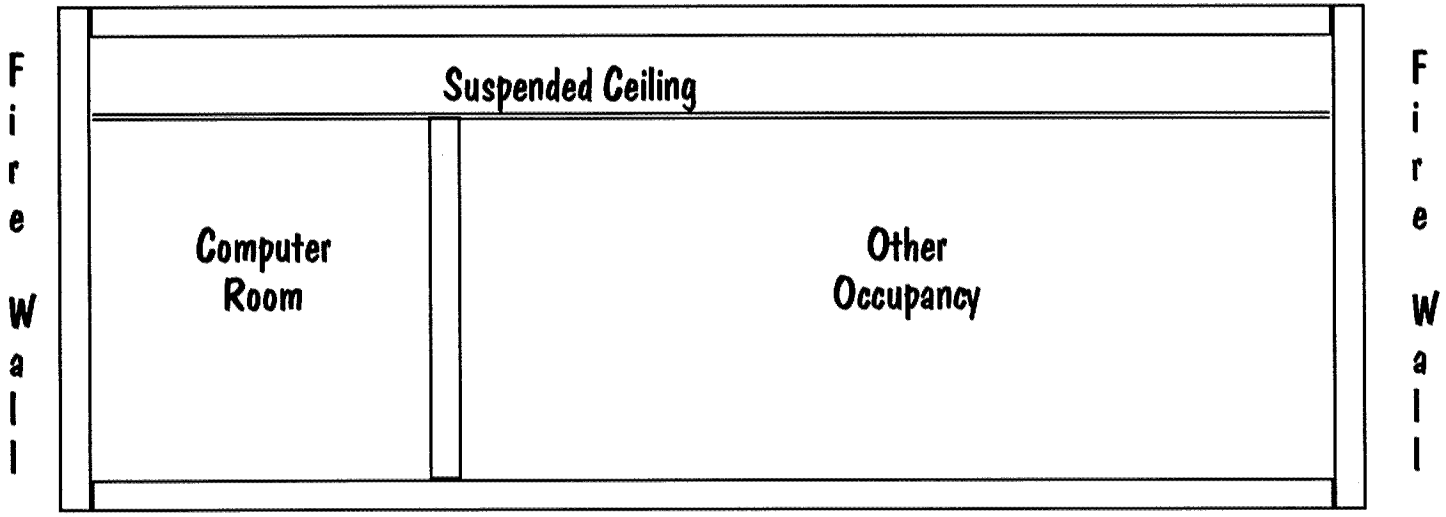
General Construction Requirements

The facility should be housed in a fully sprinklered building of non-combustible construction.

The area should be separated from other occupancies within the building (including atria or other open-space construction) by fire-resistant rated construction. The fire resistance rating should be commensurate with the exposure but not less than one hour.

The fire-resistant rated enclosure(s) should extend from the structural floor to the structural floor above or to the roof.

Common Error - Incomplete Fire Separations



Section View

High speed printers

High speed printers and paper forms bursting operations should be housed in fire-rated enclosures, separate from other electronic equipment.

The air handling system for high-speed printer facilities should be separate from the air-handling system for the other electronic equipment. Otherwise, fine paper dust generated from the printing operations will build-up on underfloor cables and electronic equipment power supplies, resulting in a significant fire risk.

Interior Construction Materials

Noncombustible wall and ceiling finishes should be used.

Special care should be taken when selecting sound absorbing materials.

Interior floor finishes used in computer areas should be selected considering performance in a fire, should facilitate housekeeping and not interfere with access to below floor cable chases.

Exposed cellular plastics should not be used in construction.

Electrical Wiring - Power Supply Wiring

The branch-circuit supply conductors to receptacles or field-wired equipment should be in rigid metal conduit, rigid nonmetallic conduit, intermediate metal conduit, electrical metallic tubing, metal wireway, surface metal raceway with metal cover, flexible metal conduit, liquidtight flexible metal or nonmetallic conduit, Type MI cable, Type MC cable, or Type AC cable. These supply conductors shall be installed in accordance with the requirements of the Electrical Code.

Electrical Wiring - Power Supply Wiring

Interconnecting cables and wiring between units, power cords, plugs, and connectors should be considered as part of the computer system and listed as suitable for installation on the floor or under a raised floor

Electrical Wiring - Power Disconnect

A means should be provided to disconnect power to all electronic equipment in the electronic computer/data processing equipment room and area.

There should also be a similar means to disconnect the power to all dedicated HVAC systems serving the room and area and to cause all required fire/smoke dampers to close. The control for these disconnecting means should be grouped and identified and should be readily accessible at the principal exit doors. A single means to control both the electronic equipment and HVAC systems would be acceptable.

Drainage

The structural floor should incorporate provisions for drainage from domestic water leakage, sprinkler operation, coolant leakage, or fire-fighting operations.

Raised Floors

The underfloor area should not be used as a common fresh air plenum to serve fire separated areas.

Raised Floors (continued)

Structural supporting members for raised floors should be of noncombustible material.

Decking for raised floors should be noncombustible.

Wood or similar core material that is encased on the top and bottom with sheet, cast, or extruded metal, with all openings or cut edges covered with metal would also be acceptable.

Access sections or panels should be provided in raised floors so that all the space beneath is accessible.

Raised Floors (continued)

Tools needed to provide access to the underfloor space should be located in the room and their location(s) should be well marked.

Electric cable openings in floors should be made smooth or otherwise be protected to minimize the possibility of damage to the cables.

Computer Equipment

Each individual unit should be constructed in such a way that by limiting combustible materials, or by use of enclosures, fire is not likely to spread beyond the unit where the source of ignition is located.

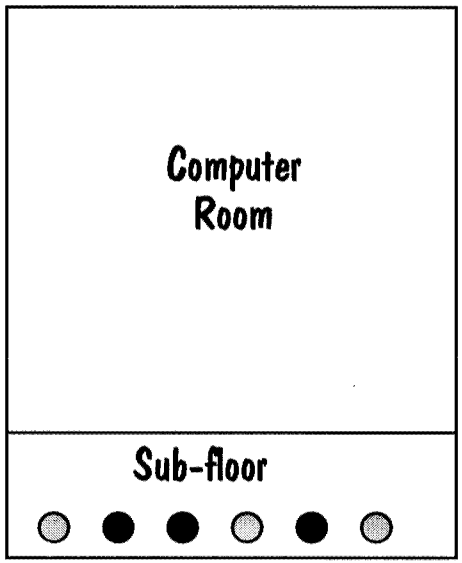
Air filters for use in the cooling systems of individual units should be listed. They should be arranged in such a way that they can be readily removed, inspected, cleaned, or replaced when necessary.

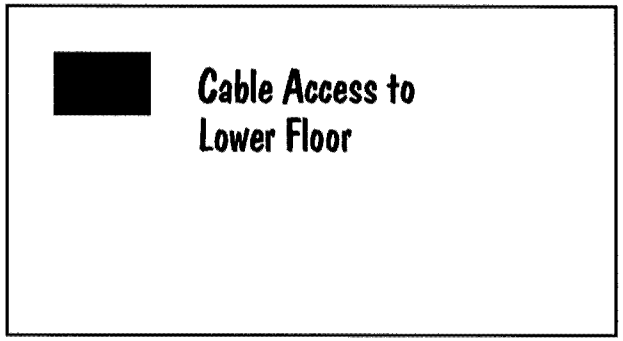
Cable Openings and Other Penetrations

Cable openings or other penetrations through required fire-rated assemblies should be fire stopped with a properly installed listed fire-stopping material that has a fire resistance rating equal to the fire resistance rating of the penetrated barrier.

Where any openings (e.g., pass-throughs or windows) are installed in any fire-rated wall each opening should be equipped with an automatic fire-rated shutter. The shutter should be operated automatically by the presence of either smoke or fire on either side of the wall.

Common Error - New Cable Penetrations NOT Fire Stopped





○ Original Cable Penetrations
● New Cable Penetrations

Materials and Equipment Permitted in the Area

Paper stock, inks, unused recording media, and other combustibles within the computer room should be restricted to the absolute minimum necessary for efficient operation.

Any such materials in the computer room should be kept in totally enclosed metal file cases or cabinets or, if provided for in individual machine design, should be limited to the quantity prescribed and located in the area designated by the equipment manufacturer.

The space beneath the raised floor should not be used for storage purposes.

Abandoned cable should be removed from the underfloor area.

Materials and Equipment Permitted in the Area (continued)

Self-extinguishing-type trash receptacles should be used.

Protection of Records

As a minimum, all vital and important records should be duplicated and the duplicates stored in a remote location that would not be exposed to a fire involving the original records. Duplicate records should be stored in fire-resistive rooms in accordance with NFPA 232, *Standard for the Protection of Records*. The degree of fire resistance should be commensurate with the fire exposure to the records but not less than two hours.

The duplicate records storage room should only be used for the storage of records. All other operations, including splicing, repairing, erasing, reproducing, cataloging, etc., should be prohibited in this room.

A written plan and schedule should be established and followed to manage the back-up of vital and important records. The plan and performance should be reviewed at least quarterly.

Emergency and Recovery Procedures

The following plans and procedures should be developed and implemented:

Emergency Fire Plan - a management-approved written, dated, and annually tested emergency fire plan.

Damage Control Plan - a management-approved written, dated, and annually tested damage control plan.

Recovery Procedures Plan - a management-approved written, dated, and annually tested plan covering recovery procedures for continued operations.

Automatic Detection Systems

A smoke-detection-type automatic detection equipment should be installed and maintained in accordance with NFPA 72, *National Fire Alarm Code*. Automatic detection devices should be installed in the following locations:

(a) At the ceiling level throughout the area;
(b) Below the raised floor; and
(c) Above the suspended ceiling.

Where interlock and shutdown devices are provided, the electrical power to the interlocks and shutdown devices should be supervised by the fire alarm control panel.

Automatic Detection Systems (continued)

The alarms and trouble signals of the automatic detection system, the sprinkler system and if provided, the gaseous extinguishing system, should be arranged to annunciate at a constantly attended location.

Automatic Sprinkler Systems

An automatic sprinkler system should be provided to protect the building housing the electronic equipment facilities and the rooms or areas containing the electronic equipment. The automatic sprinkler systems should be installed in accordance with NFPA 13, *Standard for the Installation of Sprinkler Systems.*

Sprinkler systems protecting computer areas should be valved separately from other sprinkler systems. The sectional isolation valve should be located outside and immediately adjacent to the protected space.

Automatic Sprinkler Systems (continued)

Use a conventional wet-pipe sprinkler system in conjunction with an early warning fire detection system.

Type of System	A Failure of the	Results in
Separate Sprinkler and Detection System	Detection System	No alarm transmitted. Sprinkler system continues to operate.
Separate Sprinkler and Detection System	Sprinkler system	No automatic fire extinguishing capability - fire alarm system not impaired.
Pre-Action System	Detection system	Total failure - no alarm capability - no fire extinguishing capability
Pre-Action System	Sprinkler system	No automatic fire extinguishing capability - fire alarm system not impaired.

Gaseous Fire Protection Systems

Gaseous agent extinguishing systems are not a substitute for any of the previously discussed fire protection measures and are not an equivalent to a water sprinkler system.

If implementation of all of the preceding measures does not attain an acceptable degree of risk reduction then a gaseous fire protection system should be considered.

The new gaseous agents do not perform or extinguish fires in the same way that halon 1301 did.

Gaseous Fire Protection Systems (continued)

Generic gaseous agent system choices are:

(1) Halocarbon agents
(2) Inert gases

The new halon alternative gases extinguish fires by physical mechanisms:

Halocarbon agents extinguish fires by heat absorption

Inert gases extinguish fires by oxygen reduction

Gaseous Fire Protection Systems (continued)

Gaseous agents are not suitable for partial protection applications such as sub-floors.

If a supplementary gaseous fire protection system is to be installed, all spaces within the fire rated compartment should be protected simultaneously.

For example: The sub-floor, equipment room and interstitial space

Gaseous Fire Protection Systems (continued)

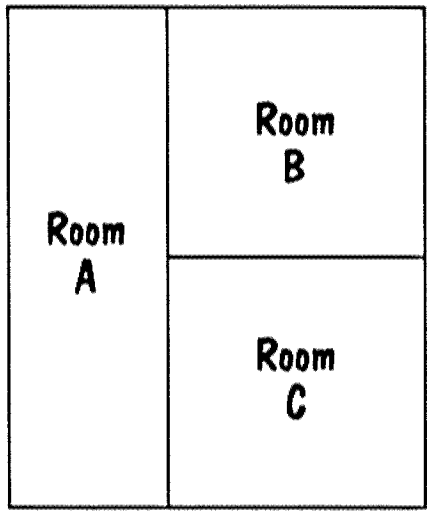
Lessons learned from the halon phaseout

Enclosure integrity is critical to achieve effective fire protection using gaseous agent systems.

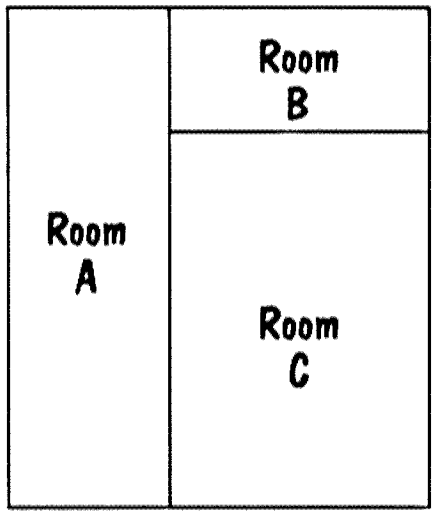
Changes to the hazard including configuration changes of the hazard must be evaluated as part of an ongoing maintenance effort.

Gaseous Fire Protection Systems (continued)

Changes to the hazard including configuration changes of the hazard must be evaluated as part of an ongoing maintenance effort.



Original Room



Modified Room

More help

NFPA 75

1995 Edition

Standard for the Protection of Electronic Computer/Data Processing Equipment

Copyright © 1995 NFPA, All Rights Reserved

This presentation has used NFPA 75 as a basis - supplemented by personal experience. NFPA 75 is an excellent tool for evaluating an existing facility or planning a new facility, however users should always remember that like all NFPA Standards, NFPA 75 is a minimum. Your facility may require additional appropriate measures.

More than a choice of extinguishing systems.

Although fire incidences are quite low, site inspections of a number of existing facilities has indicated that current protection levels were much lower than the facility operator realized.

In many cases these evaluations were triggered by environmental concerns regarding halons. In over 50% of the cases the halon system would not have performed to meet the original design criteria due to changes in the facility. As well, other practical fire protection measures had not been implemented due to a misplaced confidence in the ability of the halon system to handle any fire threat.

Is it time to check the fire protection of your vital electronic facilities?

NASA Issues Related To Use Of Halon: Past, Present, Future

Michelle M. Collins, P.E.
NASA, JJ-D
Environmental Program Office
Kennedy Space Center, FL 32899
(407) 867-4270, Fax: 407-867-8040
Michelle.Collins@ksc.nasa.gov

INTRODUCTION

NASA began an official halon phaseout program in 1990. NASA has led the way in halon bank management and has participated in the search for halon alternatives. NASA representatives participate in technical committees of the National Fire Protection Association and United Nations Environment Program providing guidance on Halon Phaseout and acceptance, design, installation, and maintenance of Halon Alternatives. This paper addresses some of the key issues that are leading the agency away from dependence on halons for fire protection.

Although the groundwork was being laid a year earlier, NASA officially began their Halon Phaseout Program in 1990. The program was comprehensive in that it addressed all aspects of phaseout and bank management; including defining "critical" for the agency, identifying critical uses, development of a plan to phaseout non-critical systems, upgrading of critical systems and their hazard enclosures, establishment of recycling and storage, setting aside backup systems, upgrading of maintenance procedures and documentation, updating policies and fire protection guidelines for the agency, participating in the standards making process and decision-making process on both a national and international level, and participating in R&D for alternatives. Many of the aforementioned steps were accomplished in the first five years of the program. NASA is still underway with the phaseout according to the original schedule. At the time the agency embarked upon this program, there were no alternatives available. All plans had to be made based on the possibility that alternatives would not be found along with the flexibility to adapt to alternatives if and when they did become available. The agency continues to participate in the regulatory process affecting halon use and replacements, as well as, participating in R&D to expand replacement options. The following three sections address specific aspects to NASA's past experience in phasing out halons, NASA's present fire protection activities, and NASA's future plans.

NASA's **Past** Experience with Halon Total Flooding Systems:

This section is split into three areas; 1) Lessons Learned, 2) Maintenance Issues, and 3) Documentation-Related Issues. The lessons learned and difficulties encountered will be the same for the use of any total flooding agent/system whether it is a first or second-generation halon replacement or an inert gas system. Before making a decision to install a total flooding system, the user and Authority Having Jurisdiction (AHJ) must be aware of the additional responsibilities, maintenance, and documentation associated with a total flooding gaseous system. Some of the more notable lessons learned are listed as follows:

Lessons Learned:

- Although a hazard area is manned 24 hours per day, experience showed that the occupants may not evacuate the space nor apply/manually-activate a fire suppressant.
- Tape storage, in many instances, was not located in a separate hazard area from the "essential electronic equipment", and hazard areas were not always separated.

- Occupancies had changed, and a halon fire suppression system was no longer necessary for the hazard area.
- Hazard enclosures had been changed in size and configuration without modifying the halon system (rendering it insufficient or ineffective).
- Cylinders were below design fill levels (again rendering the system insufficient for the fire hazard) as a result of slow leaks.
- Many systems were not capable of suppressing a fire in their state and the state of the enclosure, thus giving a false sense of security.

Maintenance Issues:

- Cylinders were from many different manufacturers, which made it difficult to maintain and stock adequate spares. The maintenance crew had to be trained on each different type of system and the training kept up-to-date. This is difficult to achieve and expensive to sustain. The cylinders, actuators, detection, and controls were outdated and more leaky and accident prone. Upgrades were performed for those systems deemed "critical" by the agency.
- Softgoods must be replaced on a regular basis.
- Leak detection must be performed regularly during maintenance. Cylinder heads were found to be leaking into the manifold.
- Rewrite maintenance instructions to reflect each individual system. If a boilerplate is used, it is very likely accidental discharges will occur during maintenance.
- Establish critical spares. If a total flooding system is deemed essential, and the investment is made, then a standby replacement bank should be an integral part of that system (unless the user can afford the down-time necessary to recharge the system).
- Fan pressurization testing can be very useful in determining the enclosure leakage and to verify the design agent concentration. Kennedy Space Center's (KSC) experience has been mixed with regard to the fan pressurization test. Some users do not like it; it "appears" disruptive to their operations. The rooms with raised floors and drop ceilings were the most difficult to locate leaks and seal up. In many cases the configurations of the rooms around the hazard area were not conducive to the fan test as the control of doors and pressures in adjacent spaces would skew test results. In addition, it is difficult to maintain a trained crew to perform the tests.
- Make sure the owner has the means to perform or contract adequate maintenance. A total flooding system is a large investment. It is NASA's policy that total flooding systems for electronic areas should be secondary fire suppression systems with wet pipe sprinklers as the primary for total loss control. In many cases funding was not available for both, and the primary system became the total flooding system. This put the entire facility at risk. NASA is a government agency (self-insured) and should have had a primary wet pipe sprinkler system first.
- The total flooding system must be tied into the HVAC system and/or appropriate dampers installed to isolate the enclosure.

Documentation-Related Issues:

- Ensure the agent/system is UL Listed or FM Approved and listed in the NFPA Standards.
- Replacement lifetime should be considered along with occupancy plans. Perform life cycle cost analysis before making final selection.
- Stay informed of changes in NFPA standards ; become involved.
- Ensure maintenance documentation is in place and reflects each individual system.
- Provide awareness and training to users on the system.
- Label hazard enclosure walls, floor, and ceiling (i.e. "Do not modify or make penetrations without contacting responsible fire protection engineer").
- Maintain control of the agent. Bar-coding of cylinders has been useful in tracking changes in agent quantities on an annual basis. Data entry occurs during maintenance. Accidental or unnecessary loss can cause a great deal of downtime (which translates to $) and large sums of $ for some of the replacement agents.

NASA's PRESENT Plans For Facility Fire Protection:

NASA has implemented procedures to minimize leakage and accidental discharges as outlined above. These procedures are applicable to any total flooding system and have resulted in significant cost savings and a minimization of impact to the users. As the agency moves forward with its phaseout of halon there are a number of activities that are important both to the phaseout program and the optimization of a successful fire protection program. Some of these key activities are listed below.

- Maintain accurate, up-to-date documentation including NASA's and Agency Center's Fire Protection Standards which address applications not covered in NFPA Standards.
- Ensure the fire department is aware of the special applications; response time must be adequate if a secondary system is not used. At KSC the response time is less than four minutes.
- Install wet pipe sprinklers as primary protection for major loss control. NASA is self-insured meaning that any fire loss must be absorbed within the existing annual budget allocation.
- In the case of special electronic equipment rooms or facilities, a secondary system like a total flooding clean agent can be installed if the contents are high value and funds are available and/or the application of water could cause loss of life or loss of vehicle (space shuttle).
- Install advanced detection systems; VESDA, AnaLASER, etc. Types of detection systems in use at KSC include Spot Heat, Spot Smoke, Beam, Aspiration, Linear Wire, Heat UV, and UV/IR.
- The agency does not have plans to install any of the halon replacements currently available.
- Most NASA Centers have personnel for on-site engineering, maintenance, and operations. Fire inspectors conduct daily walk downs and Fire Protection Engineers perform Fire Risk Surveys on every major facility on a periodic basis. A Fire Risk Review Board, consisting of upper management, reviews fire protection deficiencies and they decide to either fund the solutions or make the programmatic decision to accept the risk. In addition, Fire & Safety Engineers from each NASA Center meet annually for technical interchange.
- Fundamental Fire protection engineering is practiced at all NASA Centers. This includes utilizing fire retardant materials, separating hazards, building in redundancy, backing up electronic data on a regular basis, etc.

The FUTURE of Fire Protection without Halon at NASA Facilities:

NASA is proceeding with a sound plan for facility-based fire protection by practicing good fire engineering fundamentals, participating in the decision-making and standards-making processes, staying abreast of the latest technologies available, and participating in research and development of advanced fire suppression. NASA's halon phaseout is proceeding on schedule as a result of grounding ourselves in solid fundamental fire protection practices. The future begins now with the following steps being taken by the agency ...

- Modifications to the "Firing Rooms" in the Launch Control Facility at KSC consist of double-interlock pre-action sprinkler systems with smoke aspiration systems for early warning and gaseous portable extinguishers for early response.
- The agency will continue to invest into R&D for halon alternative options.
- NASA plans to stay involved in the Standard's making process and Decision making process; this involvement allows the agency to influence its future and stay abreast of changes in halon replacement options.
- NASA plans to team up R&D efforts with the DOD to address special needs.

As halon alternatives continue to evolve, NASA will continue to evaluate their applicability and adapt its fire protection program to incorporate them as appropriate.

Implementation of Precision Verification Solvents on the External Tank

Mike Campbell
Materials Science
Lockheed Martin Michoud Space Systems

LOCKHEED MARTIN

4630-5/28/98.9

Background

- 1,1,2-Trichloro-1,2,2-Trifluoroethane (CFC 113) was phased out of production and cannot be purchased from the original manufacturer after Dec'95

- CFC 113 can be used until depleted from stock.

- MSFC-SPEC-164 is governing document that requires use of CFC 113, 1,1,2-Trichlorethylene (TCE), or 1,1,1-Trichloroethane (TCA) or alternative solvents if approved by MSFC to verify Non Volatile Residue(NVR) and particulates.

- All solvents that are used for verification must be approved in JSC, SE-S-0073 by KSC, JSC, Boeing-Rockwell and Rocketdyne divisions, MSFC etc,.

Solvent Usages

- TCE used at Michoud Assembly Facility (MAF) since the early '60s to verify NVR/particlates on the liquid oxygen (LOX) tank and water used to verify liquid hydrogen(LH2) tank,

- TCE has a threshold limit value (TLV) of 50 ppm and has been handled safely during the interval.

- CFC 113 used to verify smaller parts, e.g., 20 foot feedlines, manhole covers, nuts/bolts, etc.

TCE Reduction

- TCE sprayed inside the entire LOX tank surfaces (≈8000 ft^2) to verify NVR/ particulate

- TCE usage about 5,000 gals/tank

Future Work

- To fully asses the safety of HCFC 225, personal protective gear is being worn and the solvent emissions measured to ascertain the need for required protective gear.

- HCFC 225 will be implemented for use to verify the LOX tank to replace TCE

- Pursue the use of GN2 to verify pressurization lines.

- Ongoing development of alternative solvents (Vertrel MCA) or alternative methods (high pressure water) to minimize exposure to hazardous chemicals.

Implementation of Precision Verification Solvents on the External Tank

- New local pollution laws allow for 900 pounds (75 gallons) yearly emissions

- Comparative studies done over five LOX tanks to compare reduced usage(5 gallons/ET) of TCE with full flow values of TCE

- Reduced flow TCE gives comparable values and is implemented (1994).

- Further on-going work with alternate verification solvents continues.

Solvent Replacement Studies

- 1991-1994 Review of all commercially available solvents narrows the choice down to TCE and isopropyl alcohol (IPA)

- TCE and isopropyl alcohol(IPA) qualified in late 1994 for general usage on the ET. No issues with material compatibility.

Implementation of Precision Verification Solvents on the External Tank

Note 1: Comments from the technical community require that IPA be verified as removed after final verification as IPA is NOT LOX compatible.

Note 2: Approval within the technical community to amend the paper work takes 1 year.

- June 1995 two things occur,

1) As implementation progresses to implement IPA/TCE at MAF, EPA approves 3,3-Dichloro-1,1,1,2,2-pentafluoropropane (45%)/1,3-dichloro-1,1,2,2,3-pentaflouropropane (55%), HCFC 225, as an acceptable solvent for precision cleaning

- All toxicological and exposure data for HCFC 225 complete. TLV limit is 50 ppm

2) KSC issues final report that a water/ surfactant solution can be used to verify LH2 systems. The solution contains a surfactant (DuPont Zonyl FSN® at 25 ppm in demineralized water)

Implementation

- Change of direction occurs and a decision is made to qualify HCFC 225 and water /surfactant.

- HCFC-225 passed the cleaning test and the material compatibility tests for flight hardware.

- Water /surfactant testing from KSC accepted as valid, e.g., materials compatibility, solution performance, etc.

Note 3: Due to the interaction of the NOET team from MSFC with other shuttle contractors, testing was minimized because of KSC involvement on the team.

- Documentation changed for approval of HCFC 225 and water / surfactant solution (LH2 verification only).

Note 4: Based on pre-coordination of effort, approval takes 4 months from submittal

- MAF decides to implement HCFC 225 only for all uses

Problems Occurring During Implementation

- In retrofitting the existing CFC 113 system, it is discovered that some internal fitting are Buna N which is attacked by HCFC 225. Concern is raised over other non flight tooling that cannot be taken apart or that are old in which there are no substitute parts available.

- Re-thinking at MAF about usage of HCFC 225 on non-flight parts and the concern about the TLV limit of 50 ppm lead to the decision to use water surfactant on LH2 parts/tooling that have no faying surfaces HCFC 225 on only LO2 parts/tooling and the possibility of using GN2 for testing of pressure gauges.

Implementation of Precision Verification Solvents on the External Tank

- A separate water /surfactant system is constructed and the existing CFC 113 facility retrofitted for use with HCFC 225 with modifications to handle the solvent.

Note 5: During the validation of water /surfactant, tooling problems are noted such as the puddling of water so that the dryness of the part could not be verified. Tooling was modified so that there is no standing water within the tool.

- As of this paper, HCFC is qualified for all LOX/LH2 parts and water surfactants for LH2 parts.

A Review of Production Cleaning Processes

Alan Brown
Vonnie Douglas
The Boeing Company
Rocketdyne Propulsion and Power
Canoga Park, California

ABSTRACT

Rocketdyne has been using aqueous based cleaning processes since the successful elimination of all ozone-depleting chemicals in 1996. These new processes consist of an ultrasonic cleaning line, a high-pressure flush cleaning process for larger hardware, and both aqueous based and solvent based verification techniques. In addition, self-contained cleaning equipment has increased the reliability of in process cleaning of hardware. These systems have been fully implemented and have been working very successfully. The success of these processes has depended on the design of the new cleaning equipment and the results of Taguchi experiments in developing robustness. Added benefits from these new processes include reduced cycle time, cost advantages over solvent-based systems, as well as higher quality cleaning.

INTRODUCTION

Trichlorotrifluoroethane (Freon-113) and 1,1,1-trichloroethane (TCA) were eliminated at Rocketdyne by early 1996. This elimination was made possible through the use of alternate aqueous precision cleaning methods. These methods required the development, evaluation and implementation of new processes, facilities and equipment. In order to replace vapor degreasing, a study of many different alternatives was conducted to find a suitable alternative. Rocketdyne was searching for processes that complied with all existing and/or foreseeable future regulation and would be applicable to a wide variety of hardware. In this way it would be a wise investment in new processes with a future. The verification processes were developed to be direct replacements to the standard processes utilizing TCA or Freon-113. Aqueous cleaning techniques are more dependent on mechanical action rather than chemical action such as with TCA. The mechanical techniques selected for the precision cleaning processes was ultrasonic cavitation or a high flow flushing process. The cleaning capability at Rocketdyne consists of an ultrasonic aqueous precision cleaning process and a high-pressure closed loop aqueous flush facility; both of which employ new verification techniques that are not dependent on ozone-depleting solvents. These processes have been in use since 1995 with very good success.

AQUEOUS PRECISION CLEANING

The ultrasonic aqueous precision cleaning facility at Rocketdyne consists of six tanks, two tanks with 25 kHz ultrasonic transducers, one tank with 40 kHz ultrasonic transducers, two 270° spray rinse tanks and one immersion rinse tank. These were selected based on the results of a study that was conducted to choose the most effective ultrasonic cleaning system for meeting precision cleaning requirements. The lower frequency; 25 kHz in steps 1 and 2, was designed to remove most of the soil and the higher frequency; 40 kHz in step 3, was designed to remove the last microlayer of soil in the final cleaning step for enhanced cleaning effectiveness. The general capabilities of the facility are shown in Table 1. Selection of the aqueous cleaning agents was based upon extensive testing of over 200 products including cleaning effectiveness on typical Rocketdyne soils as well as compatibility of the various alloys that comprise Rocketdyne hardware. The cleaning agents currently in use consist of an emulsion degreaser, Turco 3878 LF-NC, a mild alkaline cleaner, Turco 4215 NC-LT and a nonionic detergent, Turco 4215A Additive. Selection of the process was based upon existing aqueous processes used at various industry and government facilities as well as upon development work conducted at Rocketdyne. The equipment was designed and constructed in conjunction with equipment manufacturers in keeping with the desired process. Similar equipment to that which was proposed was evaluated and proven to perform prior to committing

to actual equipment to ensure it met the cleaning requirements. This evaluation consisted of using contaminated complex geometry samples to determine the ability of the process and equipment to clean.

Cleaning Line Equipment

- Tank Capacity
  - 665 gallon capacity
  - Accommodates hardware 3 ft x 3 ft x 3 ft
  - Turn over rate 4 volumes per hour
  - Steam heat exchangers
- Rinsing Capabilities
  - 2 rinse tanks with 270° spray coverage
  - 1 immersion rinse tank
- Ultrasonic Capability
  - 2 tanks with 25 kHz transducers (1024)
  - 1 tank with 40 kHz transducers (1024)
  - Adjustable to 43 watts/gal maximum
- Built-in Versatility
  - Hand held spray rinse wands
  - Hose attachments for flushing (60 gpm, max.)

Table 1: Aqueous Precision Clean Facility Equipment Capabilities

Due to the unavailability of large numbers of scrap hardware and the desire to generate a significant amount of data to substantiate the process, standard complex test specimens were fabricated and utilized for process definition. 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. These samples were used both to evaluate the equipment to procure as well as to develop the process once the equipment was purchased. The sample configuration is depicted in Figure 1. The contaminants used for this validation consisted of Cool-Tool, manufactured by Monroe Fluid Technology, Hilton, NY; CRC 3-36, manufactured by CRC Industries, Inc., Warminster, PA; metallic fines obtained from typical metal fabrication processes; and DTE 26, manufactured by Mobil Oil Corp., New York, NY. Specimens were contaminated with lubricant applied to specified areas (Figure 1) and metallic fines were then applied on top of the lubricant and the specimens were then baked to simulate soils resulting from a machining process. These were used to evaluate the performance of the various processes possible with this equipment.

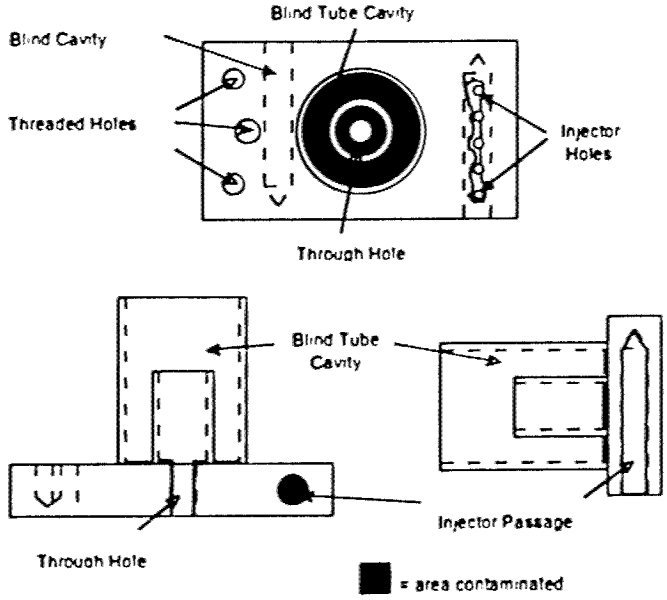


Figure 1: Standard Complex Test Specimen Configuration and Placement of Contamination

In order to develop a process for cleaning of hardware in the newly constructed facility, a Continuous Process Improvement (CPI) Team was established and was comprised of members from Manufacturing, Manufacturing Technical Support, Quality Assurance, Quality Engineering and Materials Engineering. The goal was to provide an efficient, controlled, robust process using aqueous ultrasonic cleaning methods to achieve contractual requirements. Taguchi test methodology was utilized in defining key processing parameters to ensure the selection of a robust process that met quality, cost, and schedule requirements.

The general cleaning process flow chart is provided in Figure 2. This cleaning procedure depicts a maximum requirement as it was demonstrated that all three cleaning steps were not required except under extreme conditions of hardware complexity and/or hard to remove soils. The facility permits several process parameters to be adjusted or varied for optimization of the cleaning process. These parameters are 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 and temperatures.

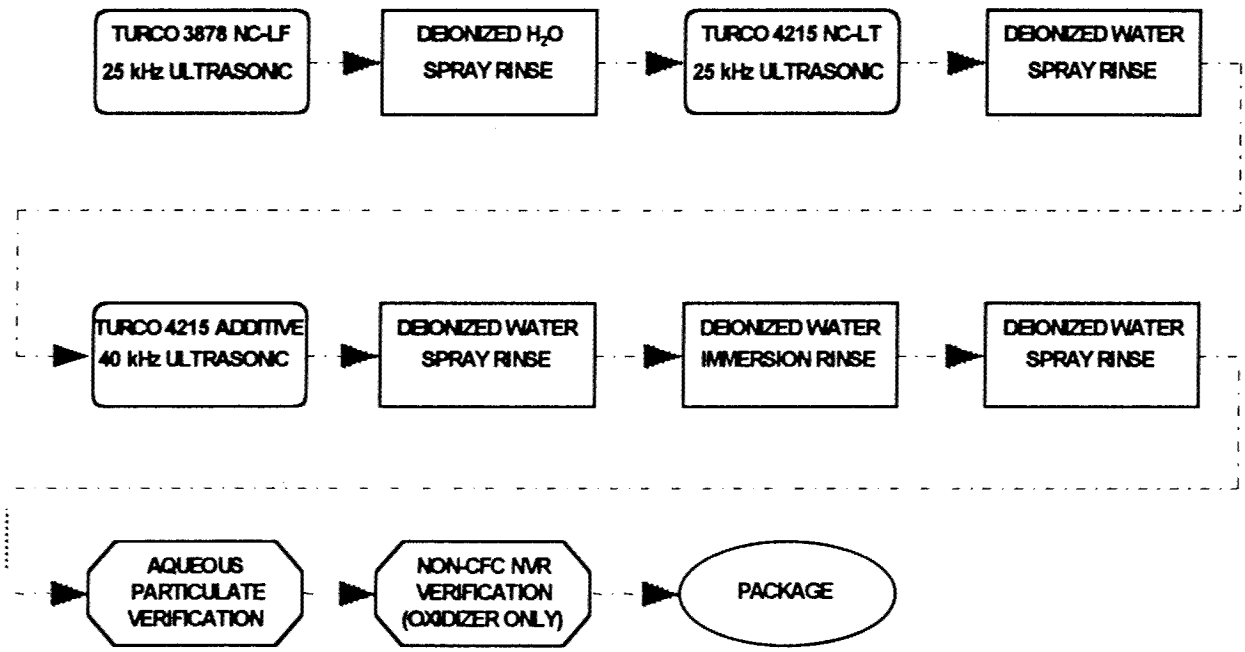


Figure 2: Aqueous Precision Process

Three different cleaning step processes were evaluated. The first included a process of all three cleaning solutions (Figure 2) or Process Option #1. The second included the aqueous cleaner Turco 3878 NC-LF followed with the nonionic surfactant Turco 4215 Additive (Process Option #2). The third consisted of the mild alkaline cleaner Turco 4215 NC-LT once again followed with the nonionic surfactant Turco 4215 Additive (Process Option #3). These processes are currently on line at Rocketdyne being used on a production basis.

AQUEOUS CLOSED LOOP FLUSH FACILITY

For large hardware, an aqueous closed loop flush facility was designed and constructed. This facility is capable of flushing hardware at flow rates that vary up to 50 gallons per minute and pressures that vary up to 80 psi. The facility utilizes a three step cleaning process in which the hardware is flushed with a very dilute mild alkaline cleaner, Turco 4215 NC-LT, followed by an intermediate deionized water rinse, followed by a low flow, high purity, final deionized water flush. Particulate analysis is accomplished through the use of an in-line filter and non-volatile residue analysis, when required, is performed by surface sampling techniques. The facility is equipped with a hot gaseous nitrogen purge capable of 300°F maximum and a vacuum capability for drying the hardware when the aqueous process is complete. Additional oven capability exists within other locations that are also used as necessary for drying. The facility capability is summarized in Table 2. The process is depicted in Figure 3.

Aqueous Flush Equipment Parameters

- Physical Capacity
  - 500 gallon solution tanks
  - Accommodates large hardware
  - Flush at 50 gpm/ 80 psi maximum
  - Steam heat exchangers for elevated temperature
  - GN_2 at 300 °F
  - Vacuum pump
- Rinsing Capabilities
  - Intermediate rinse (0.1 megohm)
  - Final Rinse (1.0 megohm)
- Built-in Versatility
  - Variable flow rates, pressures

Table 2: Aqueous Flush Facility Capability

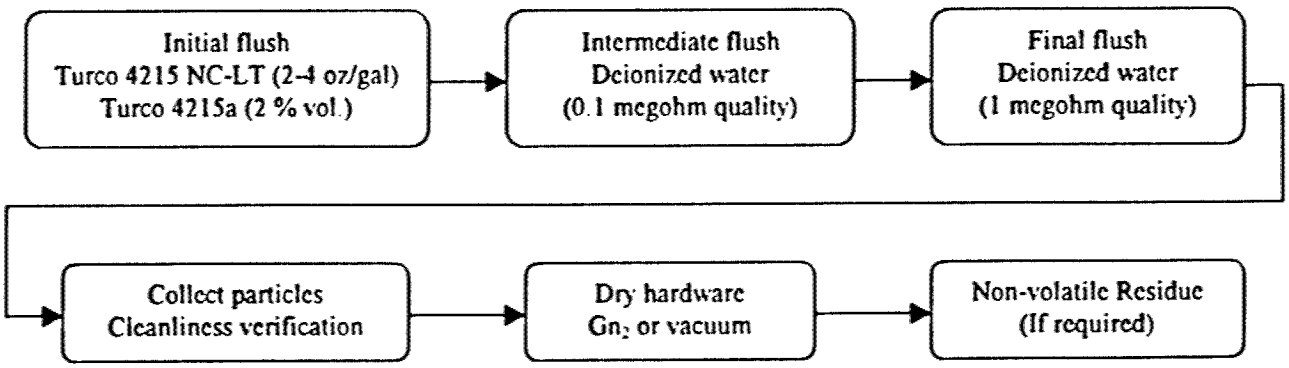


Figure 3: Aqueous Flush Facility Process

This facility is currently used to clean nozzles, combustion chambers, powerheads, large ducts, long lines and turbopump housings. The processing area contains a large overhead crane with which to handle these components and the area has a containment area in the event of a leak or a spill. In addition, some of these components have handlers that can be rotated during the procedure to enable the hardware to be manipulated during cleaning. This helps ensure that complex areas are flushed and areas that might entrap air are avoided.

NVR CLEANLINESS VERIFICATION TECHNIQUES

Two methods of cleanliness verification, which do not utilize ozone-depleting compounds, have been implemented at Rocketdyne. Test results have shown that both techniques are as sensitive and show equivalent or less variation the previously used 1,1,1-trichloroethane method. One technique is a solvent flush method, utilizing cyclohexane as the verification solvent. The other technique is an aqueous method, which involves ultrasonic agitation of hardware in a heated water bath, followed by subsequent analysis on a total organic carbon (TOC) analyzer.

Aqueous TOC Nonvolatile Residue Analysis

Aqueous verification is performed by ultrasonic agitation of the part in deionized water and analysis of the water for total organic carbon content. The hardware is placed in a previously cleaned stainless steel container, which is filled with deionized water and suspended in a Blackstone 25 kHz ultrasonic bath heated to 125°F. The part is then ultrasonically agitated for 10 minutes and a 200 μl sample of the water is withdrawn. The sample is injected into a Rosemount Dohrmann DC-190 High Temperature Combustion Total Organic Carbon Analyzer (TOCA) which has been previously calibrated. The total organic carbon content is measured, the volume of water in the stainless steel pan is measured and the equivalent NVR is calculated as detailed below. Due to the limits of detection of the Rosemount TOCA, to reliably detect an NVR level of 1 mg / sq. ft., the water volume to hardware surface area ratio must not exceed 3 liters/ sq. ft.

$$NVR = \frac{TOC \times V}{Cc}$$

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)

= 0.68 for Rocketdyne contaminants

The term Cc is the weight fraction of organic carbon in a given material. A value of 0.68 is employed by Rocketdyne as it is representative of the contaminants normally used at Rocketdyne, and therefore those that would be expected to be present on the hardware. Each potential contaminant has a different carbon content and the value of Cc can vary. If a manufacturer uses contaminants, such as silicones, which typically have much lower carbon weight fractions, the value of Cc must be adjusted appropriately. In addition, silicone and fluorocarbon greases, and paraffin waxes are more difficult to remove from surfaces using heated water and do not readily form homogeneous emulsions. If the method is to be used for these applications, additional development is required to develop greater sensitivity to these materials.

In general, hardware that can be aqueously cleaned in the ultrasonic facility is suitable for verification by the aqueous method. Material compatibility testing performed during the development of the ultrasonic precision cleaning process identified one area of concern with regard to the cleaning of aluminum. Test results showed that anodized aluminum is not degraded by multiple 15-minute duration exposures to ultrasonic agitation. Chemical film treated aluminum is degraded by exposure to a duration greater than 10 minutes. Bare aluminum surfaces

show visual surface erosion after exposure to ultrasonic agitation. Based upon past testing, it is acceptable for anodized and chemical film treated aluminum to be verified aqueously provided the exposure duration does not exceed 10 minutes. Bare aluminum is usually not encountered on finished hardware due to the lack of inherent corrosion properties, however, it should not be cleaned or verified using aqueous ultrasonic methods without further evaluation. Testing was also performed to evaluate the effect of ultrasonic agitation on electrodeposited coatings and no evidence of degradation was noted on any of the panels tested

Hardware verified by the aqueous/TOC method is analyzed immediately after particulate verification. This eliminates the 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 due to this cycle time reduction.

Cyclohexane Nonvolatile Residue Analysis

Verification using cyclohexane is performed using a gravimetric method similar to the previously used TCA method. The hardware is flushed with 500 ml of solvent, which is collected, filtered and a gravimetric analysis performed. The only exception is that the final oven drying temperature used during the gravimetric NVR was reduced to the range of 185 to 195°F. The standard drying temperature range for TCA was 221 to 230°F. Use of this elevated drying temperature with cyclohexane causes excessive evaporation of the contaminant residue. This was verified by preparing standard solutions of contaminants in cyclohexane and performing gravimetric NVR measurements using each of the two drying temperatures. The lower drying temperature provided the more accurate results.

Implementation of the cyclohexane method requires special consideration due to the fact that cyclohexane is flammable and classified as a Volatile Organic Compound (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 is oven dried before flushing with cyclohexane to prevent the mixing of water and solvent. After the hardware has been dried and allowed to cool to room temperature, it is placed in a self-contained 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 the aqueous technique.) The hardware is flushed with 500 ml, nominal, of cyclohexane and a gravimetric NVR is performed.

A self-contained cyclohexane flushing system 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 supply 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 that 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 surface sampling techniques.

Cyclohexane is not compatible with oxidizers and special precautions must be taken to ensure hardware is adequately dried. Hardware flushed with cyclohexane is subsequently exposed to a vacuum oven drying process. After the final drying procedure, a hydrocarbon analyzer is used to detect the concentration of any residual solvent that may be left on the hardware and thus verifies complete removal of the cyclohexane.

Alternatively, the cyclohexane sample collected from flushing the hardware may be analyzed for hydrocarbon determination using Fourier Transform Infrared (FTIR) methods. FTIR techniques have been developed which do not utilize ozone-depleting compounds.

Surface Sampling Verification Techniques

A surface sampling cleanliness verification method was developed for hardware that can not 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 that 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. This verification method is limited to hardware that can not be verified using the aqueous/TOCA technique or by solvent flushing.

Particulate Verification

Testing has demonstrated that TCA and water yielded comparable results for particulate verification in the particulate range of 300 to 800 microns applicable to SSME hardware. Based upon these results, aqueous particulate verification was proven to be an acceptable alternative to the previous TCA method and has been implemented in the Precision Clean Facility. 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 that is faster and more convenient.

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.

CONCLUSIONS

Rocketdyne has successfully converted from ozone-depleting solvent based cleaning and verification methods. For most processes, aqueous methods have been utilized as alternatives. These processes have been evaluated and have been proven to be at least as effective as the solvent methods they have replaced. 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. The aqueous ultrasonic precision clean process, the aqueous closed loop flushing facility, and the various verification techniques have been fully implemented on a production basis. The TCA vapor degreasers have been demolished and removed from the facilities in Canoga Park.

REFERENCES

1. Becker, J. F., "Ultrasonic Frequency Selection for Aqueous Fine Cleaning", Aerospace Environmental Technology Conference, A. F. Whitaker, ed., NASA CP- 3298, 3/95.

2. NAVSEA Report on: "Aqueous Oxygen Cleaning Products and Processes", Naval Sea Systems Command, dated 3/24/94.

3. Stern, S. M., "Aqueous Precision Cleaning of Engine Components", Second Aerospace Environmental Technology Conference, A. F. Whitaker, ed., NASA CP- 3349, 3/97.

PRECISION CLEANING AND VERIFICATION PROCESSES USED AT MARSHALL SPACE FLIGHT CENTER FOR CRITICAL HARDWARE APPLICATIONS

By

Salvadore V. Caruso
NASA/Marshall Space Flight Center

Jack A. Cox
Kathleen A. McGee
Artificial Intelligence Signal
Research Corporation, Inc.

PRECISION CLEANING AND VERIFICATION PROCESSES USED AT MARSHALL SPACE FLIGHT CENTER FOR CRITICAL HARDWARE APPLICATIONS

ACKNOWLEDGMENTS: For Valuable Assistance in Providing Information and Advice

Marceia Clark-Ingram
NASA/Marshall Space Flight Center

Tammy L. Townsend
NASA/Marshall Space Flight Center

Bobby W. Ellenburg, Jr.
Artificial Intelligence Signal
Research Corporation, Inc.

Robert W. Graves

1. INTRODUCTION

BACKGROUND

Marshall Space Flight Center Operations and Responsibilities

- Propulsion
- Microgravity Experiments
- International Space Station
- Space Transportation System
- Advance Vehicle Research

MSFC ORGANIZATION

- Center Organization
- Science & Engineering Directorate
- Materials and Processes Laboratory
  - Fabrication Services Division
    (Cleaning Services)
- Project and Environmental Engineering Division
  (Chemistry, Verification Testing)

2. "SPECIFICATION-DRIVEN" CLEANING AT MSFC

- **MSFC-SPEC-164a, Cleanliness of Components for Use in Oxygen, Fuel & Pneumatic Systems, specifies CFC 113 and Trichloroethylene (TCE) and Trichloroethane (TCA)for precision cleaning, field cleaning and as the cleanliness verification test solvent for Nonvolatile Residue (NVR) and particulate analysis.**

- **MSFC-SPEC-164a is applied to MSFC fabrication and testing activities and is a contract requirement for Space Shuttle propulsion elements:**

  - **External Tank (ET)**
  - **Space Shuttle Main Engine (SSME)**
  - **Alternate Turbopump Development (ATD) and Production**
  - **Solid Rocket Booster (SRB)**

- **MSFC-SPECT-164b supersedes MSFC-SPEC-164a as of November 1994. This revised specification is "performance based" versus "how to" and provides for alternative cleaning/verification methodologies and media. However, replacements must be base-lined to CFC-113. It does not address the aspect of CFC-113 not being available.**

- **Trichloroethylene (TCE) is a replacement for CFC-113 in specification (Engineering Requirements) driven cleaning applications at MSFC. Trichloroethylene is not necessarily the alternative for MSFC Shuttle contractors.**

3. CLEANING FACILITIES

- "Rough Cleaning", Metal Treating and Electro-Plating (Figures 1, 2, 3, 4)
- Precision Cleaning (Figures 5, 6, 7, 8, 9)
- Verification Testing Laboratory (Figures 10, 11, 12)

4. CLEANING PROCESSES

- Liquid Oxygen, Fuels and Pneumatic Systems (MSFC-SPEC-164b)
  - Manufacturing Procedure for Vapor Degreasing of Metallic Surfaces-Tetrachloroethylene (Perchloroethylene) MP206
  - Cleaning Procedure for Low Strength Steel & Steel Alloy, High Strength Steel & Alloy & Aluminum Alloy MP200
    - Vapor Degrease - Handwipe - Sand Blast (as necessary)
    - Alkaline bath-Turco 4215***
    - Etch - Caustic Solution
    - Acid Bath
    - Electro-Clean (Turco Surj.)***
    - Deoxidizing Solution - Turco Smut-go 1***
    - DI Water rinse - Hot & Cold
    - Forced High Purity Air Dry

*** TURCO is a registered trademark of Elf Aquitaine, Inc.

- **Component Cleaning**

- **Non-Lox Service**

Optics	**Electronics**	**Computer Electronics**
Film	**Load Cells**	**Photographic Components**
Flow Meters	**Ball Bearing Testers**	

5. VERIFICATION TESTING

- **Non-volatile Residue (NVR) determination by gravimetic procedure**
- **Particulate count by microscopic visual examination**
- **NVR & Particulate Procedure base-line with CFC-113 solvent**

6. CFC-113 REPLACEMENT FOR VERIFICATION TESTING

- **ODC Solvent Study at MSFC**
  - **CFC-113 - Isopropyl Alcohol - Trichloroethylene - AK225* - Vertrel MCA****

- **Trichloroethylene (TCE) was selected for use at MSFC. Significant data base exists from Saturn to Shuttle which supports the implementation of TCE as an alternate verifications solvent.**

*** AK225 is a registered trademark of ASAHI Glass Co., Ltd.**
**** Vertrel is a registered trademark of DuPont**

- Advantages of TCE
  - Short atmospheric lifetime
  - Non-ODC
  - Cost is many times less than other alternate solvents
  - No foreseeable punitive taxation/restrictions
  - Removed from list of potential carcinogens per ACGIH and MSDS
  - Very small volume used (Only for NVR and Particulate)

- Disadvantages of TCE
  - Hazardous Air Pollutant (HAP)
  - Water & Ground Pollutant
  - Associated Toxicity Problems
    - OSHA PEL = 50 ppm
    - MSFC PEL = 25 ppm

- TCE Implementation - Guidelines & Precautions

  - Minimize solvent usage for cleanliness verification
  - Assure material compatibility
  - Special handling procedures to protect personnel & equipment
    - Containment barriers to protect groundwater
    - Personnel protective equipment
    - Personnel Training

- Safe Handling procedures
- Emergency procedures in-place
- Adequate air handling system
  - 25 ppm maximum PEL
  - Filtered make-up air
  - Exhaust scrubbers as required

7. ALTERNATE CLEANING AND VERIFICATION STUDIES

- Critical Cleaning Evaluation and Implementation for Chlorofluorocarbon Replacement- Study by CH2M Hill Southeast, INC. for the Environmental Engineering and Management Office, Marshall Space Flight Center
  - Task 1 Printed Wire Board Acceptance
  - Task 2 CFC Distillation Implementation
  - Task 2A Development of a Pharmacy System Concept
  - Task 2B Alternatives to ODS Cleaning
  - Task 3 Alternative CFC Cleaning for TBE
  - Task 4 Transition from CFC-113 for Engine Test Activities
  - Task 5 Evaluation of an Alternative Cleaner for Ion Pumps
  - Task 6 Implementation Status of Non-ODS Alternative Recommendations
  - Task7 Development of Air Emissions Data for ADEM Fee Assessment

- CFC-113 Replacement Project By Daniel E. Adams, Mechanical Systems Test Branch, Propulsion Laboratory (Handwipe cleaning replacement study for CFC-113)

8. CONCLUSION

- CFC-113 usage (Cleaning - Verification) at MSFC has reduced from 64,000lbs.(CY93) to 30,000lbs.(CY94) to close to zero in 1998. Remaining stock re-distilled for very special requirements.
- MSFC will utilize TCE as an interim replacement for CFC-113 for Verification testing.
- The MSFC-managed Space Shuttle contractors are providing "lessons learned" for implementation of aqueous and semi-aqueous cleaning.
- MSFC will continue to use the perchlorethylene degreasing solution. The current cleaning processes are essentially water-based. Chromate solutions will be replaced with no-chromate solutions.
- Studies are planned for maximizing use of aqueous cleaning and water verification

AQUEOUS CLEANING AND VALIDATION FOR SPACE SHUTTLE PROPULSION HARDWARE AT THE WHITE SANDS TEST FACILITY

Steven D. Hornung and Paul Biesinger
AlliedSignal Technical Services Corp. Team
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

Mike Kirsch, Harold Beeson, and Kathy Leuders
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

INTRODUCTION

The NASA White Sands Test Facility (WSTF) has developed an entirely aqueous final cleaning and verification process to replace the current chlorofluorocarbon (CFC) 113 based process. This process has been accepted for final cleaning and cleanliness verification of WSTF ground support equipment. The aqueous process relies on ultrapure** water at 50 °C (323 K) and ultrasonic agitation for removal of organic compounds and particulate. The cleanliness is verified by determining the total organic carbon (TOC) content and filtration with particulate counting. The effectiveness of the aqueous methods for detecting hydrocarbon contamination and particulate was compared to the accepted CFC 113 sampling procedures. Testing with known contaminants, such as hydraulic fluid and cutting and lubricating oils, to establish a correlation between aqueous TOC and CFC 113 nonvolatile residue (NVR) was performed. Particulate sampling on cleaned batches of hardware that were randomly separated and sampled by the two methods was performed.

This paper presents the approach and results, and discusses the issues in establishing the equivalence of aqueous sampling to CFC 113 sampling, while describing the approach for implementing aqueous techniques on Space Shuttle Propulsion hardware.

BACKGROUND

The application of aqueous cleanliness verification is based on a Kennedy Space Center developed procedure, which has been adopted as ASTM method 131-96,[1] and the method for sampling for residual organics is based on ASTM method G-144-96.[2] In the cleaning verification procedure, parts are sampled in 50 °C (323 K) ultrapure water using a 25-kHz, 1000-W ultrasonic bath. The organic content of this water is then determined using a high temperature, catalytic combustion TOC analyzer. The particulate is determined by filtration and counting the particulate on the filter as a function of size.

Cleaning operations at WSTF encompass support for materials, components, propulsion test systems, and a large Shuttle depot activity. As part of these operations, components and piece parts are cleaned for a variety of services including oxygen, hydrogen, hydrazines, and nitrogen tetroxide. The majority of the parts is constructed of stainless steel and is resistant to corrosion in aqueous media. Cleanliness levels to 50A are required for high pressure oxygen service. For precision cleaned parts, the standard cleaning process consists of two major elements: precleaning and final cleaning, and cleanliness verification. The precleaning process is shown in Fig. 1. Parts are first inspected, and any gross contamination is removed. For stainless steel parts, the cleaning consists of an alkaline cleaner with ultrasonic agitation, rinse, a phosphoric acid cleaner with ultrasonic agitation, rinse, and then drying in a HEPA-filtered oven. Following drying, the parts are visually inspected, and if passed, are transferred to the Class 100 clean room. The accepted CFC-based final cleaning, shown in Fig. 2, is a CFC 113 rinse, followed by a final rinse of 100 mL per 0.1 m^2 (1 ft^2) of surface. The rinse is then collected for filtering and NVR. The results

** Ultrapure water defined having resistivity of 12.5 to 18 MOhm.

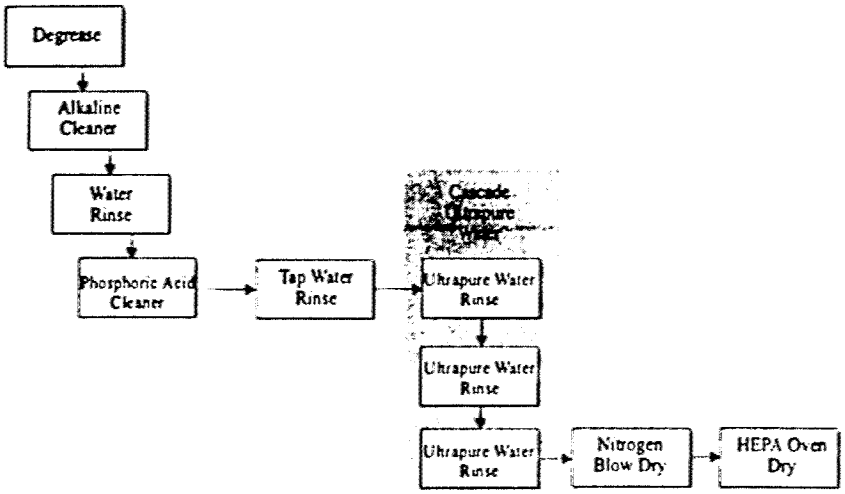


Fig. 1. Standard Precleaning Process

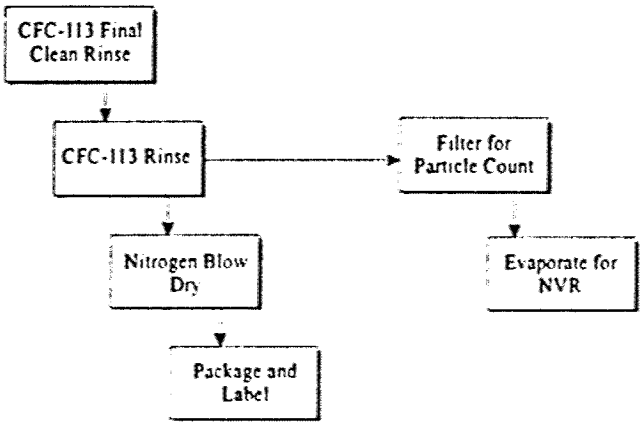


Fig. 2. CFC Final Cleaning and Verification Process

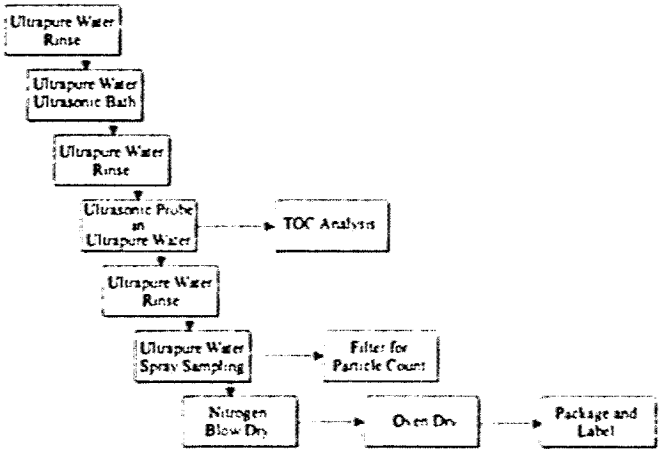


Fig. 3. Aqueous Final Cleaning and Verification Process

of the NVR and particulate sampling are expressed in *passing levels* defined in the cleaning specifications, such as JHB 5322.[3] For NVR, the levels are <1, <2, <3, and <4 mg/ft^2 of sampled surface area and are designated A, B, C, and D, respectively. Particulate levels are usually defined by the largest particle acceptable, 50, 100, 200, 300, and 400μ per 0.1 m^2 (1 ft^2) of sampled surface area. The proposed aqueous final cleaning and verification process is shown in Fig. 3. The final cleaning procedure consists of a rinse with filtered hot ultrapure water, agitation with ultrapure water in a 1000-W ultrasonic bath, followed by final rinse. Cleanliness verification consists of a 1.27-cm (0.5-in.) tip ultrasonic probe delivering approximately 600 W of power into the sampling container for a total of 30 seconds. A small aliquot of the solution is then removed for sampling by TOC, and the remainder of the water is filtered for the particle count. The use of the ultrasonic probe allows a higher ultrasonic energy density in the sampling container. This aqueous process is directed at piece parts which are not corrosion or ultrasonic sensitive, and do not have small passages or entrapment spaces.

APPROACH

The testing used to certify the aqueous alternative to CFC 113 sampling was divided into three phases: development, batch parts sampling, and process validation. In the development phase, equipment and procedures were tested to determine the most promising method of aqueous cleanliness verification. Development testing was also performed to determine that there was a relationship between the contaminant levels and the sampling response. The batch parts sampling was aimed at assessing the efficiency of contaminant removal, both organic and particulate, compared to CFC 113. More extensive batch parts sampling tests were then conducted to compare the efficiency of removal of contaminants. The batch parts sampling was performed only to establish the efficiency of the cleanliness verification and did not include the final cleaning step. CFC 113 was used as the standard against which the results were compared. Process validation was performed to determine the reliability of the process.

ORGANIC CARBON METHODS

In the development testing, numbered stainless-steel and -aluminum plates, 5 X 7.6 cm (2 X 3 in.) were used. These plates were fabricated according to ASTM-G121.[4] A representative plate is shown in Fig. 4. A tare weight on each plate was obtained and either single contaminants or contaminant mixtures in a CFC 113 carrier contaminated the plate. These contaminants were representative of the types of contaminants encountered in WSTF cleaning operations. The plates were re-weighed; to determine the contaminant loading, then sampled using the aqueous process. The results of the TOC analysis were compared with the original contaminant loading to determine percent recovery for each of the contaminants. These tests were performed over a range of contaminant loading, and a slope of the fitted data determined the efficiency of recovery.

In batch sampling, representative batches of fittings numbering between 10 and 30 parts were contaminated by a mixture of compounds in CFC 113, allowed to dry, then divided into two groups at random. An example of these fittings is shown in Fig. 5. One group was sampled by the aqueous method and the other using CFC 113. In both cases, a final cleaning or rinse did not precede the sampling, as is usually the case with CFC 113 cleanliness verification. The TOC response was compared to the CFC 113 NVR. Results were tabulated in the form of JHB-5322 passing levels. Because Krytox® is often used as a thread lubricant in the assembly of systems, it was treated separately from the other contaminants.

PARTICULATE COUNTING METHODS

Because of the difficulty of uniformly contaminating plates or a batch of parts at a low enough particulate level, cleaned batches of parts were used for the particulate studies. The particulate contamination on these parts was due to residual particles that were not removed during the cleaning process.

The development testing and the batch sampling for the particulate consisted of cleaning batches of fittings numbering between 10-30 parts and separating them into two groups at random. One group was sampled by the aqueous method and was followed by filtering to collect the particles. The other group used CFC 113 with the standard filtering technique. In both cases, a final cleaning or rinse did not precede the sampling, as is usually the case with CFC 113 cleanliness verification. The total number of particles on the filter was counted according to size. The passing levels for the aqueous and CFC 113 sample pairs were tabulated using JHB-5322 passing levels.

ORGANIC AND PARTICULATE PROCESS TESTING

Process testing was performed on actual hardware. The aqueous method, which included an aqueous ultrasonic final cleaning step, was followed by the accepted CFC 113 method. Particulate and NVR passing levels were recorded for each batch. This sequential sampling was performed to assess the possibility of obtaining a passing level with the aqueous method followed by a failure with the CFC 113 method. The viability of this technique in a production environment was also evaluated in terms of throughput and recleaning required due to excessive failures. A wider variety of parts were sampled in this testing and included disassembled valves and filters as well as fittings and short lengths of tubing. An example of a disassembled filter assembly is shown in Fig. 6.

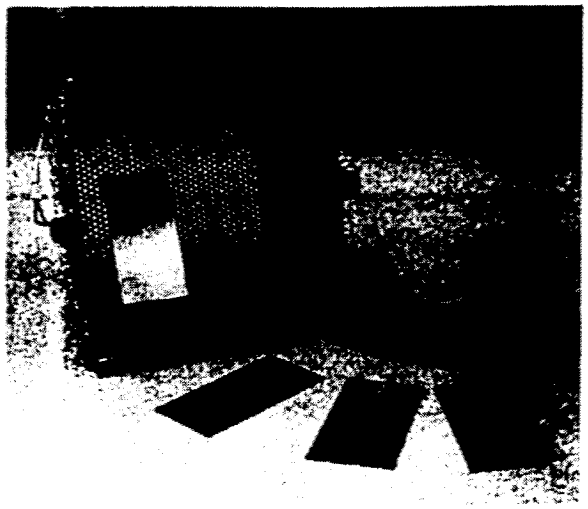


Fig. 4. Representative Plates

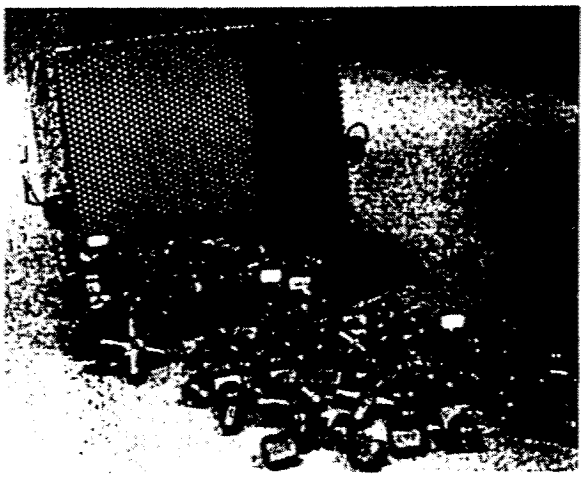


Fig. 5. Example of Fittings

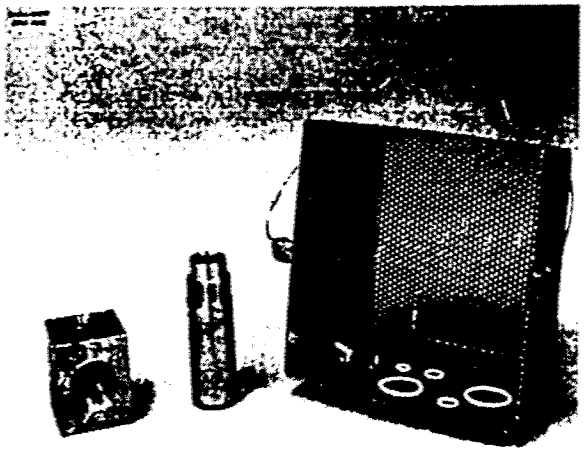


Fig. 6. Disassembled Filter Element

RESULTS

ORGANIC CARBON METHODS - DEVELOPMENT TESTING

Tare weights were obtained on numbered stainless-steel plates 5 by 7.6 cm (2 by 3 in.). A contaminant mixture consisting of 0.5 grams of each contaminant, including hydraulic, vacuum pump, lubricating, and cutting oil were dispersed in 200 mL of CFC 113. Approximately 0.25 mL of this contaminant mixture was placed on each plate and allowed to air dry. The mass of the plate plus the contaminant was determined. For higher contaminant levels, this procedure was repeated several times. Before each sampling, the TOC was determined on the water to serve as a blank or reference.

The coupon was placed in a 600-mL beaker and covered with 400 mL of ultrapure water at 50 °C (323 K). The coupon was agitated ultrasonically for 1 minute with 0.3-second pulses for a total ultrasonic exposure time of 30 seconds. A gastight syringe was used to remove 250 μL of the water, which was injected into the TOC analyzer. From the measured concentration, the mass removed by this technique was calculated. The results of this testing is represented by a graph in Fig. 7. This initial testing showed a good correlation with a slope of approximately 0.65. This slope indicates there is a linear increase in the TOC response with the contaminant mass.

To assess the recovery of Krytox® by the aqueous method, approximately 2 mg was deposited on the coupon directly from the tube and sampled as previously described. No TOC response could be found in this case. However, Krytox® was detected in the form of particles when the water was filtered. Further work on the sampling for Krytox® was done from this particle count data. An example of Krytox® particles detected by aqueous ultrasonic sampling is shown in Fig. 8.

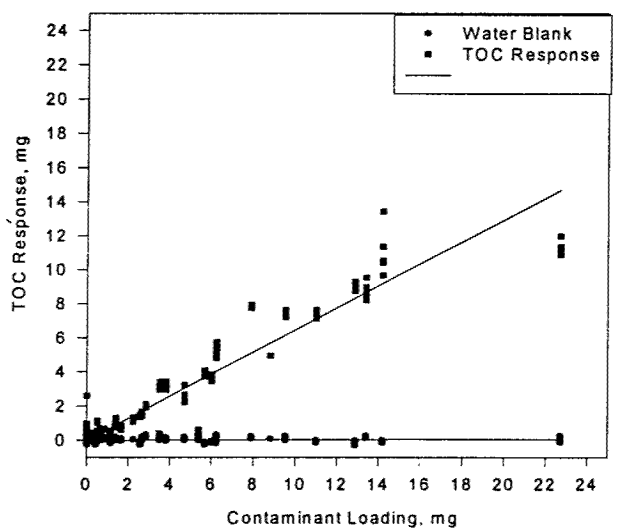


Fig. 7. Recovery of Organic Contaminants

ORGANIC BATCH TESTING

The batches of parts, primarily fittings, numbering at least 10-30 pieces were contaminated using the same solution as in the development testing. These were then dried, and the batch was split into two groups at random. One group was added to a 600-mL beaker, covered with 400 mL of 50 °C (323 K) ultrapure water and ultrasonicated for 60 seconds. 250 μL was then removed for TOC analysis. The second group was sampled using the standard CFC 113 rinse with 100 mL from which the nonvolatile residue was obtained in mg. The equivalent TOC was calculated from the concentration obtained from the TOC by the following equation:

$$\text{Equivalent TOC (mg)} = C(\text{ppm}) * V(L)/S(\text{mg CFC/mg TOC}) \quad \textbf{(1)}$$

where

C = the concentration obtained from the TOC
V = the volume of ultrapure water used in liters, and
S = the experimentally determined sensitivity factor

The sensitivity factor was obtained in this case by plotting the milligram response (ppm by volume) of the TOC versus the results obtained from the NVR to determine the slope of the line.

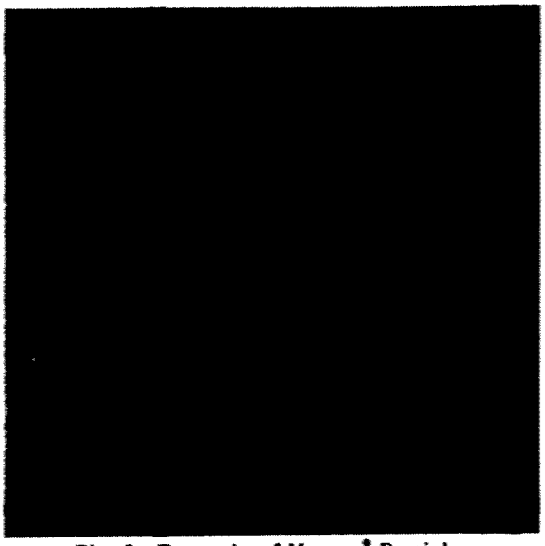


Fig. 8. Example of Krytox* Particles

From the batch testing, a sensitivity factor of 0.4 was determined and applied in all subsequent tests. To compare the NVR and TOC sampling methods, the results were distributed into the discreet, integer passing levels used in the cleaning specifications. For example, a result of 1.4 mg would pass a 2 mg or *B* level; a result of 0.8 mg would pass a 1 mg or *A* level. A *figure of merit*, ΔW, which expresses the relative efficiency of the two sampling techniques was also calculated by subtracting the CFC 113 passing level from the aqueous passing level. When ΔW is zero, the results of the two sampling techniques are equal. When ΔW is negative, the CFC 113 showed more contamination on the parts. When ΔW is positive, the aqueous method showed more contamination on the parts.

The number of observations of each result was then tabulated to give a distribution of the number of observations for each value of ΔW. In Fig. 9, ΔW is plotted versus number of observations. The mean or average passing level is 1.2 ΔW, and is on the side of the distribution where the aqueous technique is more effective. The mode, or most likely occurring value of ΔW is zero, where the two techniques yield equal results. The median ΔW, the value with equal numbers of observations above and below, is 1, is also on the side of the distribution where the aqueous technique is more effective. From this set of data, the aqueous ultrasonic sampling is equal to or more effective than CFC 113 and samples 91 percent of the time in detecting residual contamination.

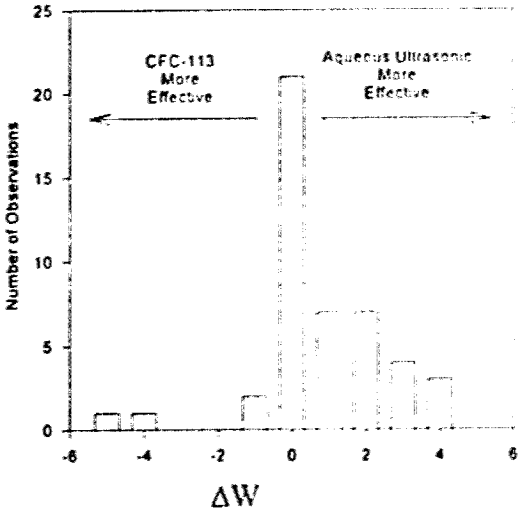


Fig. 9. Distribution of ΔW for Organic Passing Levels on Batch Parts

PARTICULATE BATCH TESTING

The batches of parts (primarily of at least 10-30 pieces or fittings) were precleaned and transferred to the Class 100 clean room where the batch was split into two groups at random. One group was then added to a 600-mL beaker, covered with 400 mL of 50 °C (323 K) ultrapure water, and ultrasonicated for 60 seconds. All of the 400 mL was filtered, and the total number of particles on the filter was counted. The second group was sampled using a rinse of 100 mL of CFC 113, which was then filtered. The total number of particles on the filter was counted as a function of size. Using the passing levels from the cleanliness specification, the aqueous and CFC 113 particle counts were then assigned the appropriate passing level.

A *figure of merit*, ΔP, which expresses the relative efficiency of the two sampling techniques was also calculated by subtracting the CFC 113 passing level from the aqueous passing level. When ΔP is 0, the results of the two sampling techniques are equal. When ΔP is negative, the CFC 113 detected a higher particulate level on the parts. When ΔP is positive, the aqueous method detected a higher particulate level on the parts. The number of observations of each result was then tabulated to give a distribution of the number of observations for each value of ΔP. In Fig. 10, ΔP is plotted versus number of observations. The average ΔP is 53 and is on the side of the distribution where the aqueous technique is more effective. The mode, or most likely occurring value of ΔP is zero, where the two techniques yield equal results, and the median ΔP with equal numbers of observations above and below is also 0. From the tabulated data, the aqueous sampling for particulate is equal to or more effective than the CFC 113 and samples 73 percent of the time.

KRYTOX® BATCH TESTING

The studies and experience gained at WSTF indicate through the CFC 113 cleanliness verification and the aqueous ultrasonic sampling that Krytox® is detected in the particulate count rather than the NVR. To assess the effectiveness of the aqueous technique in detecting Krytox® by particle count, six batches of four threaded fittings were contaminated by a heavy application and distribution of Krytox® grease over the threads. These batches were cleaned using the precleaning process. Following precleaning and inspection, three batches were sampled aqueously without the final cleaning step; and CFC 113, without the final cleaning step, sampled three batches. Out of the three batches, aqueous sampling detected Krytox® in one batch of fittings, and CFC 113 detected Krytox® in two batches of fittings. The CFC 113 sampled batches all passed a level A, or 1.0 mg NVR. To relate this particulate detection of Krytox® to a comparable number for NVR, a calculation was performed to determine the mass, which would result from a particulate passing level if all the allowed particulate were Krytox®. As shown in Table 1, a sample passing the 200 level with the maximum allowable number of Krytox® particles would have less than 0.90 mg of Krytox® present. This represents the *worst case* NVR equivalent of a Krytox® particle count.

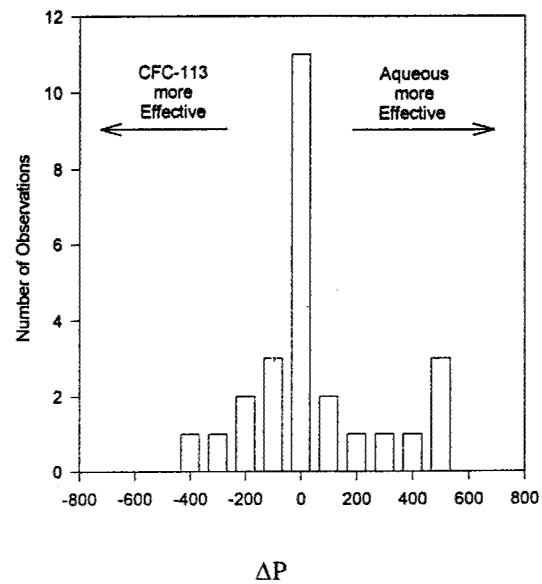


Fig. 10. Distribution of ΔP for Particulate Passing Levels on Batch Parts

Table 1. Worst Case NVR Equivalent

Specification Passing Level	Mass Equivalent as Krytox® (mg)
300	1.62
200	0.90
100	0.10
50	0.01

Process Testing

In this phase of testing, batches of hardware were final cleaned and sampled using aqueous methods, and then final cleaned and sampled using CFC 113 methods. To accomplish this, the glass beakers for the ultrasonic sampling were replaced with a metal container along with an internal basket. The metal container and basket generated particulate during the ultrasonic exposure.

The process was changed to use a rinse of 50 °C (323 K) water for the particulate sampling. The sampling for organics was unchanged from that used for the batch testing. The passing levels were compared for both particulate and organic recovery. Out of a total of 300 trials, the aqueous ultrasonic with TOC detection registered five failures and CFC 113 NVR gave no failures at the A passing level. For particulate counts, the figure of merit ΔP, was applied to 92 sampling runs. The results are tabulated in Fig. 11 where ΔP is plotted versus number of observations of each value of ΔP. The mode, or most likely occurring value of ΔP is 0, where the two techniques yield equal results. The average ΔP is 32, and the median value of ΔP with equal numbers of observations above and below is zero. Based on this testing, this process has been accepted for final cleaning and cleanliness verification of WSTF ground support equipment.

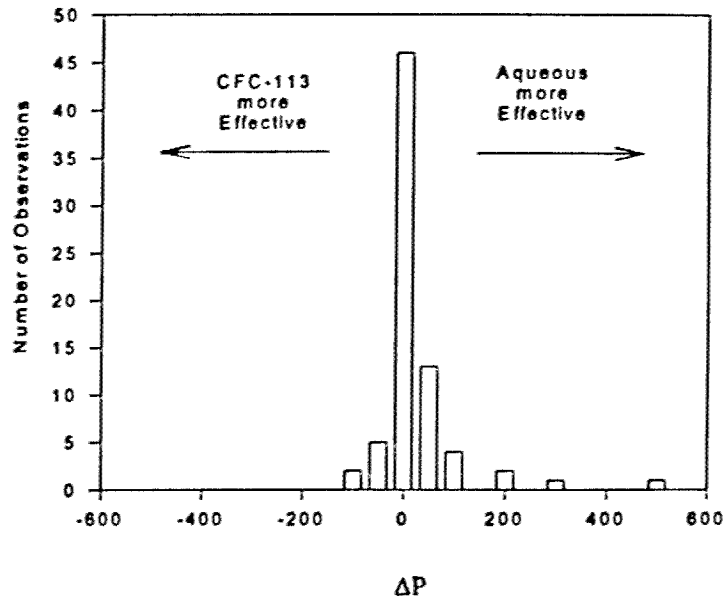


Fig. 11. Distribution of ΔP for Particulate Process Testing

AQUEOUS CLEANING FOR PROPULSION HARDWARE

CFC replacement is a critical issue for Space Shuttle Propulsion hardware. Adaptation of a new process required a clear technical approach to the selection of alternative verification methods. This technical approach consisted of a part-by-part analysis with consideration given to configuration, materials, and types of contaminants.

Part configurations were considered critical, especially evaluating any potential entrapment areas where drying processes may not be effective. Since most of the flight hardware repair work involves total unit disassembly, down to its piece-part level, the part configurations during cleaning are generally very simple. Therefore, piece-part configurations were perfect candidates for using the water-verification process. In addition, where there were potential ultrasonic damage concerns, either testing was performed to verify that there were no harmful effects or the configuration in question was deemed to be suitable for a solvent verification. Examples of this include filter assemblies and anodized parts.

The part material was also a consideration. All soft goods were cleanliness verified using solvents. Although many soft goods could have been cleaned and verified aqueously, many have questionable aqueous verification applications. The aqueous verification method was also discarded where there were corrosion concerns, specifically when drying methods were in question. Materials such as 400-series stainless or titanium are specific examples of materials that will not be verified aqueously.

The final evaluation criteria dealt with the types of contaminants likely to be found on the Shuttle. Most of the flight hardware requiring cleaning at WSTF is exposed to nitrogen tetroxide or monomethylhydrazine propellants or their combustion products. All of these contaminants are soluble in water, and therefore the water cleaning and verification method is effective. The other main types of contaminants are assembly lubricants, such as fluorocarbon grease. The WSTF data indicate that aqueous verification methods are effective at verifying the presence of this class of contaminants.

CONCLUSIONS

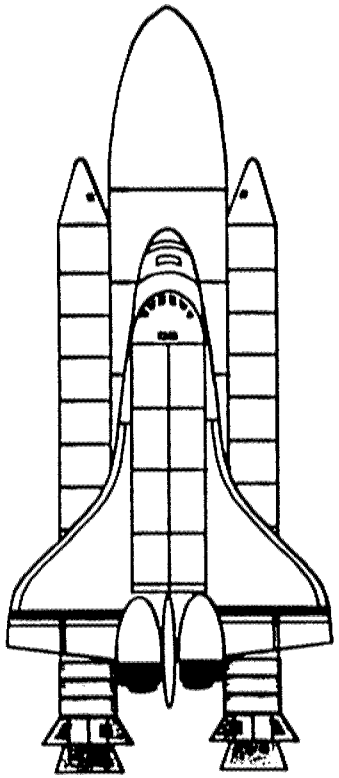
These results apply to piece parts which were primarily stainless steel and resistant to corrosion in aqueous media. Contaminants used in this study were representative of those encountered at WSTF. The following conclusions are made:

- Aqueous ultrasonic cleanliness verification does not increase the risk of passing a contaminated part over the current CFC 113 cleanliness verification technique.
- The use of the aqueous ultrasonic sampling with TOC detection as a substitute for the CFC 113 NVR is effective and was found to be more conservative than CFC 113.
- The use of aqueous ultrasonic sampling followed by rinse sampling for particulate is effective and was shown to be equivalent to CFC 113 particulate sampling.
- Detection of Krytox® is by particulate count and is conservative for particulate levels below level 200.
- Aqueous methods are applicable to propulsion type hardware, although, rigorous engineering evaluations including configuration, material, and contaminant reviews, must be thoroughly documented especially when changing certified processes.

REFERENCES

1. ASTM G-131-96. *Practice for Cleaning Materials and Components by Ultrasonic Techniques*. ASTM Vol. 14.02, pp. 1431-1435.
2. ASTM G-144-96. *Standard Method for Determination of Residual Contamination of Materials and Components by Total Carbon Analysis Using a High Temp. Combustion Analyzer*. ASTM Vol. 14.02, pp. 1454-1457.
3. NASA. *Contamination Control Requirements Manual*. JHB 5322, Revision C, NASA Johnson Space Center, Houston, TX.
4. ASTM G-121-93. *Standard Practice for Preparation of Contaminated Test Coupon for the Evaluation of Cleaning Agents*. ASTM Vol. 14.02, pp. 1381-1384.

CFC-113 REPLACEMENT PLAN FOR THE BNA PALMDALE FACILITY



Eric Eichinger

3rd AET Conference

Huntsville, 6/2/98

Session B-2

Topics

- Summary Of Orbiter & GSE Hardware Cleaned In Palmdale
- Contaminants Of Concern
- Proposed CFC-113 Replacement Process
  - Supporting Technical Data
- Required Paperwork
- Required Equipment & Facility Modifications
- Summary

A Certification Approach For Palmdale Has Been Developed

- Objective
  - Provide A New & Safe Facility To Utilize CFC-113 Replacements For Precision Cleaning & Verification
  - Perform Facility Modifications & Certification With Minimal Schedule Impact To Manufacturing
  - Update Documentation To Include All Appropriate Replacements

- Background
  - Development & Qualification Testing Completed During 94-97
  - Implementation This Year Will Allow A Reserve Of CFC-113
    - Some Hardware May Still Require CFC-113
  - Orbiter Implementation Effort Has Had To Consider;
    - The Identification Of A LOX/Hardware Compatible Solvent Which Will Remove A Diverse Array Of Contaminants
    - The Existing Paperwork Process
    - Changing SE-S-0073
    - How To Do Things Under The SFOC Contract

Orbiter & GSE Hardware Cleaned In Palmdale

- Orbiter Hardware
  - 17" Quick Disconnect
  - Support Hardware For The ET Umbilical Installations
  - GSE/Flight Interface Hardware (Type I)
    - Quick Disconnects/Flex Lines/Filters

- GSE (Type II) For OMDP Supports
  - Fluid Distribution Systems
  - Test Support Hardware
  - About 100 Systems/Models Are Used During OMDP
    - Each System/Model Consists Of Several LRUs & Assemblies

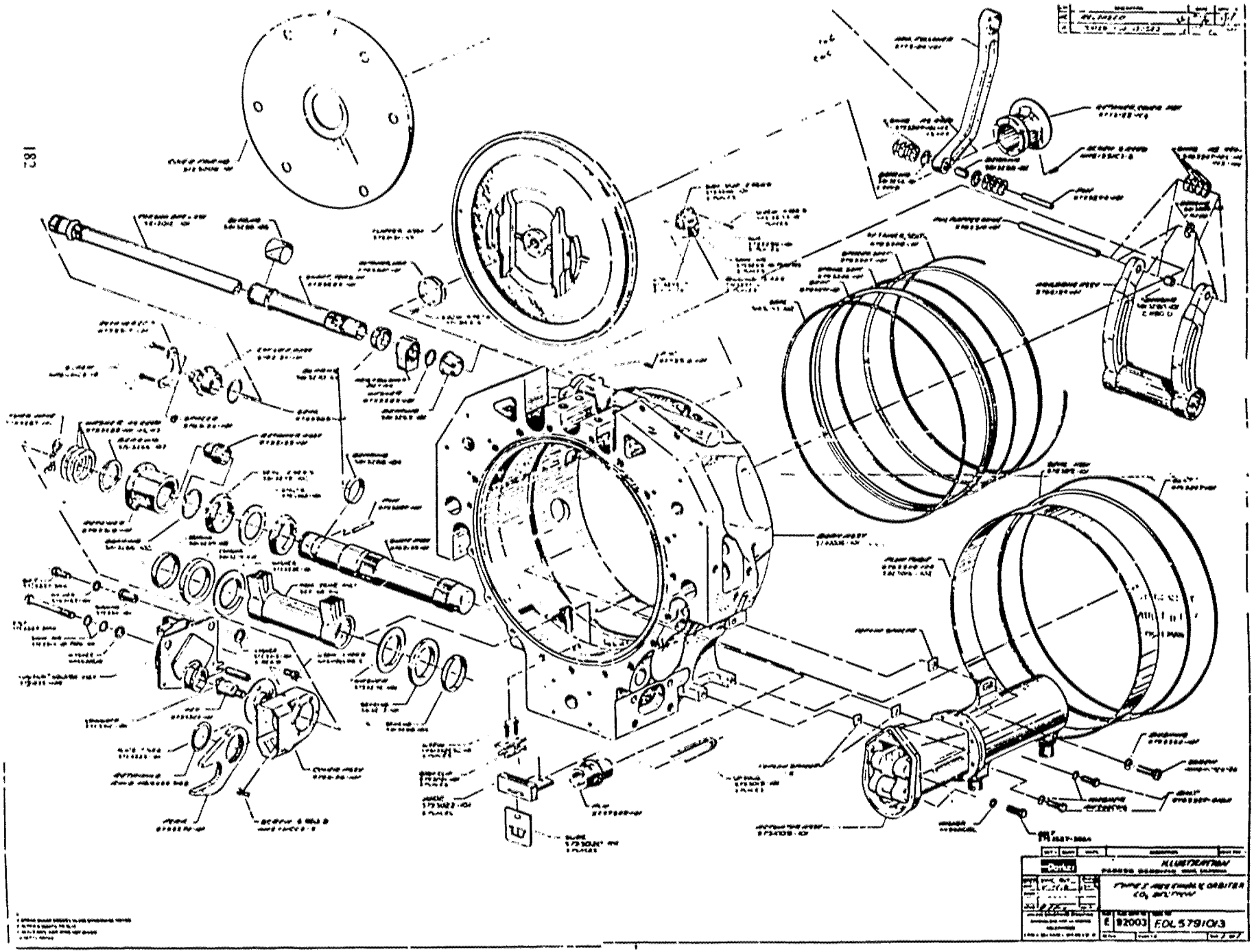
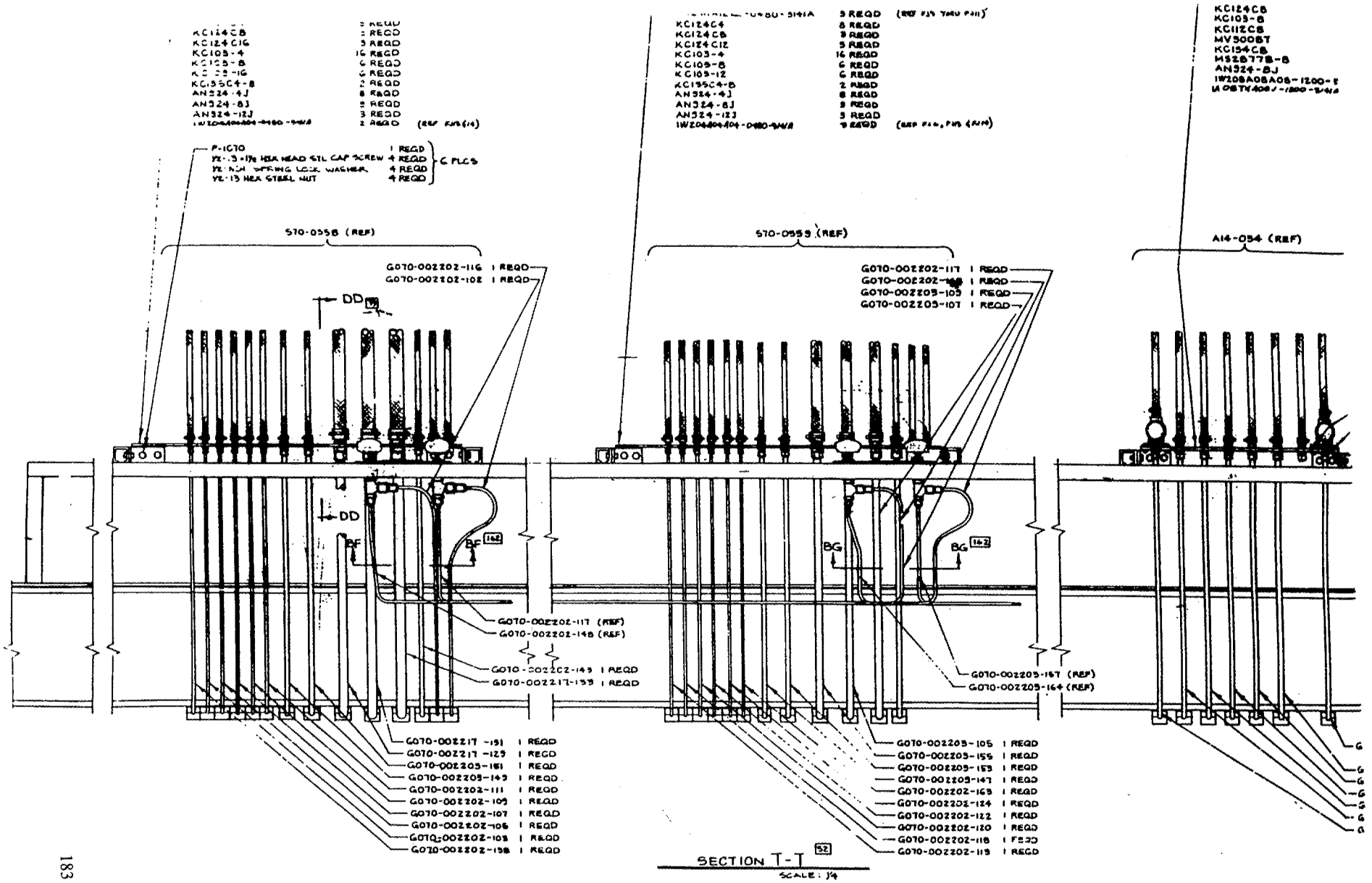
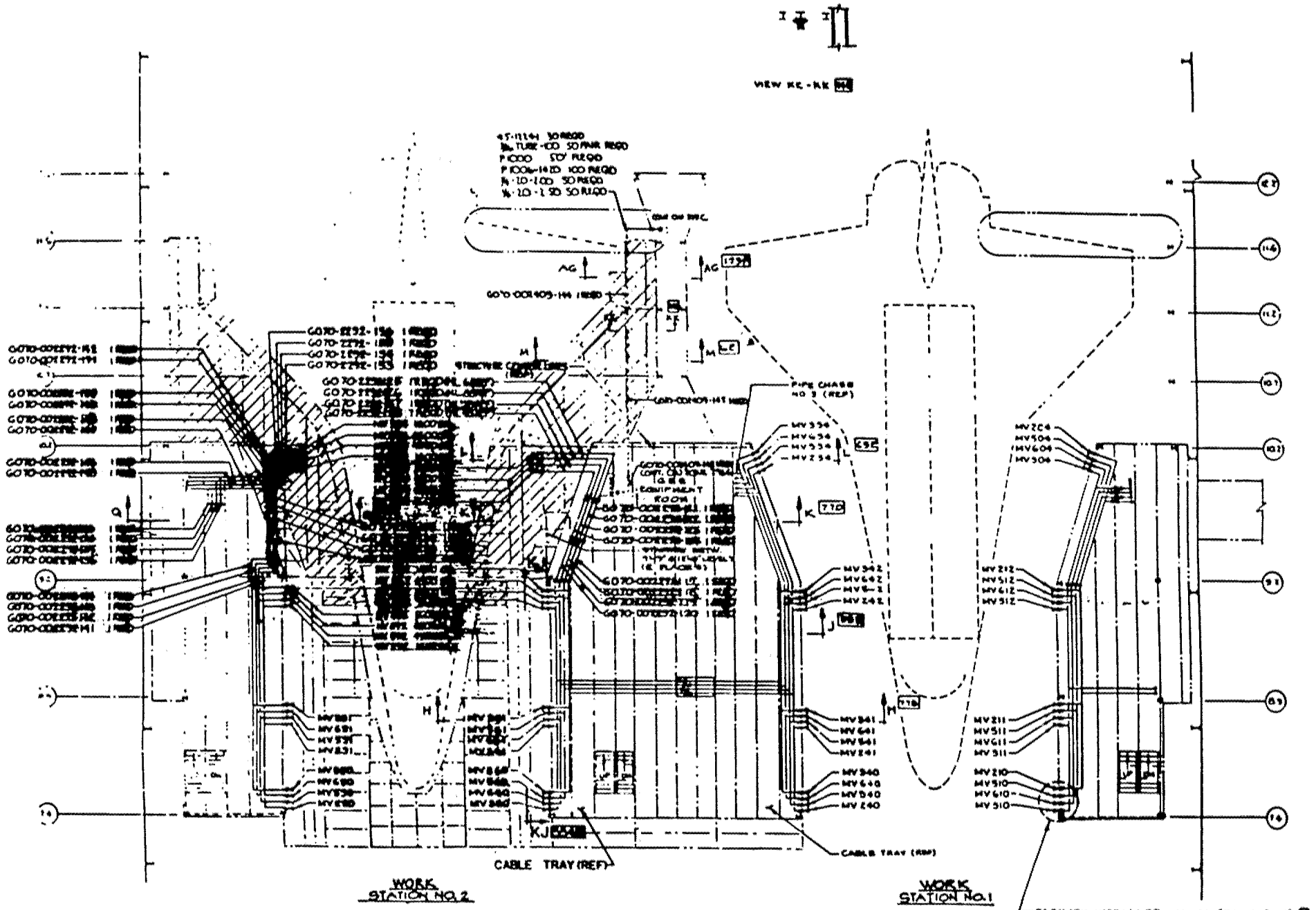


ILLUSTRATION
E 92003
EOL 5791013


KC124CB 5 REQD
KC124CIG 5 REQD
KC105-4 5 REQD
KC105-8 16 REQD
KC105-16 6 REQD
KC195C4-8 6 REQD
AN324-4J 2 REQD
AN324-8J 8 REQD
AN324-12J 5 REQD
3 REQD
2 REQD (REF FIG 14)
P-1070 1 REQD
1/2-13-1 1/2 HEX HEAD STL CAP SCREW 4 REQD
1/2 NOM SPRING LOCK WASHER 4 REQD
1/2-13 HEX STEEL NUT 4 REQD
C PLCS
570-0558 (REF)
G070-002202-116 1 REQD
G070-002202-102 1 REQD
DD
BF
BF 162
G070-002202-117 (REF)
G070-002202-148 (REF)
G070-002202-143 1 REQD
G070-002217-159 1 REQD
G070-002217-151 1 REQD
G070-002217-129 1 REQD
G070-002205-161 1 REQD
G070-002205-149 1 REQD
G070-002202-111 1 REQD
G070-002202-109 1 REQD
G070-002202-107 1 REQD
G070-002202-106 1 REQD
G070-002202-103 1 REQD
G070-002202-158 1 REQD
KC124C4 8 REQD
KC124CB 9 REQD
KC124CIZ 9 REQD
KC103-4 16 REQD
KC109-8 6 REQD
KC109-12 6 REQD
KC195C4-8 2 REQD
AN324-4J 8 REQD
AN324-8J 9 REQD
AN324-12J 5 REQD
1W204404-404-0480-9AWB 9 REQD (REF FIG 14, FIG 14H)
570-0559 (REF)
G070-002202-117 1 REQD
G070-002202-148 1 REQD
G070-002205-103 1 REQD
G070-002205-107 1 REQD
BG
BG 162
G070-002205-167 (REF)
G070-002205-164 (REF)
G070-002205-105 1 REQD
G070-002205-155 1 REQD
G070-002205-153 1 REQD
G070-002205-147 1 REQD
G070-002202-163 1 REQD
G070-002202-124 1 REQD
G070-002202-122 1 REQD
G070-002202-120 1 REQD
G070-002202-118 1 REQD
G070-002202-119 1 REQD
KC124CB
KC103-8
KC112CB
MV500BT
KC154CB
MS28778-8
AN324-8J
1W208A08A08-1200-E
A14-054 (REF)
G
SECTION T-T 52
SCALE: 1/4
88
87
86
85
84
83
82



MEZZANINE (12 FT LEVEL-UNLESS NOTED)

HARD LINE ROUTING SHOWN ON UNDERSIDE OF PLATFORM STRUCTURE

QTY	CODE IDENT	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	MATERIAL	DATA: SPECIFICATIONS, SHEET, NOTES, SUPPLIERS	ITEM
		-145				141
		-144				141
		-143				148
		-142				147
		-141				148
		-140				132
		-139				149
		-138				107
1		6010-002217-137	TUBE ASSY			154
1		6010-002217-136	TUBE ASSY			100
		-135				86
		-132				100
		-131				86
		-130				98
		-129				86
		-128				141
		-127				141
		-126				121
		-125				123
		-124				133
		-123				131
		-122				130
		-121				130
		-120				130
		-119				130
		-118				130
		-117				133
		-116				132
		-115				133
		-114				131
		-113				130
		-112				131
		-111				130
		-110				131
		-109				131
		-108				130
		-107				130
		-106				110
		-105				130
1		6010-002217-104	TUBE ASSY			130
-001		GW10-002200	INSTALLATION			-

(11) 27. 2" HP 86-0001 VALVE MAY BE SUBSTITUTED FOR 2" HP 86-01 VALVE.

(16) 26. MARK PART NUMBER PER MA0104-501, CODE 84-05-NG-15 FOR SIDE. LOCATED APPROX AS SHOWN

(19) 25 SHORTEN HANDLE TO DIMENSION SHOWN

(14) 24. SAFETY WIRE OPEN/CLOSE PER APPLICABLE TEST DOCUMENT, USING MS20259H31 WIRE PER MA0110-501.

(12) 23. MAKE FROM EXISTING HANDLE SUPPLIED WITH 2" HP 86-01 VALVES

QTY	CODE IDENT	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	MATERIAL	DATA: SPECIFICATIONS, SHEET, NOTES, SUPPLIERS	ITEM
8		[illegible]				84
1		11303-F04-F04-1200-3414	HOSE ASSY		PARKER HANNIFIN HARBOR CITY, CA (1)	144 (22)
1		11303-F08-F08-1200-3414	HOSE ASSY		PARKER HANNIFIN HARBOR CITY, CA (1)	147 (22)
2		AN929-16-X	CAP		(1)	204
30		P12718	CLAMP		UNITRUT CORP WEYNE, MICHIGAN	116
(18) 22		4L-13439	HEX HD BOLT CAP SCREW		UNITRUT CORP WEYNE, MICHIGAN	1001 108
2		2B4-24	CHECK VALVE		MASKEL BULB (2)	1[illegible]
4		AN929-8K	CAP		(2)	277
7		AN929-4K	CAP		(2)	277
6		45-11453	REDUCER		(2)	206
1		6010-002261-151	TUBE ASSY			229
1		6010-002261-124	TUBE ASSY			229
1		46-13511	TEE		AMERICAN INSTRUMENTS (1) [illegible]	239
5		45-11370	PLUG			223
4		45-14524	ADAPTER			234
4		45-11262	NIPPLE			234
10		45-11360	[illegible]			234
4		45-18904	1/4 AN ADAPTER			116
5		45-11320	PLUG			[illegible]
2		44-15194	1/4 [illegible] VALVE			[illegible]
8		46-11310	NUT			230
1		46-13396	3/4" ELBOW			236
10		46-17250	3/4" BHD UNION			116
7		46-17240	1/4" BHD UNION			116
4		46-14856	3/4" TEE			239
1		45-14511	1/4" TEE			236 [illegible]
20		45-12436	3/4" UNION			116
18		45-12406	1/4" UNION		(1) ANGEL MANUFACTURING CO SALEM, MASS.	116
2		MS24509H12	TEE		(2)	140
5		MS27[illegible]-0058-0409	CAP ASSY		(1)	116
23		MS27[illegible]-0055-0803	CAP ASSY		(1)	116
65		AN924-8J	NUT			116
164		AN924-4J	NUT			116
2		MS24401J8	ELBOW		(1)	[illegible]
10		MS24401J4	ELBOW		(1)	[illegible]
1		MS24583J8	TEE		(1)	230
1		MS24577J56	REDUCER			230
4		MS24403J4	CROSS			[illegible]
19		MS24402J8	TEE			116
8		MS24402J4	TEE			116
16		MS24583J4	BHD UNION			116
12		MS24530J4	BHD TEE		(1)	116
-001		GW10-002200	INSTALLATION			-

(22) 22 TO EXPEDITE DELIVERY, ALL PROCURED ITEMS MAY BE CLEANED IN HOUSE (ROCKWELL INTERNATIONAL, SPACE DIVISION) PER MA0110-501 LEVEL 600 PLANNING VERIFY.

(11) 21 SEE DRAWING GS10-002200 FOR VALVE DESIGNATION & PART NUMBERS. MAJORITY OF VALVES INSTALLED BY FACILITY CONTRACT.

20. REF DRAWING GP10-300016 FOR GSE/GSE/FDS INTERFACE.

QTY	CODE IDENT	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	MATERIAL	DATA: SPECIFICATIONS, SHEET, NOTES, SUPPLIERS	ITEM
49		1/4-20 x 4.00	HEX HD STL CAP SCREW		UNITRUT CORP WEYNE, MICHIGAN	116
2		45-11438	REDUCER		ANGEL MANUFACTURING CO SALEM, MASS. (1)	223
(17)(2) 5		CPX 90398	PLUG		AEROQUIP CORPORATION ERIE, PA (1)	
8		MS27[illegible]-0004-0003	QUICK DISCONNECT		(1)	183
3		MS27[illegible]-0024-0007	QUICK DISCONNECT		(1)	183
8		MS28774-110	SPLIT RING			
1		MS28778-12	O-RING		(1)	140
(17)(2) 1		MT[illegible]	BALL VALVE		[illegible] (1)	[illegible]
8		6010-002226-146	TUBE ASSY			[illegible]
1		-146				189
1		-149				131
1		-142				133
1		-141				131
1		-140				133
1		-139				131
6		-138				187
6		-136				139
1		-134				133
1		-132				133
1		6010-002226-[illegible]				133
12		6010-002215-002				170
24		6010-002215-001	TUBE ASSY			170
1		6010-002211-001	PANEL			176
1		6010-002209-001	MANIFOLD			187
1		6010-002208-001	PANEL			80
1		6010-002207-001				184
1		6010-002206-001				188
1		6010-002205-001				[illegible]
1		6010-002204-005				68
1		6010-002204-002				[illegible]
1		6010-002204-001	PANEL			[illegible]
(17)(1) 4		MV60T108B	VALVE		CIRCLE SEAL, BURBANK, CA	177 [illegible]
(17)(2) 6		MV80T108B	VALVE		CIRCLE SEAL, BURBANK, CA	[illegible]
1		8410-002208-170	TUBE ASSY			81
		-169				81
		-168				86
1		6010-002209-167	TUBE ASSY			89
-001		GW10-002200	INSTALLATION			-

15. A MINIMUM OF 10% OF ALL WELDS SHALL BE X-RAYED. IF MORE THAN 10% ARE UNACCEPTABLE, ADDITIONAL INCREMENTS OF 10% OF THE REMAINING WELDS SHALL BE X-RAYED UNTIL LESS THAN 10% ARE REJECTED.

18. WELD SYMBOL PER STD 50C002GP

(9) 17 WELD, CLEAN AND INSPECT PER ASME/BOILER CODE, SECTION 8.

(8) 16. TO BE USED FOR CLAMPING TUBE ASSYS TO EACH OTHER FOR ADDED SUPPORT.

GW10-002200 | SHT 1 | REV

15 | 14 | 13 | 12 | 11 | 10 | 9

New Processes Are Required For Cleaning & Verification

- For Precision Cleaning In Palmdale;
  - Piece Parts Will Be Cleaned Using Aqueous Based Detergents & Ultrasonics
  - Assemblies & Sub-Assemblies Will Be Cleaned Using Vertrel MCA

- For Cleanliness Verification In Palmdale;
  - All Verification Work Will Be Done Using The Vertrel MCA

Many Potential Contaminants Affect Palmdale Cleaning

- Contaminants Utilized For Precision Clean Evaluations
  - Braycote 601 - Fluorinated Grease
  - Dow Corning DC-33 - Silicone Grease
  - Mil-H-83282 Hydraulic Fluid - Medium Hydrocarbon
  - Mil-H-5606 Hydraulic Fluid - Medium Hydrocarbon
  - Houghto Draw Bending Oil - Heavy Hydrocarbon
  - Titan Lube Bending Oil - Heavy Hydrocarbon

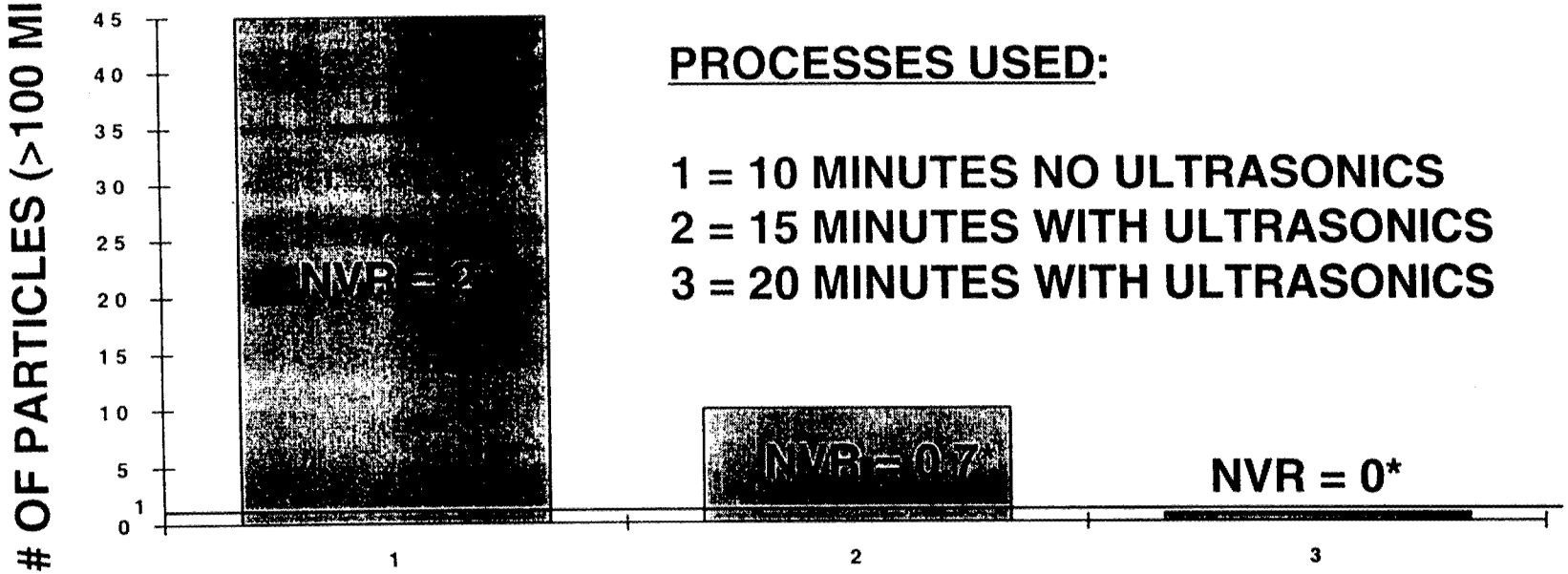
- Contaminants Utilized For Precleaning Evaluations
  - Mill Markings - Solvent Based Ink
  - Dykem - Solvent Based Dye
  - EDM Cutting Fluid - Water/Hydrocarbon Emulsion
  - Duct, Aluminum, & Masking Tape - Tape Residue
  - GS-37 Sealant - Vacuum Seal Putty
  - Braycote 601 & DC 33 Greases

Orbiter Frequently Requires Cleanliness Level 100A

Cleanliness Level	Particle Size (microns)	Maximum Number of Particles per Sample	Maximum NVR per 100 ml
100A	< 25	No silting	1 mg
	25-50	68	
	>50-100	11	
	>100, Nonmetallic	1	
	>100, Metallic	0	

AQUEOUS PRECISION CLEANING WITH ULTRASONICS MEETS CLEANLINESS REQUIREMENTS

- 8 Types of Detailed Parts Considered
- 7 Contaminating Agents Applied
- Aqueous Process Developed During FY 1995 Utilized
  - Brulin Cleaner
  - Deionized Water Rinse
- Particulate Requirement = 1 (<100um) Per 100 ml Max
- NVR Requirement < 1 mg/100 ml



PROCESSES USED:

1 = 10 MINUTES NO ULTRASONICS
2 = 15 MINUTES WITH ULTRASONICS
3 = 20 MINUTES WITH ULTRASONICS

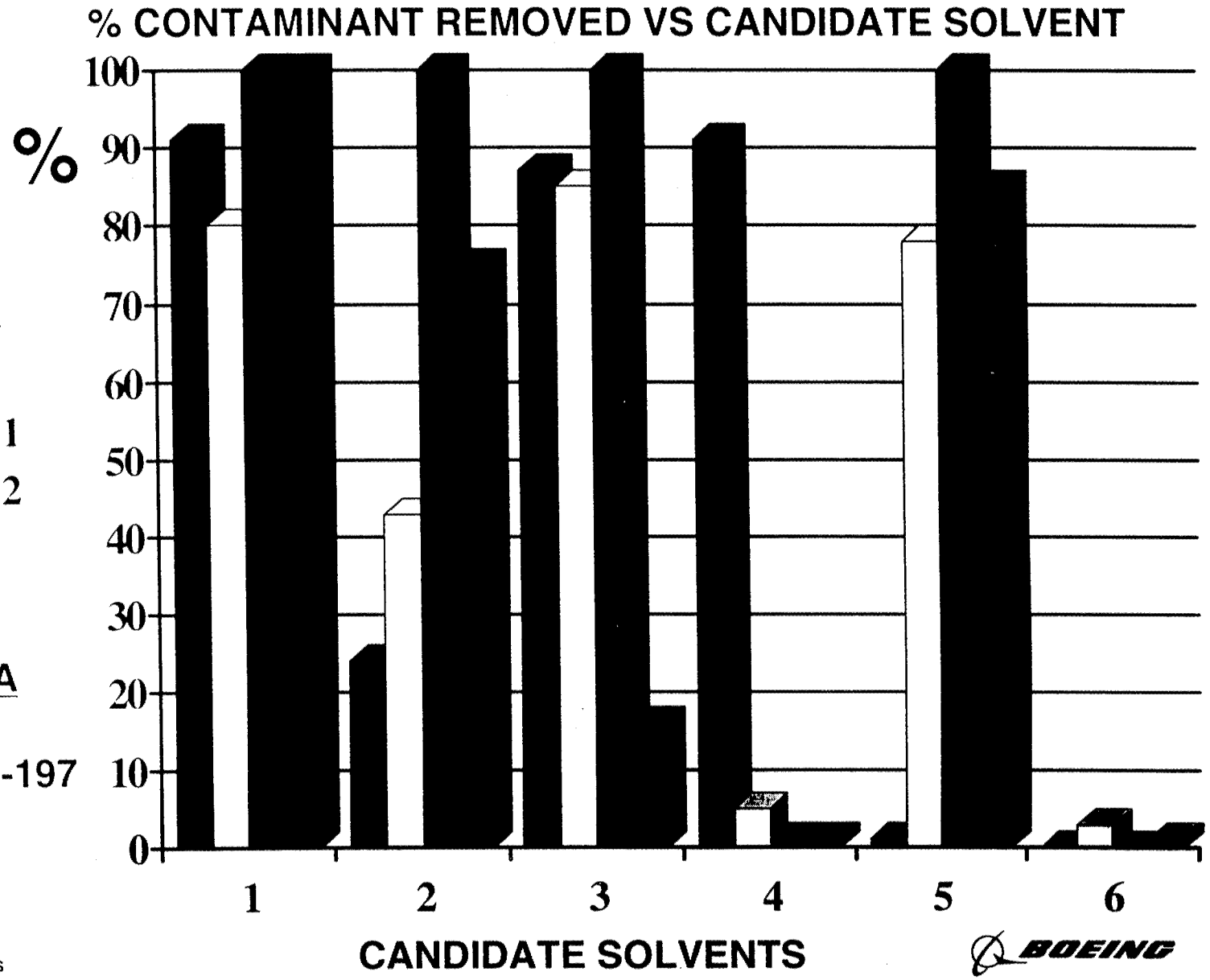
* = MG/100 ML

9 Verification Solvents Tested For Performance

Candidate Fluids
Freon TF (CFC 113)
DuPont **Vertrel XF** (HFC 43-10 *mee*)
DuPont **Vertrel MCA** (HFC 43-10 *mee* & trans 1,2-dichloroethylene azeotropic mixture, both with and without nitromethane)
Asahi Glass Asahiklin **(AK) 225** (HCFC 225 *ca* & *cb*, 45:55)
3M **HFE 7100** (n- & iso-perfluorobutyl methyl ether)
3M **HFE 7100 & trans** 1,2-dichloroethylene azeotropic mixture
EnviroTech Int'l **Ensolv** (halocarbon)
EnviroTech Int'l **Ensolv & Petroferm** ART-98 (hydrocarbon cosolvent)
Albemarle **Abzol** VG

Lab Data:

VERTREL MCA, & AK 225 EFFECTIVE ON ORBITER CONTAMINANTS



■ Flourocarbon
□ Silicone
■ Hydrocarbon 1
■ Hydrocarbon 2

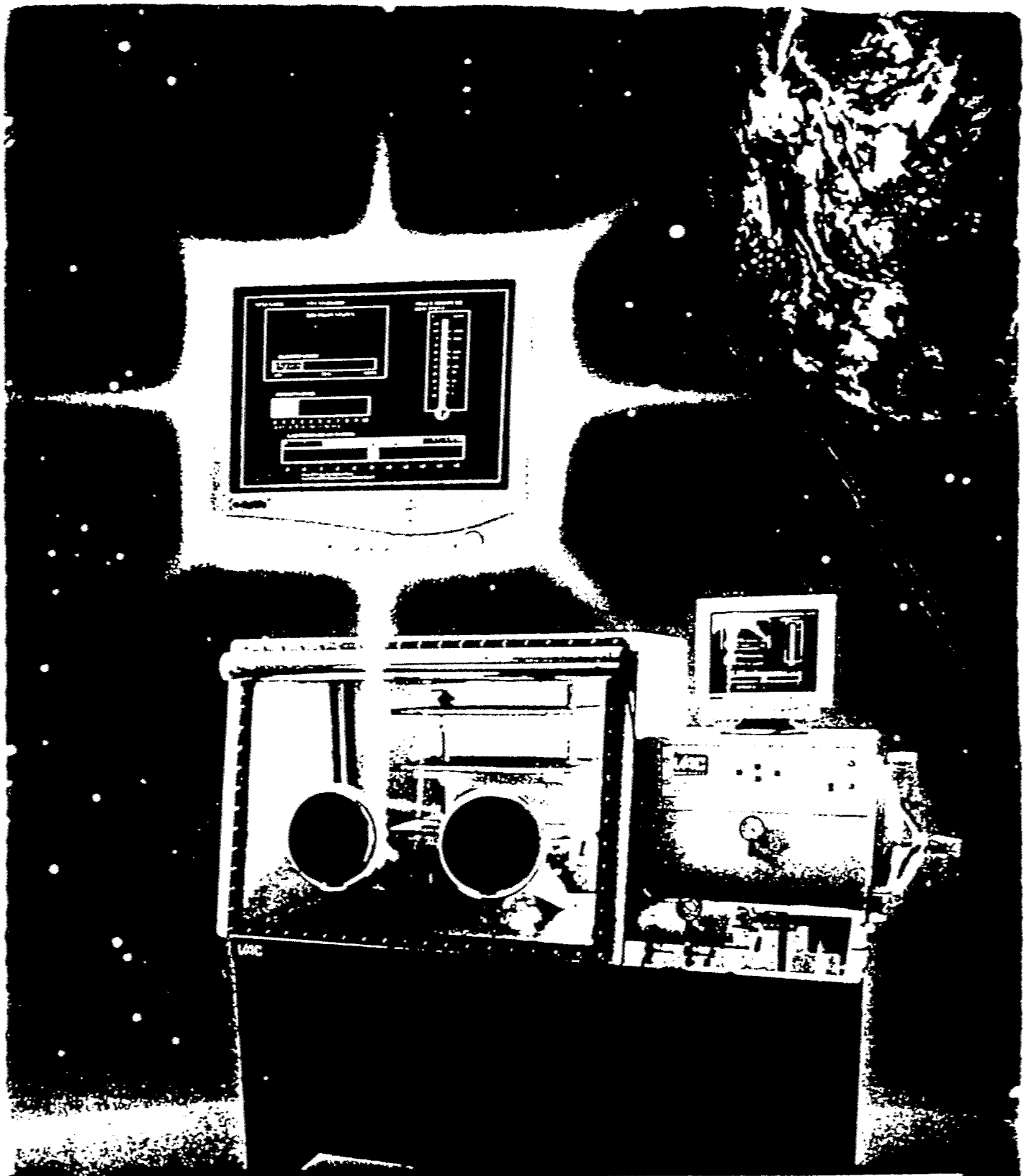
1=FREON 113
2=VERTREL MCA
3=AK 225
4=TRIBOLUBE F-197
5=BOROTHENE
6=NO SOLVENT

Proposed CFC-113 Replacement Processes Meet Palmdale Requirements

- BNA Proposes Aqueous Cleaning For Detail Parts
  - LTR 5985-2495 - Brulin 815GD Is A Superior Detergent
  - LTR 6333-4024 - Brulin Can Precision Clean Tubing
  - LTR 6512-4060 - Brulin Can Precision Clean Tubing
  - LTR 6609-4088 - Brulin Can Clean Misc. Details
  - LTR 6853-4075 - Brulin Compatibility
  - WSTF, KSC, Rocketdyne, & Industry Success
- BNA Proposes Vertrel MCA & AK 225 For Cleaning Assemblies, Sub-Assemblies & For All Verification
  - LTR 6608-4083 - Vertrel & 225 Recommended For Cert.
  - LTR 6887-4097 - HFE 7100 Not Recommended For Cert
  - LTR 6718-2000 - Vertrel (Stabilized) & 225 Certified
  - LTR 6933-2000 - HFE 7100 Failed Cert. Testing
  - LTR 6673-4093 - Vertrel & 225 Compatibility
  - WSTF-IR-97-0078 - HFE 7100 Compatibility

Palmdale Certification Requires Additional Equipment

- Cleaning System Will Allow Solvent Use & Control
  - Large & Small Glove Boxes
  - Enclose & Ventilate Flex Line Tank
  - Distillation Recovery Unit
- Facility Will Be Changed To Accommodate New Solvent
  - Construct Wall To Segregate The Cleaning Area
  - Relocate Existing Equipment
- If HCFC 225 Is Ever Utilized New Building Systems Needed
  - One Additional Air Handler (H.V.A.C.)
  - Exhaust System Enhancements
  - Solvent Monitoring Equipment

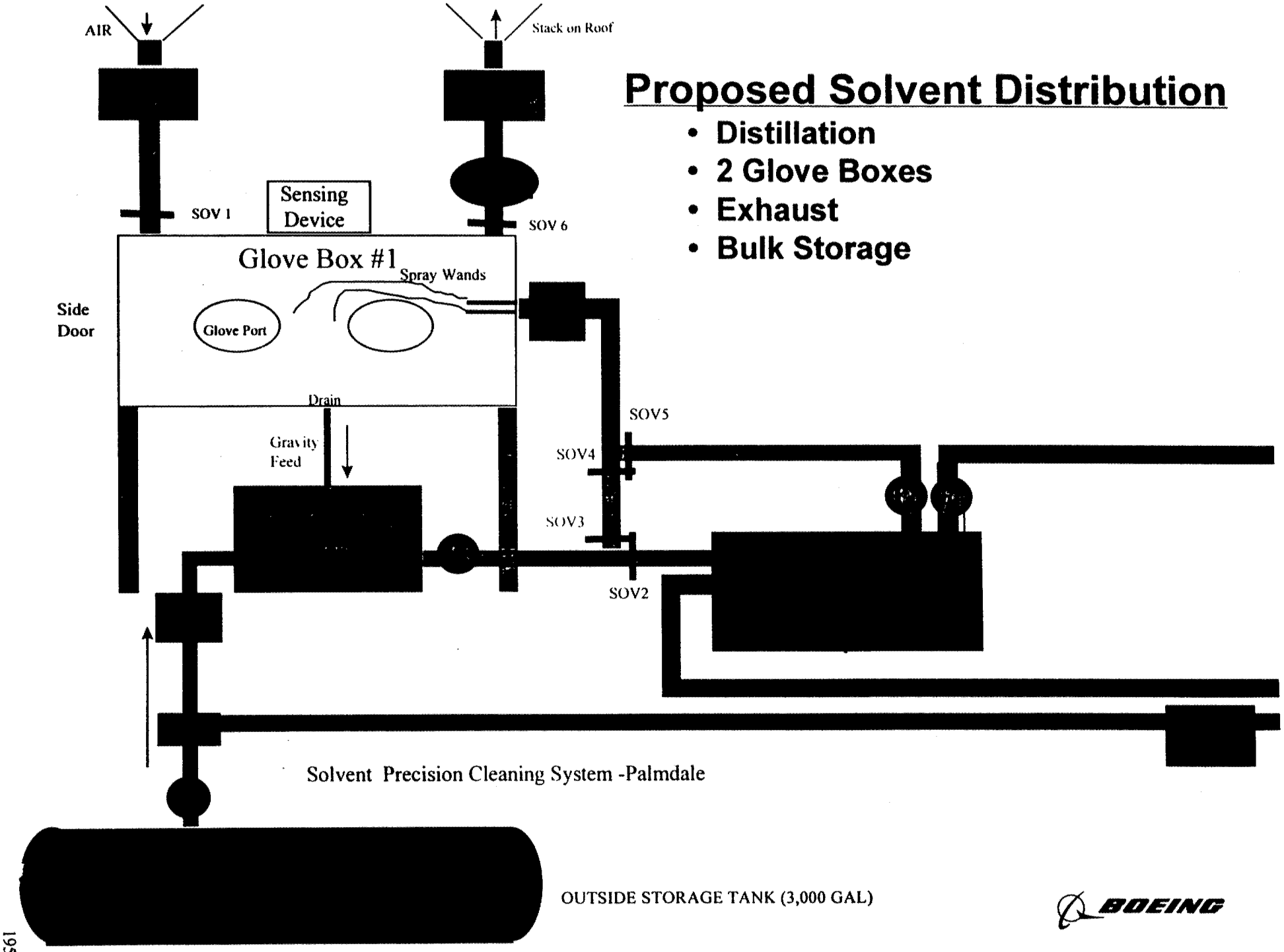


VAC

Controlled Atmosphere Technology for the 21st Century

Proposed Solvent Distribution

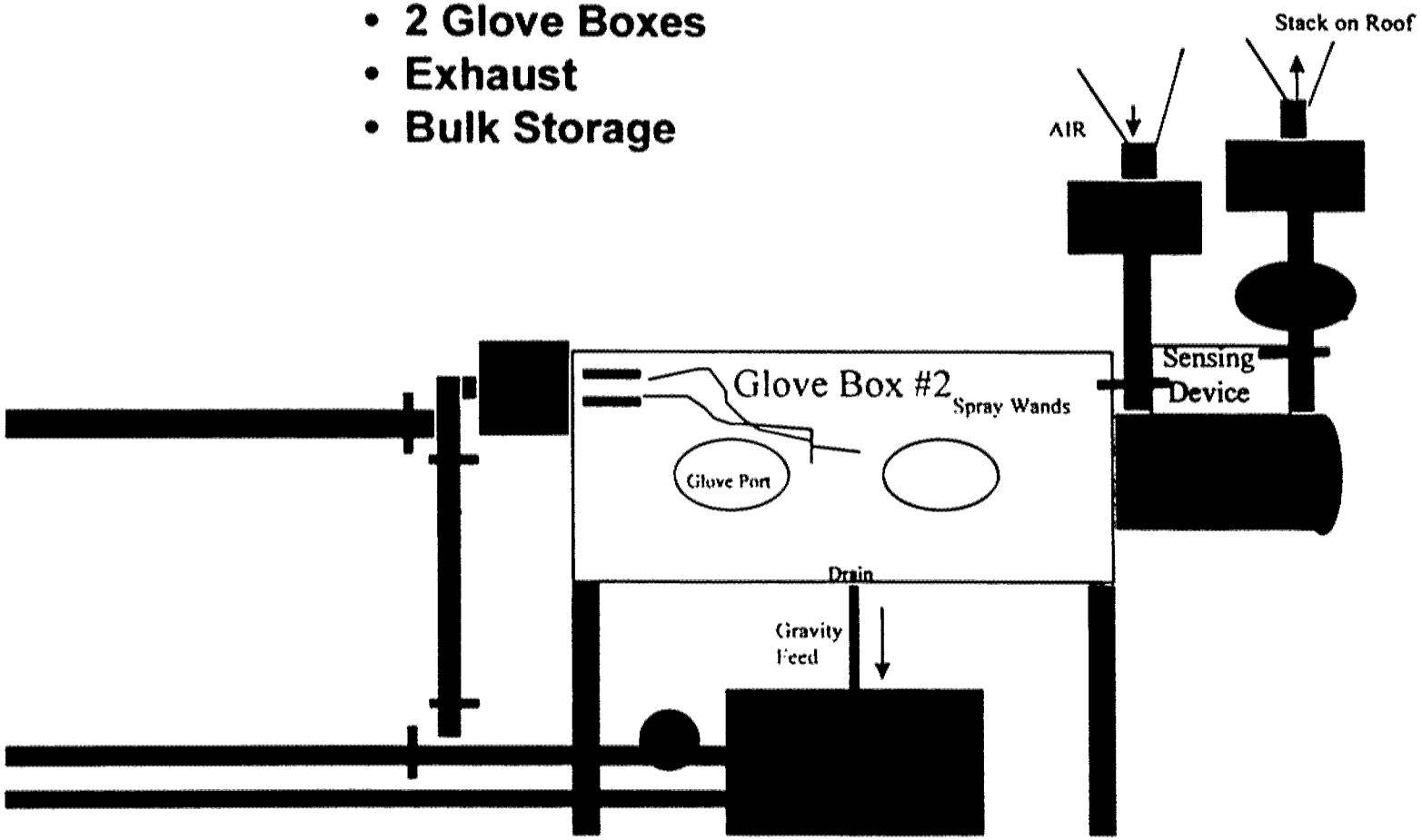
- Distillation
- 2 Glove Boxes
- Exhaust
- Bulk Storage

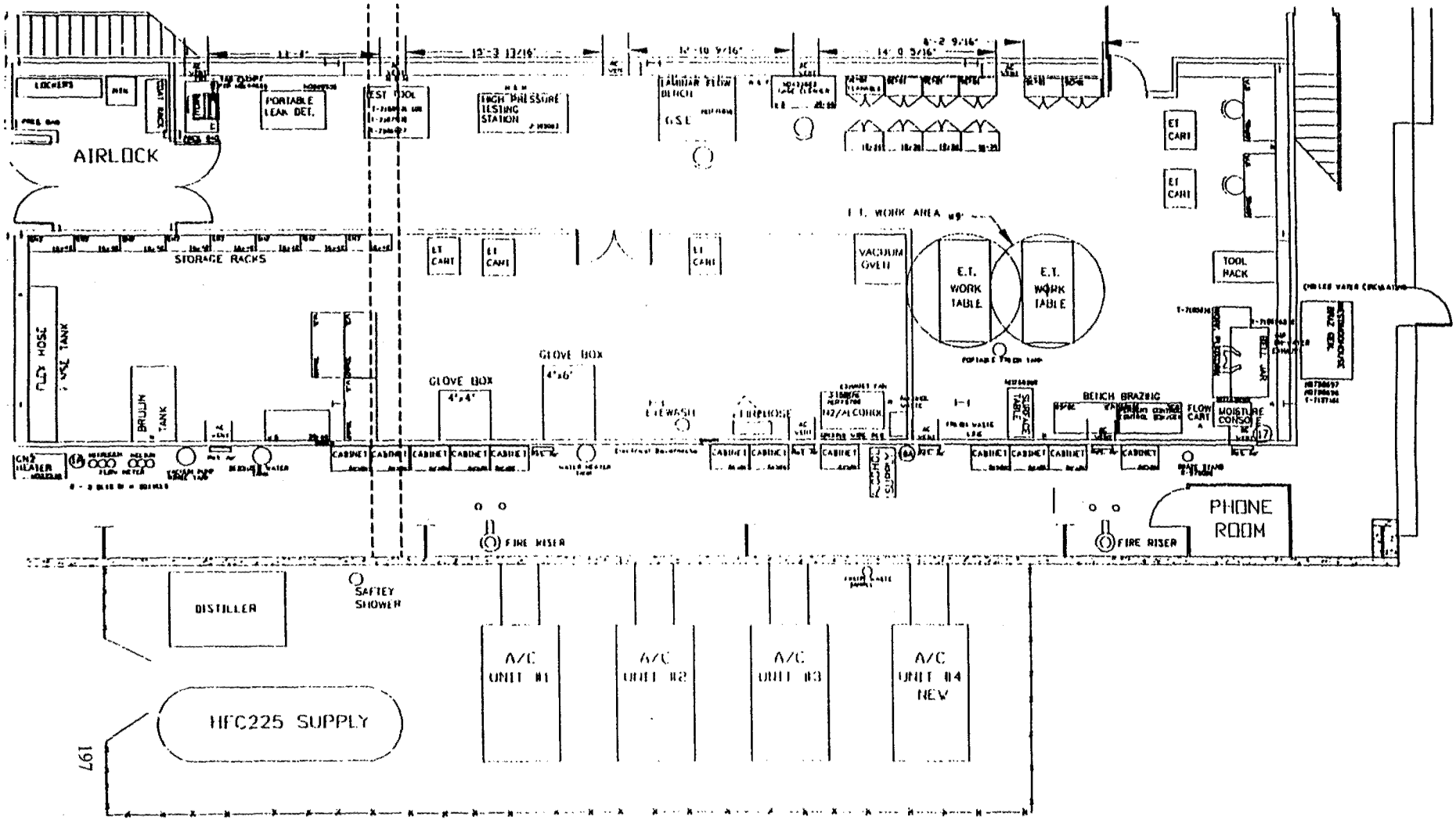


BOEING

Proposed Solvent Distribution

- Distillation
- 2 Glove Boxes
- Exhaust
- Bulk Storage




AIRLOCK
LOCKERS
PORTABLE LEAK DET.
EST TOOL
HIGH PRESSURE TESTING STATION
LAMINAR FLOW BENCH
GSE
ET CART
ET CART
STORAGE RACKS
ET CART
ET CART
ET CART
E.T. WORK AREA
VACUUM OVEN
E.T. WORK TABLE
E.T. WORK TABLE
TOOL RACK
FLEX HOSE
BRUSH TANK
GLOVE BOX 4'x4'
GLOVE BOX 4'x6'
EYEWASH
FIREHOSE
N2/ALCOHOL
SURFACE TABLE
BENCH BRAZING
FLOW CART
MOISTURE CONSOLE
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
CABINET
FIRE RISER
FIRE RISER
PHONE ROOM
DISTILLER
SAFTEY SHOWER
A/C UNIT #1
A/C UNIT #2
A/C UNIT #3
A/C UNIT #4 NEW
HFC225 SUPPLY

Over 180 Documents Must Be Updated

- Paperwork Implementation Will Utilize A Streamlined Approach Due To Limited Time & Budget

- Palmdale Orbiter Documents To Be Changed Include:
  - ML Specs (for Test & Check-Out/Installation) - 65
  - MPP (BNA Processing Procedures) - 60
  - Parker Documents (for 17 Inch Program) - 20
  - V070/G070 - 100 (Estimated)
  - MA/MF Specs - 20
  - OMRSD - 9 (Assume 9 Fluids Subsystems)
- Ground Support Documents To Be Changed Include:
  - ML Test & Check-Out/Installation - 10
  - MPP (BNA Processing Procedures) - 4
  - MA/MF Specs - 5
  - MT & QPP Quality Documents - 18

Summary

- Palmdale Processes Flight, GSE TY I, & GSE TY II Hardware
- Precision Cleaning Will Be Done With Brulin 815 GD For Piece Parts & Vertrel MCA For Assembled Hardware
- Cleanliness Verification Will Be Done With Vertrel MCA
- Laboratory Qualification Work Is Complete
- Palmdale Certification & Paperwork Implementation Is In Work
  - Over 180 Documents Must Be Updated

Energetic Ingredients Processing in Liquid Carbon Dioxide

Robert E. Farncomb and George W. Nauflett

Indian Head Division
Naval Surface Warfare Center
Indian Head, MD 20640-5035

ABSTRACT

NSWC's Green Chemistry program requires preparation of energetic materials containing C-nitro, N-Nitro, and O-Nitro moieties using liquid carbon dioxide (L-CO_2) as the processing solvent. L-CO_2 replaced methylene chloride as the solvent in nitrations of 3-methyl-3-oxetane-methanol, glycidol, γ-cyclodextrin, and cotton linters with dinitrogen pentoxide (N_2O_5) and anhydrous nitric acid. Nitration of acid-sensitive substrates with N_2O_5 or HNO_3 are generally carried out at low temperatures in organic media, particularly chlorinated hydrocarbons or Freons. With substrates possessing both strained rings and labile groups, the reaction can be "fine-tuned" using L-CO_2. Because nitrate esters are acid-sensitive, sodium fluoride was used to form a complex with the nitric acid resulting from the nitration with N_2O_5.

The 3-nitratomethyl-3-methyl oxetane (NIMMO) was subjected to polymerization conditions in liquid carbon dioxide (L-CO_2), using gaseous boron trifluoride (BF_3) catalyst. Polymerizations in L-CO_2 simplifies solvent removal and product purification. The L-CO_2 on the small-scale batches is not recycled, but vented to the atmosphere. Supercritical carbon dioxide (SC-CO_2) was used for oligomer extraction and fractionation of the polymers.

The main focus of this effort was the design, construction, and evaluation of the processing equipment. No effort was made to optimize the conditions for polymer synthesis in carbon dioxide.

OBJECTIVE

Our principal objective is to develop and implement environmentally benign synthesis and processing methodologies for energetic materials manufacturing, using L-CO_2/SC-CO_2 as the processing solvent. This includes the elimination of toxic solvents, volatile organic compounds (VOCs), ozone-depleting substances (ODSs) and hazardous air pollutants (HAPs) during processing.

BACKGROUND

Carbon dioxide is an economical, non-toxic, and non-flammable solvent. Carbon dioxide is derived from a number of sources, including natural wells, and from industrial processes as a by-product. It is non-regulated as a waste by local, state, and federal environmental agencies. It is an environmentally responsible alternative to VOCs and ODSs for nitrations and polymerizations. Liquid carbon dioxide (L-CO_2) replaced methylene chloride as the solvent in nitrations with dinitrogen pentoxide (N_2O_5) and anhydrous nitric acid. This new L-CO_2 nitration procedure overcame many of the drawbacks of conventional mixed-acid (HNO_3/H_2SO_4) media when dealing with acid-sensitive substrates. Sodium fluoride was used to complex with nitric acid resulting from the N_2O_5 nitrations[1].

Shown in Figure 1 is a diagram of the bench-scale carbon dioxide nitration system used. It was constructed from component parts purchased from about forty different companies. The vessels and pumps were developed by Thar Design Inc. Pittsburgh, PA on an NSWC/IHD Phase I & II SBIR contracts. A 100-liter L-CO_2/SC-CO_2 pilot plant developed by Thar Design under the SBIR program was recently shipped to Indian Head and is currently being assembled. The 100-liter vessel has a pressure rating of 9,000 psi (610 atm) at 300°F (150°C). The SBIR-developed equipment used is listed below:

- Pressure vessels with finger-tight closures
  - material of construction: 17-4PH stainless, which is 60% stronger than 300 series stainless steel
  - spring-loaded graphite-reinforced Teflon cup seals
- Computer-controlled high-pressure carbon dioxide pump
- Agitator shafts (ceramic-coated for low friction and wear)
- Computer-controlled L-CO_2 pumps (0.1 to 200 grams/min)
- Cyclone separators
- Electronic flow meters
- Computer-controlled back-pressure regulators

Almost all commercially available vessels have metal-to-metal seals that require high-torque to seal, or use elastomers that swell in a high-pressure carbon dioxide environment.

The unlimited potential uses of carbon dioxide as a reaction media and processing solvent have been recognized for more than twenty years, and is an area which has attracted great interest[2]. The use of liquid carbon dioxide has been almost exclusively limited to the beverage and fire-fighting industries. Synthesis and processing of energetics, in many cases, require that temperatures as low as -55°C be used. The triple point of carbon dioxide is -56°C and 5 atm (75 psi) and its critical point is 31.1°C and 73 atm (1074 psi). L-CO_2 exists when the pressure and temperature are above the triple point, and either or both the temperature and pressure are below the critical point. A density close to the material being processed is desirable. Shown in Figure 2 are the densities of carbon dioxide at -10 through 75°C and at 200 through 4,000 psi[3]. The use of dinitrogen pentoxide (N_2O_5), anhydrous nitric acid, and carbon dioxide (50 to 140 atm) requires special handling techniques. O-Nitration of alcohols is classically carried out with nitric acid alone, or, more frequently, with mixed acid (mixtures of nitric and sulfuric acids). Selective nitration of materials with acid-sensitive moieties are commonly performed with N_2O_5 at low temperature in halogenated solvents[1]. Even though the use of N_2O_5 in L-CO_2 as nitrating agent is clean, versatile, and offers significant environmental benefits, no nitrations using N_2O_5, anhydrous HNO_3, and their admixture in L-CO_2 were previously reported.

Both N_2O_5 and anhydrous HNO_3 are soluble in L-CO_2, which allows them to be added directly to the substrate being nitrated. (Refer to Figure 1.) Preparation of N_2O_5 by the dehydration of HNO_3 with phosphorous pentoxide[1,4], as shown in eq 1, followed by distillation at 50°C, resulted in a product of unacceptable purity. It is anticipated that the N_2O_5 can be extracted with L-CO_2 at 0°C, since phosphoric acid and phosphorous pentoxide have little or no solubility in L-CO_2. The use of L-CO_2 for extraction eliminates the need for distillation of N_2O_5. The preferred method for the preparation of N_2O_5 is the gas-phase oxidation of N_2O_4 with ozone[4,5], as shown in eq 2.

$$6\,HNO_3 + P_2O_5 \longrightarrow 3\,N_2O_5 + 2\,H_3PO_4 \qquad (1)$$

$$N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2 \qquad (2)$$

The yields for both these reactions are at the 90% level or better. N_2O_5 is the anhydride of nitric acid, and is a white, thermally-labile, crystalline solid. In the pure solid state, N_2O_5 exhibits a half-life of 10 days at 0°C, and 10 hours at 20°C. The solid readily sublimes, having a vapor pressure of 51 mm at 0°C, 200 mm at 20°C, and 760 mm at 32.5°C. The chemical properties of pure nitric acid are: sp gr 1.51; mp -41.6°C; bp 86°C.

A Navy Patent disclosure has been submitted which covers the nitrations of various substrates, including polyols, in L-CO_2 with N_2O_5, anhydrous HNO3, and its admixtures[6].

The polynitrooxetane class of energetic polymers was first discovered by G.E. Manser[7,8]. Shown in Table 1 are the reported[9] properties of PolyNIMMO. These polymers were prepared using 5 to 20 monomer-to-methylene chloride ratios. Methylene chloride is an ozone-depleting substance (ODS).

Table 1. PolyNIMMO Physical and Chemical Properties[9]

Density		1.26 g/cc
Viscosity at	30°C	1500 P
	40°C	560 P
	60°C	100 P
Glass Transition (T_g)*		-25°C
Molecular Weight		5500
Functionality		~2
Heat of Formation		-73.9 kcal/mol
Heat of Explosion		28.8 kcal/mol
Onset of Decomp*		170°C
Oxygen Balance		-115.7%

*Differential Scanning Calorimetry

RESULT AND DISCUSSION

The use of L-CO_2 as a solvent for N_2O_5 and anhydrous HNO_3 offers significant safety and environmental benefits over conventional nitrating agents (such as mixed acid) used to manufacture energetic materials.

The new L-CO_2 nitration procedure generates less waste because N_2O_5 reacts instantly with the resulting water, forming nitric acid, eliminating the need for sulfuric acid. After the nitration, excess N_2O_5 and byproduct nitric acid were extracted with a flow of L-CO_2, eliminating the need to quench the reaction mixture with large volumes of water. Shown in Table 2 are the results of N_2O_5 and nitric acid nitrations, with and without sodium fluoride.

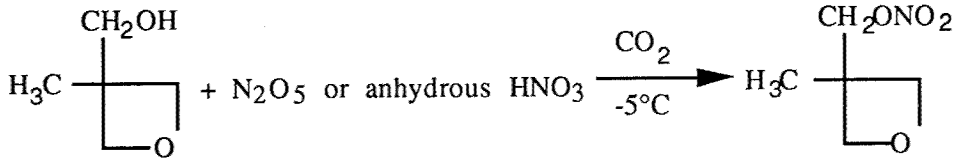
Table 2. Results of N_2O_5 and Nitric Acid Nitrations With and Without NaF

Material nitrated in 20 gram batches, 10% excess nitrating agent at 68 atm & -10°C

Material	Yield %			
	With NaF		Without NaF	
	N_2O_5	HNO_3	N_2O_5	HNO_3
3-Methyl-3-Oxetane-Methanol	-	-	95	72
Poly(3-Methyl-3-Oxetane-Methanol)	-	-	90	-
Glycidol	-	-	90	-
γ-Cyclodextrin	91	38	45	12
Cotton Linters	85	-	-	-

The monomer 3-methyl-3-oxetane-methanol was nitrated with both N_2O_5 and anhydrous nitric acid, as shown in eq 3, using L-CO_2 as the processing solvent, producing the monomer 3-nitratomethyl-3-methyl oxetane (NIMMO). The NIMMO typically contained 9.3% nitrogen (9.5% theoretical).

A black coating formed on the 316 stainless steel parts the first time the equipment was used for N_2O_5 nitration in L-CO_2, but not on the 17-4-PH stainless steel parts. The coating did not change after subsequent nitrations.



(3)

3-methyl-3-oxetane-methanol

3-nitratomethyl-3-methyl oxetane (NIMMO)

The NIMMO was subjected to polymerization conditions in liquid carbon dioxide (L-CO_2) using gaseous boron trifluoride (BF_3) catalyst. Shown in Figure 3 is a diagram of the equipment used. The reactants were added stepwise to the pressure vessel:

1. 1,4-butanetriol
2. carbon dioxide (70 atm at -20°C)
3. gaseous BF_3 using a 10-mL loop and 6 port valve at 80 atm CO_2
4. monomer (pumped 1 mL/min)
5. water (pumped at 1 mL/min)
6. the pressure was released (over 1 hour)

Polymerizations in L-CO_2 simplifies solvent removal and purification. No external energy is required for processing solvent removal. Supercritical carbon

dioxide ($SC-CO_2$) was used for oligomer extraction and fractionation of the polymers. The fractions collected are shown in Table 3. The fractions were characterized by H-NMR analysis.

Table 3. Fractions Collected in NIMMO Preparation

NIMMO grams	SC-CO2 grams	Pressure atm	Temp °C	Comments
3.5	-	170	5	viscous oil
1.3	316	136	60	viscous oil
2.8	1015	170	60	viscous oil
1.8	656	204	60	white solid
3.6	-	-	25	viscous oil from 200 mL acetone

γ-Cyclodextrin (γCD) is a large ring-structure containing eight glucose molecules connected via alpha 1,4-glycosidic linkages. It has a molecular weight of 1297 and has 24 hydroxyl groups. γCD was nitrated with both N_2O_5 and anhydrous nitric acid using $L-CO_2$ as the processing solvent, producing γ-Cyclodextrin nitrate (γCDN). Better yields (45% verses 91%) and 13.5% nitrogen content (14% theoretical) were obtained when sodium fluoride was used during the nitration. Sodium fluoride complexes with the byproduct nitric acid by hydrogen bonding. The nitric acid-sensitive γCDN was protected by the sodium fluoride/nitric acid complex. The yields of γCDN demonstrate the benefit of using sodium fluoride during the nitrations. The γCDN typically contained 13.5% nitrogen content and the DSC had an exotherm (3,090 joules/g) at 192°C.

CONCLUSION

It has been successfully demonstrated that the $L-CO_2/SC-CO_2$ process development units used for the synthesis and processing of energetic materials functioned as designed. This equipment has a variety of applications in the synthesis and processing of various energetic materials. O-Nitrations of liquids and solids were successfully performed using N_2O_5 and anhydrous HNO_3. Carbon dioxide replaced halogenated solvents as the processing solvent in the nitrations.

ACKNOWLEDGMENTS

The financial support and the technical advice provided by Steve Mitchell NSWC/IHD, is gratefully acknowledged. We thank Tom Devendorf, Horst Adolph, and Al Stern for technical discussions.

REFERENCES

1 Caesar, G.V.; Goldfrank, M., "Nitration of Starches with Nitrogen Pentoxide in Presence of Sodium Fluoride", J. Am. Chem. Soc., Vol 68, 1946, pp 372-375.

2 DeSimone, J.M.; Maury, E.E.; Menceloglu, Y.Z.; McClain, J.B.; Romack, T.J; Combes, J.R., "Dispersion Polymerizations in Supercritical Carbon Dioxide", Science (Washington, DC), Vol 265, 15 July 1994, pp 356-359.

3 SF-Solver, Version 2.5.1, ISCO Inc., Lincoln, NE, 1991.

4 Fischer, J.W., "The Chemistry of Dinitrogen Pentoxide," *Nitro Compounds: Recent Advances in Synthesis and Chemistry*; Feuer, H.; Nielson, A.T., Eds.; VCH Publishers, Inc., NY, 1990; pp 267-365.

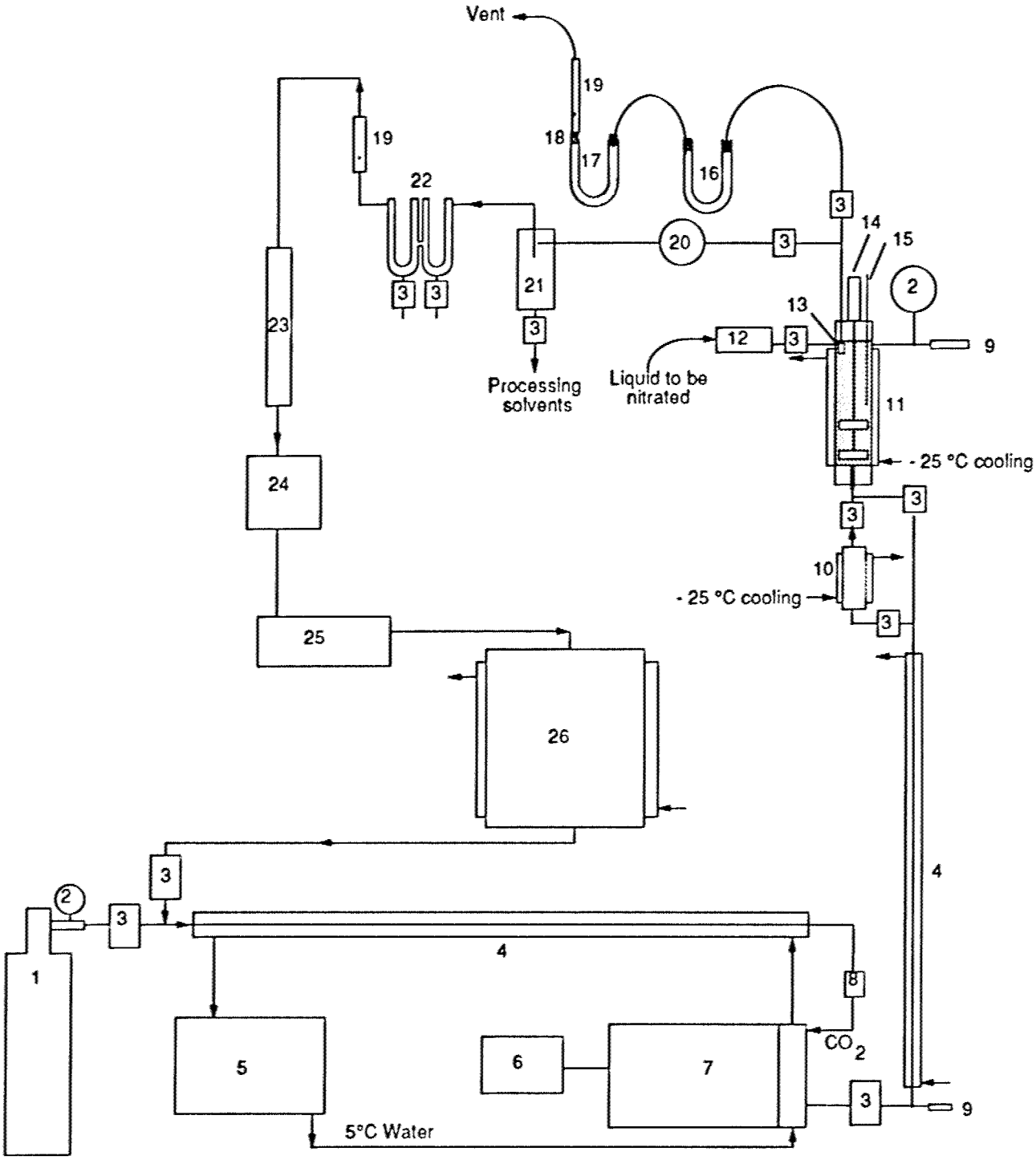
5 Devendorf, T.E. and Stacy, J.R., "Pilot-Plant-Scale Continuous Manufacture of Solid Dinitrogen Pentoxide"; *Nitration Recent Laboratory and Industrial Development*; Albright, L.F.; Carr, R.V.C.; Schmitt, R.J., Eds.; ACS Symposium Series 623, 1996, pp 68-77.

6. Nauflett, G.W., Farncomb, R.E., Patent Disclosure Navy Case No. 79,009.

7 Lindsay, G.A.; Talukder, M.A.H.; Nissan, R.A.; Quintana, R.L.; Hasting, M.A.S.; Yee, R.A.; Nadler, M.P.; Atwood, A.I.; Reed, R.; Manser, G.E., "Energetic Polyoxetane Thermoplastic Elastomers: Synthesis and Characterization", Naval Weapons Center, NWC TP 6945, December 1988.

8 Manser, G.E.; Archibold, T.G.; Malik, A.A.; Carlson, R.P.; "Synthesis of Energetic Binders", Annual Report on Contract N000014-89-C-0281, November 1992.

9 Rhein, R.A., "Handbook of Energetic Polymers and Plasticizers", Naval Weapons Center, China Lake, CA, NWCTP6720, July 1986.



(1) CO_2 cylinder; (2) pressure gauge; (3) valve; (4) heat exchanger (concentric 1/8 and 3/8 inch tubing); (5) water chiller with recirculating pump; (6) computer pump controller; (7) high pressure pump (0 to 200 g CO_2/min); (8) 5μm filter; (9) rupture disk; (10) 100-mL pressure vessel with jacket; (11) 600-mL pressure vessel with three side-inlets (for additions, rupture disk, pressure gauge); (12) addition pump (0 to 40 mL/min); (13) filter; (14) air motor with tachometer and agitator; (15) thermocouple; (16) U-tube; (17) U-tube containing sodium carbonate; (18) rubber stopper; (19) flowmeter; (20) heated depressurization ; (21) cyclone separator; (22) Dry Ice trap; (23) carbon dioxide purification; (24) flowtotalizer (25) compressor; (26) 8-liter carbon dioxide storage vessel.

Figure 1. Bench Scale Carbon Dioxide Nitration System

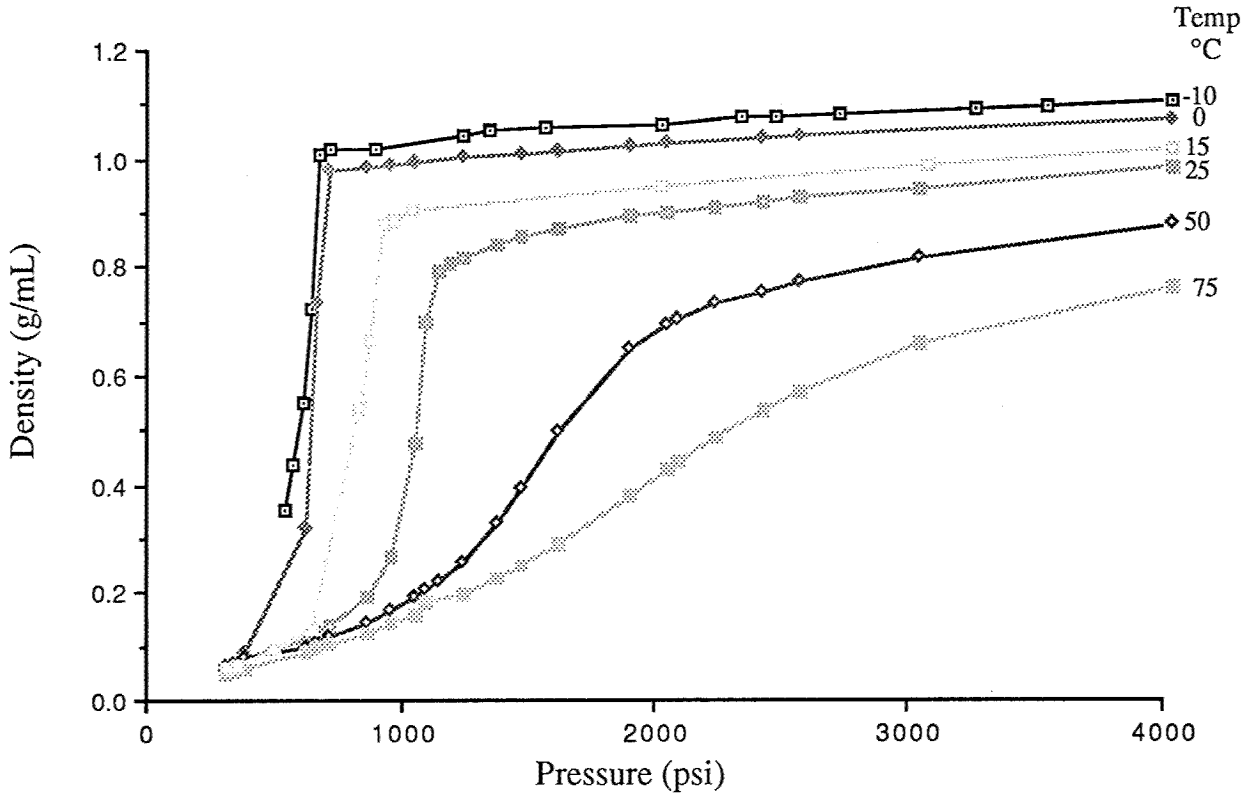


Figure 2. Density[3] of L-CO_2 at -10 to 75 °C

Hazardous Material Minimization in Adhesives and Sealants used in PATRIOT Missile System Maintenance

R.E. Morgan
AmDyne® Corporation
and
R.A. Hagler
U.S. Army Aviation and Missile Command

ABSTRACT

In response to Executive Order (EO) 12856, the Army is reviewing all weapon systems maintenance documentation to identify hazardous materials and develop alternatives for hazardous material minimization. The goal of the effort is to reduce hazardous material usage by 50% based on the quantities established in 1994. This paper describes the effort to identify the hazardous materials and more specifically focus on the minimization of EPA-17 listed materials in the adhesives and sealants used to maintain the PATRIOT Missile System. The process and resources available that are being used for this effort are described in detail.

BACKGROUND

In order to comply with EO 12856, all current technical documentation supporting the maintainability of the fielded PATRIOT Missile System has been reviewed and a database created that contains references to all Ozone Depleting Chemicals (ODCs) and other potentially hazardous materials. This document examines the effort to minimize the hazardous materials from all the adhesives and sealants used in maintaining the PATRIOT Missile System.

PLAN

The plan to reduce hazardous material usage in the PATRIOT Missile System consists of the following steps:

1. Identify and acquire all PATRIOT Missile System maintenance documentation under control of the U.S. Army Aviation and Missile Command
2. Review Documentation
3. Create ACCESS™/ORACLE Database and populate with information from document review and other sources
4. Search database for classes of HMs
5. Identify alternative materials
6. Recommend and coordinate changes through all approving parties

APPROVING BODIES

The main approving bodies that are involved in the changes are; the Depots, AMCOM Safety Office, Missile Research and Development Engineering Center (MRDEC), PATRIOT Project Office, and the Integrated Material Management Center (IMMC).

The first stop after an internal Environmental Technology Team (ETT) approval is the appropriate Depot, for the Patriot missile this is Red River Army Depot (RRAD); for the remainder of the system it is Letterkenny Army Depot (LEAD). If they do not approve the recommendation then any further action is meaningless since the depots are our ultimate customer. The AMCOM Safety Office is contacted next for their comments. Next, the alternative must be approved by a technical representative of the MRDEC. The final approval comes from the PATRIOT Project Office. The Project Office is the owner of the system and

they have their own Environmental, Safety, and Logistics people who must be satisfied with the recommendation. If the Project Office is satisfied, the changes are forwarded to IMMC who will make the proposed changes to the pertinent maintenance documentation.

If there are any objections to the proposed changes, the changes are returned to the ETT for further analysis.

TECHNICAL DOCUMENTS REVIEWED

The following number of technical documents were reviewed:

Table 1. Reference Documents

Document Type	Number Reviewed
Depot Maintenance Work Requirement (DMWR)	289
Technical Manual (TM)	114
Modification Work Order (MWO)	10
Technical Bulletin (TB)	6
Lubrication Order (LO)	2
Depot Manual (DM)	1
Depot Maintenance Reference List (DMRL)	1
Missile Interim Specification (MIS)	120
Drawings	843

DATABASE

The ETT's ACCESS™ database for PATRIOT, created by AmDyne personnel, contains 36884 entries. Each entry typically corresponds to one mention in a document of a potentially hazardous material. The materials in the database are broken down into the following categories:

- Acids/Alkalis/Oxidizers
- Adhesives and Sealants
- Cleaning Compounds and Solvents
- Corrosion Preventive Compounds
- Energetics
- Functional Fluids and Lubricants
- Paints/Varnishes/Coatings
- Soldering and Welding
- Other

Each entry has at least an item name, part number, military or commercial specification, or a National Stock Number (NSN) associated with it. By use of reference sources, such as the Federal Logistics (FEDLOG) or Master Cross Reference Data (MCRD) databases, all entries can eventually be associated with an NSN. The NSN then becomes the fundamental unit for referring to the materials.

REFERENCE SOURCES

With the NSN, one can identify the individual suppliers of materials. Four different reference sources that were used are listed below:

1. FEDLOG or MCRD Databases
2. Hazardous Material Information System (HMIS)
3. Hazardous Material Resource System (HMRS)
4. HAYSTACK Database

FEDLOG and MCRD

These CD-ROM based programs are supplied by the Defense Logistics Agency (DLA). They can be searched by NSN, part number, or item name. They also indicate the Commercial and Government Entity (CAGE) Code for the suppliers of each item. Unfortunately, only the Prime Contractor or Government Contractor and not the actual manufacturer are listed for some items.

Hazardous Material Information System (HMIS)

This CD-ROM based program is maintained by the Defense General Supply Center (DGSC). The program has Material Safety Data Sheets (MSDSs) for all of the hazardous material containing products that are stocked by the General Services Administration (GSA). The data can be searched by many criteria besides NSN. An example is a search by military or commercial specification or for a specific chemical ingredient. Some of the MSDSs are incomplete or slightly outdated and there are some minor errors in the system. The HMIS CD-ROMs are updated and distributed on a quarterly basis.

Hazardous Material Resource System (HMRS)

HMRS is a database provided by the Army Acquisition Pollution Prevention Support Office (AAPPSO). In addition to the HMIS information, this online database provides information on potential substitutes for specific NSNs.

HAYSTACK

HAYSTACK is produced by Information and Handling System, Inc., and is an extensive set of CD-ROMs which contain information on the government procurement system. Actual specifications and qualified vendor lists are found in this massive database.

DATABASE QUERY RESULTS

In the adhesives and sealants category there are 3447 records or hits in the database. These hits include reference to 34 different Missile Interim Specifications (referred here after as MIS Documents), 31 Military and Commercial Specifications and 12 products which do not have any specifications associated with them. A total of 144 different NSNs are listed in the documents. A breakdown of the various specifications and their applications is shown in Figure 1.

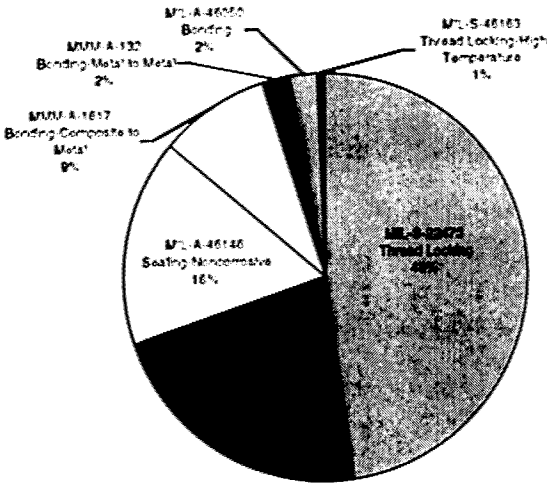


FIGURE 1 Specifications and Their Applications

The adhesives and sealants specified in MIS documents are used in a different manner. A little over one-third are used for bonding. Another third are used in operations where conductivity is a key issue or as a solder substitute.

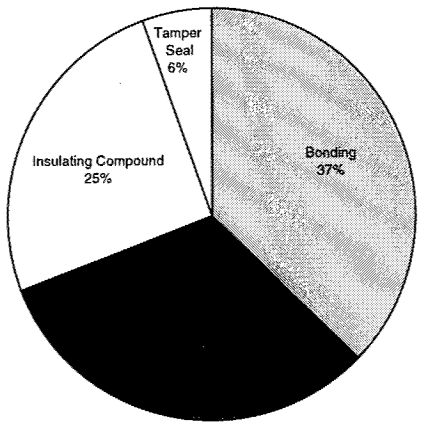


FIGURE 2. Missile Interim Specifications and their applications

One-fourth of the applications are as a thermal insulating compound and 6% are used for tamper sealing.

HAZARDOUS MATERIAL MINIMIZATION PRIORITIES

The pyramid shown in Figure 3 signifies the priority that AMCOM has chosen to apply in its Pollution Prevention effort. ODCs have the highest priority and have been identified and potential substitutes have been chosen for all adhesives and sealants used in the PATRIOT system. The next priority, and the main subject of this paper, is minimization of materials containing EPA-17 targeted chemicals. The final class of hazardous materials is those listed on Standardization Document 14 (SD-14). SD-14 consists of SARA Title 302 and 313 in addition to Class I ODCs and Volatile Organic Chemicals (VOCs). These hazardous materials will be considered with SARA Title 302 toxic materials and given more priority for replacement than SARA Title 313 materials.

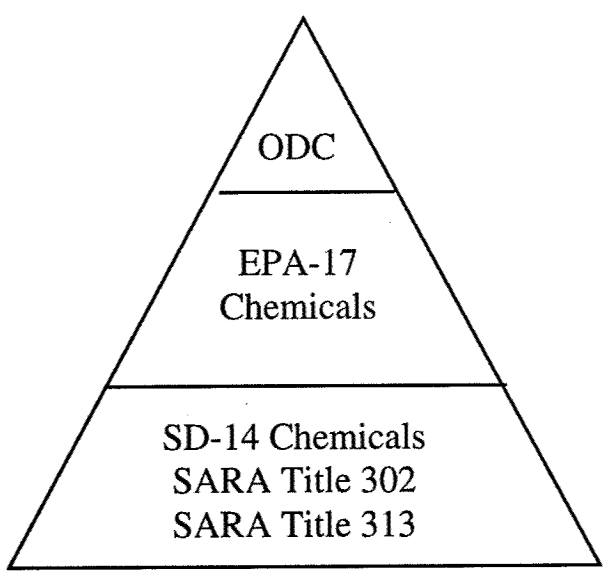


FIGURE 3. Hazardous Material Minimization Priorities

EPA-17 List

Table 2 lists the chemicals and chemical families that form the EPA-17 list of targeted chemicals.

Table 2 EPA-17 Chemicals

Benzene
Cadmium and Cadmium Compounds
Carbon Tetrachloride (Carbon "Tet")
Chloroform (Trichloromethane)
Chromium and Chromium Compounds
Cyanide Compounds and Hydrogen Cyanide
Lead and Lead Compounds
Mercury and Mercury Compounds
Methyl Ethyl Ketone (MEK or 2-Butanone)
Methyl Isobutyl Ketone (MIBK or Hexone)
Methylene Chloride (Dichloromethane)
Nickel and Nickel Compounds
Tetrachloroethylene (Perchloroethylene)
Toluene (Toluol or Methyl Benzene)
1,1,1-Trichloroethane (Methyl Chloroform, TCA)
Trichloroethylene (TCE)
Xylene (All isomers, Xylol or Dimethyl Benzene)

A search of our PATRIOT database indicated that one or more products from at least one supplier that met these specifications contained the targeted materials as shown in Table 3. GSA buys and stocks these adhesives and sealants from qualified suppliers. Purchases are made at random from different suppliers so there is always the chance that the material that ends up on the shop floor may contain a targeted hazardous material.

Table 3 Products containing EPA-17 Chemicals

SPECIFICATION	EPA-17 CHEMICAL
DOD-C-24176	Toluene, Cadmium
MIL-A-25457	Toluene
MIL-A-47317	Toluene, Benzene
MIL-S-8516	Toluene, Lead Compounds
MIL-S-8802	Toluene, Lead Compounds
MMM-A-121	Toluene, Methyl Ethyl Ketone
MMM-A-132	Toluene
MMM-A-1617	Toluene, Methyl Ethyl Ketone
MIL-A-46050	1,1,1-Trichloroethane
MIL-A-46146	1,1,1-Trichloroethane
MIL-S-22473	1,1,1-Trichloroethane

Non-ODC containing products for the last three specifications have been identified and are the subject of a previous paper entitled "ODC ELIMINATION IN ADHESIVES AND SEALANTS USED IN PATRIOT MISSILE SYSTEM MAINTENANCE" presented at the 1998 JANNAF Joint Propellant Development and Characterization/ Safety and Environmental Protection Subcommittee Meeting in Houston, Texas.

The database indicates that there are other products used in PATRIOT that contain EPA-17 chemicals. These products are listed in Table 4. MIS documents are specifications that are written for a specific missile system and each MIS usually has only one or at most two suppliers for a product. This makes finding substitutions very difficult for these materials. In addition, there are products that are procured that do not have a specification. Once again, finding substitutes for these specific materials is very challenging.

TABLE 4. Other Products containing EPA-17 Chemicals

PRODUCT	EPA-17 CHEMICAL
MIS-19895	Toluene, Methyl Ethyl Ketone
MIS-20242	Toluene, Methyl Isobutyl Ketone
MIS-34117	Methyl Ethyl Ketone
MIS-41187	Toluene
Cho-Bond 1030/1086	Toluene
Raychem S-1010	Methyl Ethyl Ketone
Cho-Bond 1086	Toluene
GE RTV-615	Toluene, Methyl Ethyl Ketone
TECK-NIT 72-00005	Trichloroethylene

SUBSTITUTION APPROACH

Since there are quite a few products to replace, it would seem that to meet the reduction goal of 50% specified by EO 12856, priority should be given to the most heavily used products. Since the MIS products and those products that have no specification will be difficult and time consuming to replace, we have chosen to focus on the military and commercial specification materials. We can rank the products by the number of times that they are called out in the document. As shown in Table 5, five specifications account for all but about 1% of the call-outs. The good news is that the first and third most used specifications have already been addressed in the previous work. This leaves the three specifications MIL-S-8802, MMM-A-1617, and MMM-A-132.

TABLE 5. Occurrence Frequency of Products containing EPA-17 Chemicals

Specification	% Times Occurring	Status
MIL-S-22473	45.4	Fixed
MIL-S-8802	20.8	TBD
MIL-A-46146	15.6	Fixed
MMM-A-1617	8.44	TBD
MMM-A-132	2.21	TBD
TOTAL	98.9	

Preferred Approach for Substitution

The preferred approach for substitution is in order of preference:

1. Substitute material with another from the same specification.

2. Substitute material with another from a similar specification.

3. Substitute material with a different type of material from a different specification.

MIL-S-8802 Alternatives

At present, there are two specifications that can potentially be used in place of MIL-S-8802. These are:

1. **AMS 3276** "Sealing Compound, Integral Fuel Tanks and General Purpose, Intermittent Use to 360 °F"
2. **MIL-S-85334** "Sealing Compound, Non-curing, Low Consistency, Silicone, Groove Injection, For Integral Fuel Tanks"

A plan is being developed to test these alternate materials as a replacement for MIL-S-8802 in PATRIOT Missile System applications.

MMM-A-132 and MMM-A-1617 Alternatives

At the current time no alternatives have been identified for these two specifications. The author is contacting adhesive manufacturers and is soliciting help in identifying potential candidates for a test program.

CONCLUSION

A database has been established that documents the usage of all chemicals in the maintenance of the PATRIOT Weapon System. All EPA-17 containing adhesives and sealants used on PATRIOT have been identified. Toluene, Methyl Ethyl Ketone and Lead are the main ingredients that must be replaced in adhesives and sealants used on PATRIOT. Although suitable replacements have been found for some of the hazardous materials, additional research and testing will be required to achieve the desired HM minimization goals.

Surface Treatment Technology

James G. Mitchell, Ph.D.
Surface Treatment Technologies, Inc.
P.O. Box 370, 207 Big Springs Avenue
Tullahoma, TN 37388

Abstract:

A newly invented process (patent pending) permits metal surfaces to be treated with additive materials that provide super-alloyed surfaces, hard and high-wear surfaces, thermal barrier coatings, oxidation-resistant coatings, and high-temperature-melting-point surfaces. This process has demonstrated capability of producing a chosen alloy or refractory of a specified thickness on substrate materials. The resulting surface is nonporous and crack-free. The metallurgical bond of the alloy resists all attempts at delamination or peeling and can accommodate a wide range of temperatures and coefficients-of-expansion. Therefore, one can provide a permanent, thin layer of protective material over substrate materials. The innovation is entitled "Laser Induced Surface Improvement", or LISI. Many materials of interest have been used in two years of research and demonstration. LISI permits the component designer to select base metals for their material qualities (strength, weight, etc.), as well as cost, without regard to surface-interface properties. Unlike many other "coatings", the LISI process requires little surface preparation, needs no special environment for application, and is environmentally friendly. The University of Tennessee Space Institute (UTSI) has invented the process, and Surface Treatment Technologies, Inc. (ST^2) is a newly formed Tennessee corporation which has acquired a license for the process and is working with the inventors to explore and evaluate applications of the technology.

What is LISI?

Coating of materials is a big business worldwide. Where does LISI fit into the hierarchy of coating processes? Table 1 lists some of the more recognized methods of coating and illustrates that LISI fits in the category of thermal surface modification.

Methods of Fabricating Coatings			
Atomistic Deposition	**Particulate Deposition**	**Bulk Coatings**	**Surface Modification**
Electrolytic Environment	**Thermal Spraying**	**Wetting Processes**	**Chemical Conversion**
Electroplating	Plasma Spraying	Painting	Electrolytic Anodization
Electroless Plating	HVOF	Dip Coating	(oxide)
Fused Salt Electrolysis	D-Gun	**Electrostatic Spraying**	Fused Salts
Chemical Displacement	Flame Spraying	Printing	**Chemical-Liquid**
Vacuum Environment	**Fusion Coatings**	Spin Coating	**Chemical Vapor**
Vacuum Evaporation	Thick Film Ink	**Cladding**	Thermal
Ion Beam Deposition	Enameling	Explosive	Plasma
Molecular Beam Epitaxy	Electrophoretic	Roll Bonding	**Leaching**
Plasma Environment	**Impact Plating**	Laser	**Mechanical**
Sputter Deposition		**Overlaying**	Shot Peening
Activated Reactive Evaporation		Weld Coating	**Thermal**
Plasma Polymerization			**Surface Enrichment**
Ion Plating			Diffusion from Bulk
Chemical Vapor Environment			**Sputtering**
Chemical Vapor Deposition			**Ion Implantation**
Reduction			
Decomposition			
Plasma Enhanced			
Spray Pyrolysis			
Liquid Phase Epitaxy			

Table 1

To further position LISI, one must move to Figure 1 which defines the power density requirements and the interaction times for a number of laser processing technologies. LISI is surface modification by way of alloying, using the laser as a closely controlled heating source.

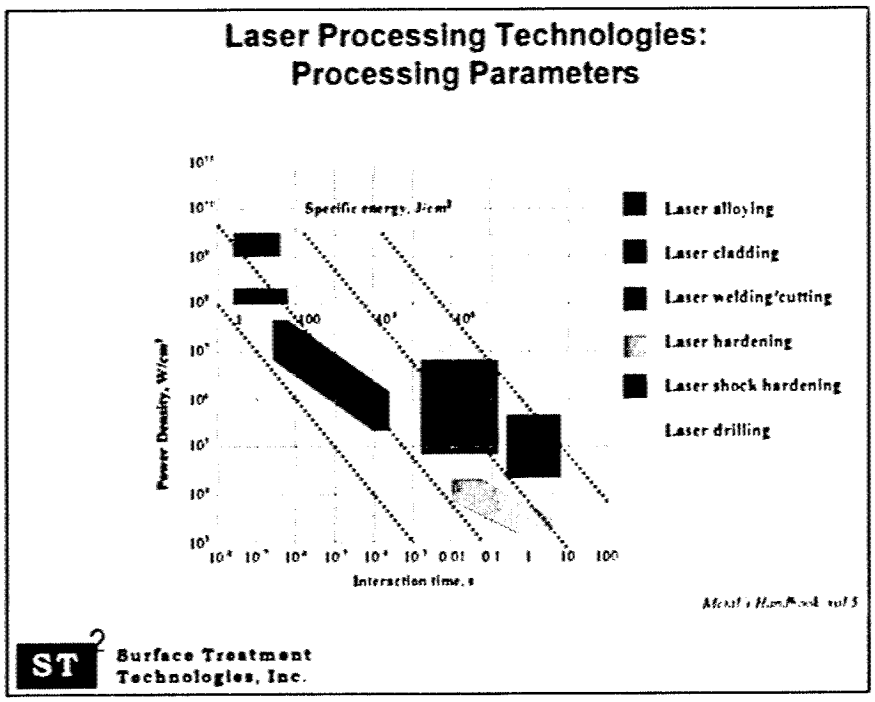


Figure 1

Metallurgists around the world for over 20 years have attempted to improve the external properties of a material via a surface-alloying technique. UTSI researchers were able to develop a process that overcame the deficits of others; i.e., surface porosity, surface cracking, and varied distribution of the surface layer to produce a uniform protective surface. The LISI process is performed by melting a precursor material into an underlying substrate using the laser as a heat source. This is shown schematically in Figure 2, which also shows the successive displacement of laser passes.

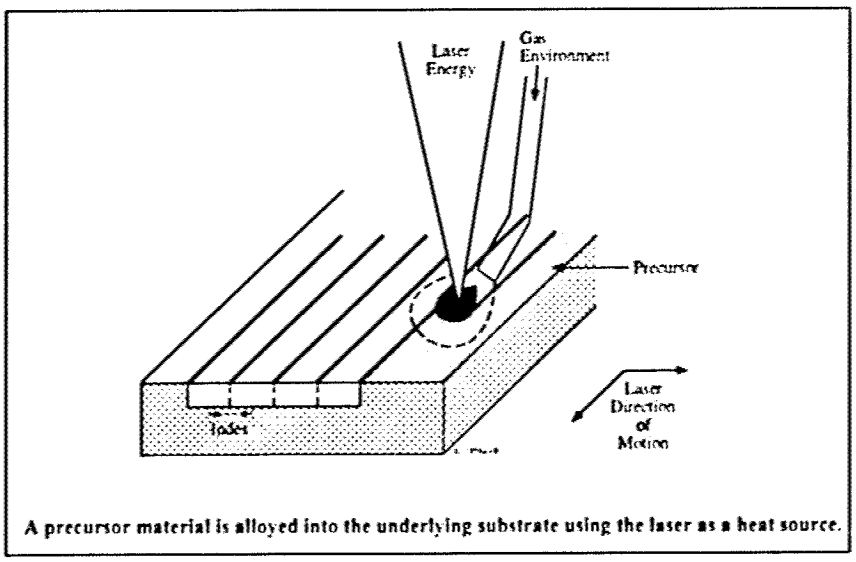


Figure 2

Since the melting occurs rapidly and only at the surface and subsurface, the bulk of the material remains cool, thus creating rapid self-quenching and solidification. The overall control of the melt and the rapid solidification allows LISI to create the chemical and microstructure states needed for corrosive and erosive protection. The process can range from straightforward "alloying", such as chromium and nickel into iron for corrosion resistance, to the more sophisticated "induced reaction", such as the formation of titanium and nitride at an iron surface for wear resistance. The intense heat of the laser vaporizes many surface contaminants while it creates a melt pool of precursor and substrate material. Surface location and configuration can complicate the application of the process, but in general, if it is possible to reach the surface, LISI can be performed on the surface (usually with fiber optics).

What makes LISI additionally attractive and interesting is the wide variety of chemical and microstructural states that can be retained because of the rapid quench from the liquid phase. These include chemical profiles where the alloyed element or infiltrated reinforcement material is highly concentrated near the atomic surface and decreases in concentration over shallow depths, as well as uniform profiles where the concentration is the same throughout the entire modified region. The LISI-induced reaction is also adaptable for the production of surfaces that require transitions from metals and other substrates to ceramics or refractory materials. Types of microstructures observed range from solid solutions with distinct crystalline phases to metallic glasses.

Technical Features:

Envision a process that can create an alloy of choice (metals, ceramic matrix composites, and refractories) on a wide variety of substrate materials, with a predetermined thickness between 10 and 1,000 microns. Further, consider that this "coating" will not separate from the substrate material from physical abuse, surface bending and twisting, or large thermal transients over a wide range of temperatures (from cryogenic temperatures to those approaching material upper limits). There is no mechanical bonding line and the metallurgical bond remains intact even when the substrate material is stressed to failure.

Figure 3 shows 1010 steel with a chromium alloy surface, which has been deformed after LISI treatment. The surface is still fully protective and has not been compromised.

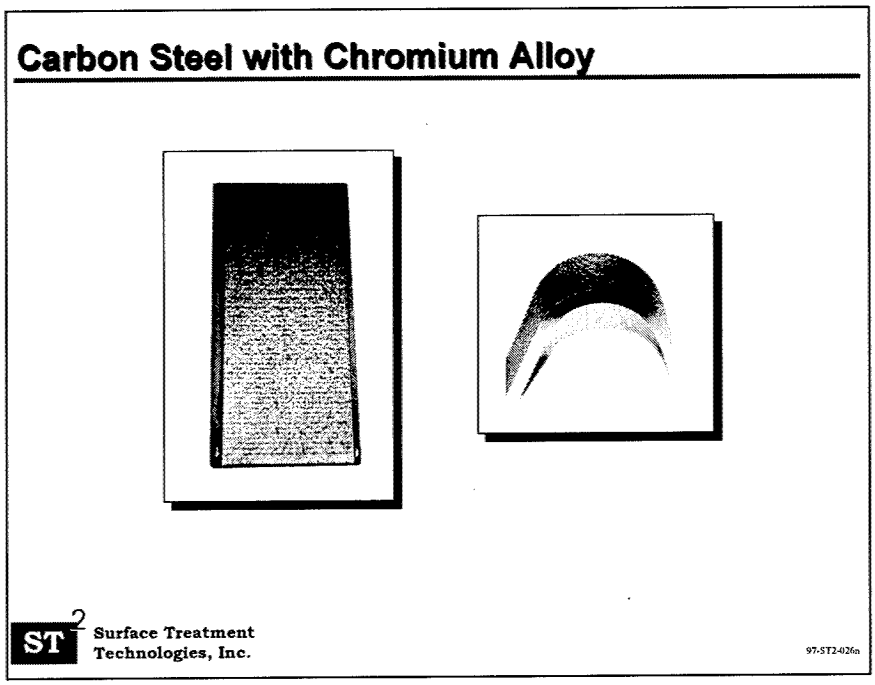


Figure 3

Figure 4 shows an electron microscope photo of tungsten carbide alloy on aluminum substrate and clearly illustrates the irregular interface between alloy and substrate.

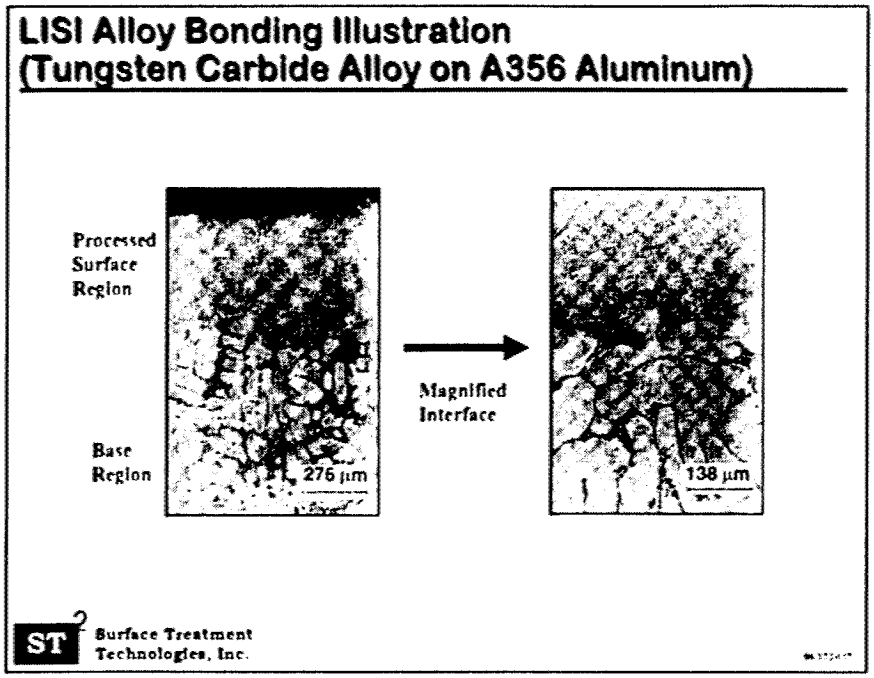


Figure 4

The LISI process requires little or no cleaning of the substrate. This characteristic reduces both costs of application and certain environmental concerns of surface cleaning. In fact, LISI has proven to be totally environmentally friendly, producing no harmful effluents or residuals that require disposal. Nor does LISI require any special environment for application (e.g., a vacuum) as do some surfacing processes and it is readily adaptable to the manufacturing floor and field.

LISI permits one to mix and select precursor materials (in powder form) that are tailored for each application. The heating rate, cooling rate, and gas environment are controlled to capture alloy constituents well outside the dictates of equilibrium phase diagrams. The resulting alloy demonstrates a very fine grain structure that is characteristic of materials that are corrosion and crack resistant, as shown in the microstructure illustration in Figure 5. Thus, this new process appears to provide all the characteristics desired for corrosion protection. It is not necessary to use a costly material for construction when only the surface must exhibit special properties. It is no longer necessary to use corrosion inhibitors or biocides in the fluids to inhibit corrosion. Substrate materials that are required for mechanical strength no longer dictate the interface qualities and limitations of the surface.

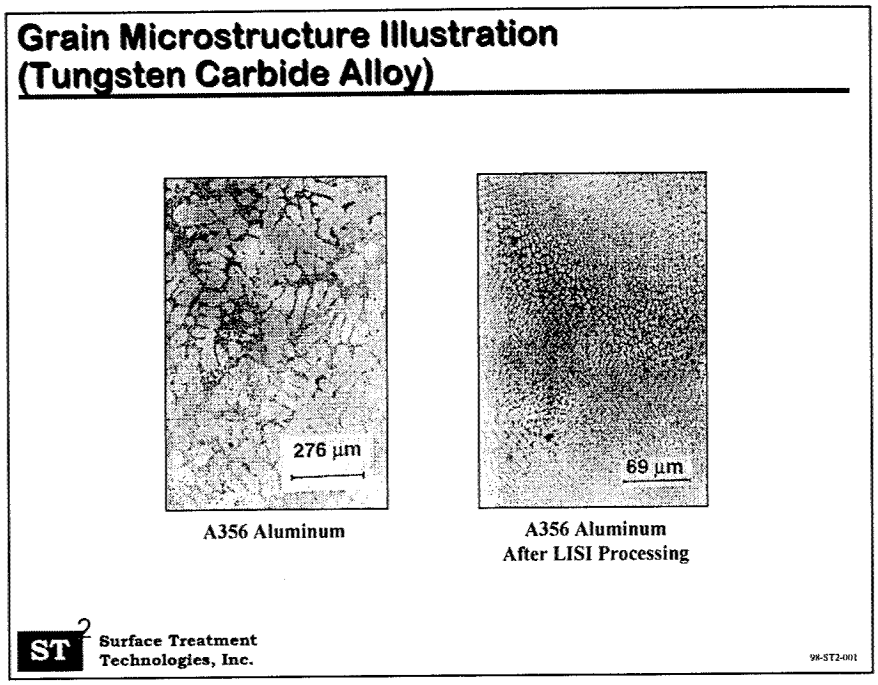


Figure 5

Some characteristics associated with the LISI process are summarized in Table 2.

Characteristics of LISI Process
• The process requires no special environment (e.g., a vacuum) and can be performed on the shop floor or in the field.
• The process has no harmful effluents, byproducts, or residuals (environmentally friendly) – a good replacement for chrome plating for many applications.
• Only the surface and subsurface region (a few microns to millimeters deep) is modified, which causes little or no change in the rest of the bulk material.
• The process produces a surface-modified layer as an inherent integral part of the substrate material and provides no distinct interface that would permit delamination and/or separation (i.e., a molecular bond that will not chip or peel).
• A very small amount of surface modifier species is required, which can provide significant savings on strategic and costly materials for some applications.
• As the process involves extremely rapid heating and cooling, it produces surfaces with unique properties that include a precipitate-free chemically homogeneous volume, novel material phases, and compositions outside those dictated by equilibrium phase diagrams. This permits surface modification of ferrous (steel) as well as nonferrous (aluminum, titanium, etc.) material systems suited for applications involving wear/erosion, corrosion, hardness, strength, toughness, creep, fatigue, thermal resistance, and diffusion resistance.
• Unlike other laser material treatments, the LISI process results in a very minimal heat-affected zone. Heat input is closely controlled and limited during both continuous and pulsed laser operation.
• The laser beam is presently delivered via fiber optic (about 30 meters long) with little loss in beam energy and quality. However, the cable can be much longer if necessary. The fiber optic beam delivery permits surface processing remotely and selectively using computer numeric control (CNC), thereby increasing accuracy and repeatability.
• Where CNC equipment is not applicable (in the field), the laser head height-above-surface can be controlled with a "feeler".
• The laser beam is traversed at speeds that are dependent upon the material system being processed and the depth below the surface to be processed. Up to 50 sq. ft./hour can be processed with existing laboratory robotics and a 2 kw laser.

Table 2

Experimental Confirmation:

Two years of testing and demonstration confirm the success of the LISI process for a number of substrate and precursor materials as shown in Table 3. Much of the emphasis has been on aluminum and steel as the substrate. It has been clearly demonstrated that both ferrous and nonferrous materials can be significantly enhanced for corrosion and/or wear properties.

Substrate Materials		Precursor or Surface Additive Materials	
Steel	Aluminum	bismuth	copper/silicon/carbide
A36	356	chromium	gold
A203	319	chromium/nickel	nickel
A285	5051	chromium/nickel/	nickel/silicon/carbide
A516	7075	molybdenum	silicon
316	5083	chromium/nickel/carbide	silicon carbide
304	6061	chromium/nickel/titanium	silicon/carbide
1010	Other	chromium/carbide/carbide	silicon/magnesium/titanium/carbide
4340	Inconel	chromium/nickel/	titanium
HY80	Nickel	silicon/carbide	titanium carbide
HY100	SiCp/Al203	copper	tungsten
	Composite	copper/bismuth	tungsten carbide
	Ti-6Al-4V	copper/silicon	Al203
		copper/silicon/magnesium	CeO2
			MoSi2
			TiN

Table 3

LISI-treated surfaces have undergone testing at Air Force, Navy, and private laboratories, along with extensive testing at the University facilities. Figure 6 shows the results of corrosion testing on LISI-treated 1010 steel in a salt fog chamber at the Air Force Materials Laboratory at Wright-Patterson Air Force Base. The chromium/nickel alloyed surface showed no corrosion after 232 hours. Similar samples have been tested in the University salt fog chamber for 1000 hours with no sign of deterioration.

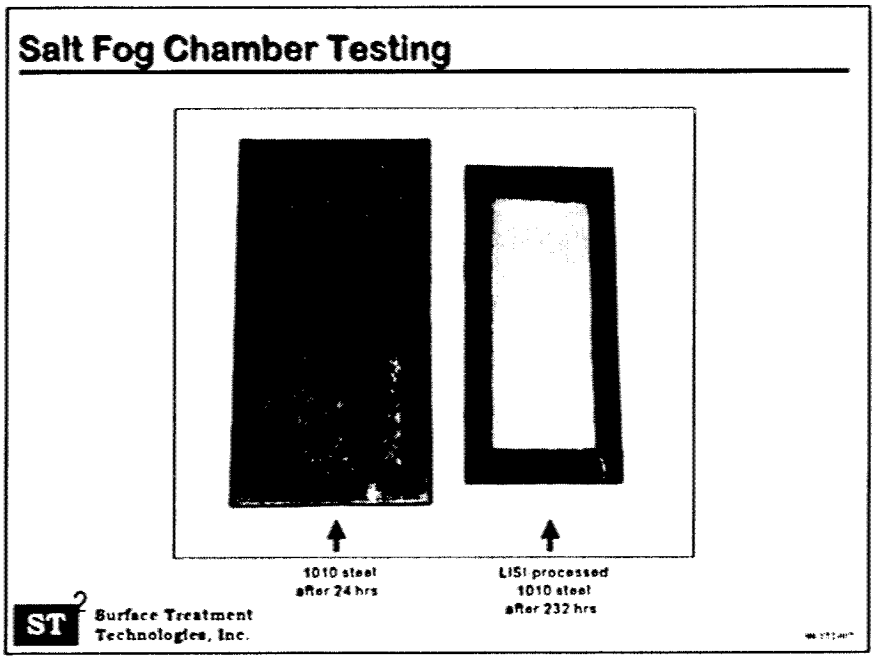


Figure 6

Quantitative data shown in Figure 7 give polarization resistance measurements on treated 1010 steel obtained at the Navy's Carderock Materials Laboratory (in this case a tungsten carbide-chromium alloy). These results confirm the visual observations illustrated in Figure 6. Note the corrosion resistance as compared with bare steel. The Navy researchers report that LISI-treated surfaces perform better than the best painted surfaces.

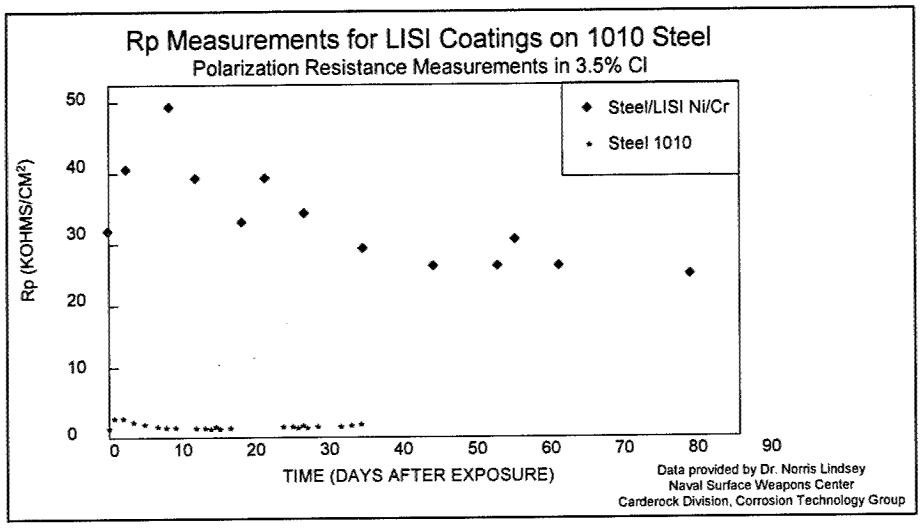


Figure 7

Unlike some other corrosion inhibiting surfaces, the LISI-enhanced surfaces not only give very good corrosion protection, but also improve wear properties. For example, chromium-rich or tungsten-carbide-rich alloys on aluminum surfaces give very good corrosion protection while significantly increasing hardness and wear. Aluminum protected surfaces were evaluated at the Navy laboratory and performed well in corrosion tests. Figure 8 shows wear curves for tungsten-carbide on a special ALCOA aluminum for several process variables. Also performing well is tungsten carbide on 356 aluminum.

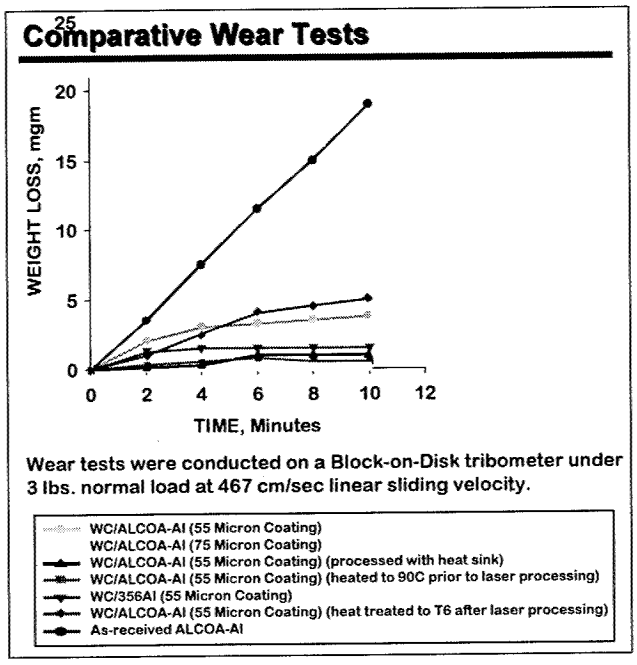


Figure 8

LISI has also demonstrated its unique ability to join dissimilar materials with widely different coefficients of expansion. LISI-treated surfaces have been exposed to temperatures ranging from liquid nitrogen to near melting point with no hint of delamination resulting from temperature cycling or temperature extremes.

Surface Finishes:

The laser path must overlap on consecutive passes and causes some variation in surface finish. The smoothest finish on aluminum and steel has been measured at 0.0003 inches surface variation. If smoother surfaces are desired, the alloy can be polished to a mirror finish. Some applications require rough surfaces. The maximum surface height variation has been measured at 0.020 inches (Figure 9). Various surface patterns can be produced by control of beam size and gas flow, as well as pulsed laser operation.

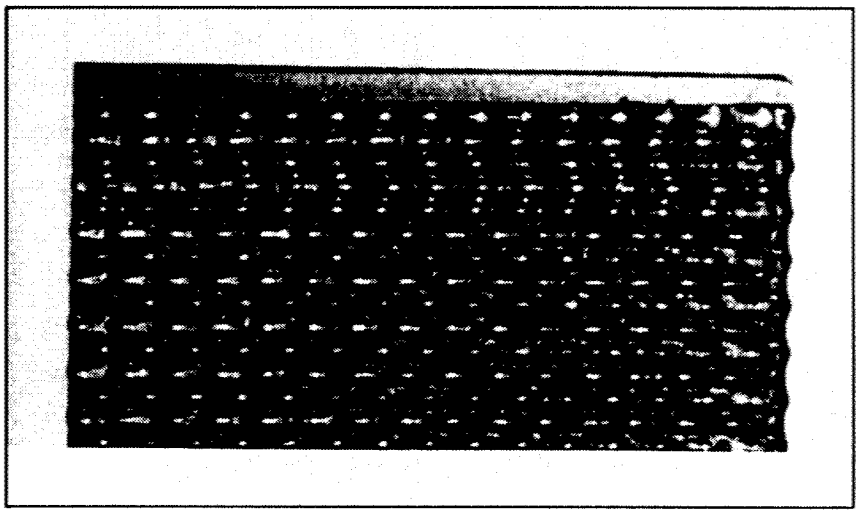


Figure 9

Concluding Remarks:

- Laser Induced Surface Improvement (LISI) joins the many other coating techniques to offer its own unique set of characteristics.
- LISI surfaces have clearly demonstrated the ability to enhance corrosion, erosion, and wear qualities.
- LISI's ability to provide a chromium-rich surface in an environmentally friendly process is of interest for chrome plating replacement for some applications.
- By realloying the base metal, LISI produces surfaces that cannot be duplicated by any other method.
- LISI is presently being compared to other coating techniques in terms of effectiveness and cost for a number of applications.
- LISI's ultimate use probably begins in the design phase. The designer may choose component materials with consideration of mechanical properties and cost, while the appropriate surface can be derived via a LISI process.

An Innovative Approach to Meeting Storm Water Discharge Requirements

Prepared for:

Third Conference on Aerospace Environmental Technology

Prepared By:
Billy B. Cress / Richard L. Bost / Kim A. Henke
Roy F. Weston, Inc.
70 NE Loop 410, Ste. 460
San Antonio, TX 78216

Gary Goodman
Kelly Air Force Base
307 Tinker Dr.
San Antonio, TX

An Innovative Approach To Meeting Storm Water Discharge Requirements

By Gary Goodman, Kelly Air Force Base; Billy B. Cress, Richard L. Bost, Kim A. Henke, Roy F. Weston, Inc.

ABSTRACT

Kelly Air Force Base (Kelly) is a large industrial complex that provides "depot" level maintenance for aircraft and approximately 75 percent of the Air Force's engine inventory. The base maintains both an Environmental Protection Agency (EPA) National Pollutant Discharge Elimination System (NPDES) permit and a Texas Natural Resource Conservation Commission (TNRCC) storm water discharge permit. Because of the complexity of the base's two discharge permits and the distance between outfalls, the base installed a system of automated storm water monitoring samplers and flow meters for its eight storm water outfalls. This paper describes the base's approach to storm water monitoring and provides insight into how the base has been able to meet storm water monitoring compliance requirements while reducing the manpower required to implement this program.

INTRODUCTION

Identifying and controlling sources of storm water pollution is critical to the pollution prevention process and is preferable, both economically and ecologically, to remediating pollution after environmental damage has occurred. The traditional approach in regulating water resources has been to concentrate on point source discharges from industrial waste water and municipal sewage. However, storm water runoff from non-point sources has emerged as the primary contributor to pollution in receiving waters. This approach to reducing the impact to surface waters by storm water runoff from non-point sources was transformed into legislation in the 1980's. The National Urban Runoff Program (NURP) and Clean Water Act (CWA) 305(b) reports submitted to Congress in the 1980's identified contaminated storm water as one of the culprits causing surface water quality impairment. The 1987 amendments to the CWA tasked the U.S. EPA to establish an NPDES permit program for storm water discharges associated with industrial activity. The final NPDES permit application regulation was published by EPA in the Federal Register on November 16, 1990. As a result of the advent of the NPDES storm water permit program and subsequent State-regulated NPDES permit programs, the monitoring and controlling of storm water runoff at industrial facilities became not only necessary but mandatory.

Due to the industrial nature of activities conducted throughout Kelly, the base was required to obtain coverage under both the EPA and TNRCC storm water discharge permits. Under these permits, Kelly is required to monitor storm water runoff from eight outfalls spread over a 3-mile radius from the center of the runways. The complexity of Kelly's storm water permits and distances between outfalls presents a challenge to the storm water monitoring program. To maintain compliance with both storm water discharge permits, Kelly installed automated storm water sampling systems at each of the eight outfalls on the base requiring sample collection. This automated system facilitates the collection of storm water samples (discrete and composite) at multiple locations during a single storm event and allows for routine downloading of real-time data without the errors associated with manual data collection and processing. Flow-data management software allows programming of flow meters, rain gauges, data loggers, scheduling of remote interrogations, retrieval of on-line status readings, interrogation of meters and transfer of data. This software also has the capacity to generate numerous reports and graphs from the collected data, thus enabling Kelly to review real-time data for compliance.

Since Kelly's installation of this system, the base has been able to meet all the storm water discharge monitoring requirements listed in Table 1 and also has relieved limited manpower resources for other important program requirements.

MONITORING REQUIREMENTS

When collection of 24-hour composite samples became an integral part of discharge permit requirements, calling for more frequent or flow proportioned composite samples, the casual method of sampling storm water with a can on the end of a stick quickly became obsolete. Kelly's discharge permits require the collection of both discrete and composite samples, along with outfall flow rate and total runoff volume, at each of the eight storm water outfalls. Table 1 summarizes Kelly's EPA and TNRCC storm water monitoring requirements for each outfall.

Table 1 – Summary of EPA and TNRCC Stormwater Discharge Monitoring Requirements

TABLE 1 SUMMARY OF EPA AND TNRCC STORM WATER DISCHARGE MONITORING REQUIREMENTS KELLY AFB, TX										
		Parameter								
OUTFALL		FLOW	BOD	COD	O&G	TDS	TSS	TEMP	WET	
002		1/Day	1/Week	1/Week	1/Week	2/Week	2/Week	1/Day	1/Quarter	
004		3/Day	1/Week	1/Week	1/Week			3/Day	1/Quarter	
005		1/Day		1/Week	1/Week					
006		1/Day		1/Week	1/Week				1/Quarter	
007		1/Day		1/Week	1/Week				1/Quarter	
008		1/Day		1/Week	1/Week					
009		1/Day		1/Week	1/Week					
010		1/Day		1/Week	1/Week					

Note:

1) BOD (Biochemical oxygen demand) is collected as a 24-hour composite sample.
2) COD (Chemical oxygen demand) is collected as a 24-hour composite sample.
3) O&G (Oil and grease) is collected as a discrete sample
4) TDS (Total dissolved solids) and TSS (Total suspended solids) are collected as 24-hour composite samples.
5) WET (Whole effluent toxicity) samples are collected as 24-hour composite samples.

The collection of discrete samples at each of these outfalls during a single storm event poses a problem with regard to the potential manpower and logistical needs associated with the collection of composite samples at each outfall during the same storm event. These types of monitoring requirements, which are outlined in Kelly's EPA and TNRCC storm water discharge permits, significantly influenced their selection of automatic storm water samplers and flow meters to satisfy their monitoring needs. Kelly's implementation of automatic storm water sampling systems at these outfalls facilitated the storm water monitoring program by not only satisfying permit requirements but also by reducing the program's overall labor effort requirements.

SYSTEM CONFIGURATION

Kelly selected and installed ISCO-brand manufactured automatic storm water collection systems at each of the eight regulated storm water outfalls. The component equipment functions as an integrated storm water collection system such that storm water samples are collected and controlled automatically, either remotely or from a central processing location. The system is structured such that samples may be collected on the basis of rain, flow, time, or a number of other selected factors.

Components of this integrated system include:

- Flow Measurement System (FMS);
- Sample Collection System (SCS);
- Rain Measurement System (RMS);
- Operating System (OS);
- Cellular Telephone System (CTS);
- Solar Power System (SPS);
- Necessary appurtenant interconnecting cables and system hardware; and
- A pressure-tested instrument enclosure.

Kelly utilizes this integrated system to:

- Measure and record rainfall amounts;
- To measure and record storm water flow in open channel flow conditions;
- To retrieve, process, and/or alter collection data and parameters remotely; and
- To collect discrete and/or composite water quality samples at pre-selected user-defined flow or time based increments, or factors thereof.

The following summarizes the functional features of the aforementioned systems which comprise the storm water collection system installed at each of the eight regulated storm water outfalls at Kelly. Figures 1 and 2 illustrate some of the components of Kelly's storm water collection system.

- Flow Measurement System (FMS) - The primary functional component of the FMS is the ISCO Model 4230/4250 flow meter. The FMS measures and records runoff level, and computes instantaneous flow using a pre-established water level to flow rate conversion for the various open channel flow conditions at each outfall. The FMS stores collected and computed data which can be retrieved via a personal computer, modem, and the system compatible software entitled Flowlink.

- Sample Collection System (SCS) - The primary functional component of the SCS is the ISCO Model 3700 automatic storm water sampler. The SCS, on an automatic user selectable/programmable basis, measures and distributes a storm water sample to a bottle, or sequence of bottles, by activation from the FMS. The SCS calculates and delivers sample volume based on liquid detection and a revolution counting mechanism associated with a peristaltic pump. The SCS collects discrete and/or composite storm water samples based on user defined input and is capable of distributing samples into 1 to 24 bottles, or any combination thereof.

Figure 1 – General Components of Auto Sampler System

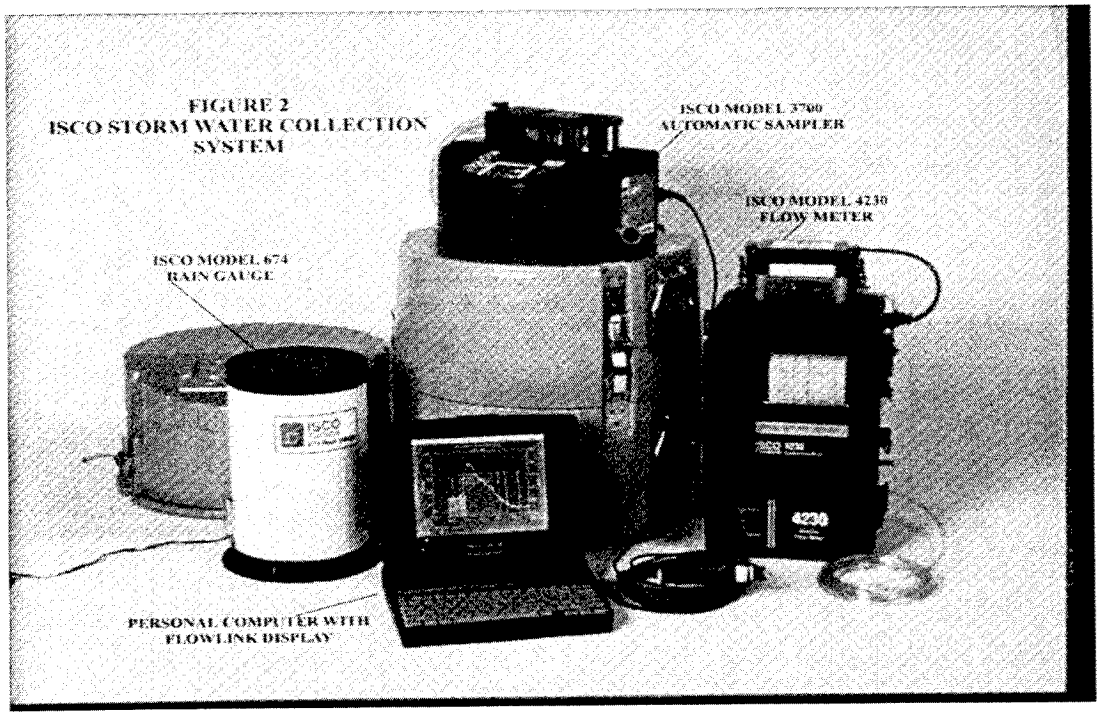


Figure 2 – Specific Components of Auto Sampler System

- Rain Measurement System (RMS) - The RMS allows rainfall to enter through an orifice and flow through a funnel to a tipping bucket. As rainfall is collected, the bucket tips and provides a contact closure to the FMS which monitors and records the rainfall level.

- Operating System (OS) - The primary functional component of the OS is the ISCO developed software Flowlink. Although Flowlink is sometimes considered a data management software, it also performs many other tasks:

  - Programming flow meters and auto samplers to begin a sampling routine based on rainfall, flow, time, or any combination thereof;

  - Retrieving real-time status readings from flow meters;

  - Interrogating flow meters and samplers, and transferring their stored data to files in the personal computer;

  - Importing flow-conversion tables and exporting data as ASCII text;

  - Editing readings to correct errors caused by clock drift, daylight savings time, or miscalibration;

  - Scheduling remote interrogations and printing jobs;

  - Generating reports and graphs of the data;

- Solar Power System (SPS) - The SPS provides power at each outfall to the FMS, SCS, and CTS. Each outfall is also equipped with a deep cycle marine battery as a reserve power source.

- Cellular Telephone System (CTS) - The CTS provides cellular access to the remote location flowmeter via a personal computer, modem, and Flowlink.

SYSTEM OPERATION

Hardware

The storm water collection system present at each of the eight storm water outfalls at Kelly integrates all of the individual components mentioned above. Each collection system is equipped with a FMS to monitor the instantaneous flow at each outfall. This flow-monitoring system has a two-fold purpose: to comply with discharge monitoring requirements stipulated in the permits and to ascertain if the minimum flow levels have been met to warrant sampling and thereby enable the SCS. The parameters monitored by the FMS that are used to trigger the SCS are water level, flow rate, flow velocity, rainfall, pH, and dissolved oxygen (DO). Water level, flow rate, and flow velocity are measured using an area-velocity sensor, rainfall data is linked directly to the FMW via the RMS, and pH and DO are measured using a parameter sensor.

Software

The operating system for the FMS consists of a micro-processor controlled circuit that stores the user programming instructions as well as collecting and storing the data monitored by the sensors. User instructions generally include those pre-determined parameters and rates that will trigger a sampling event. A real-time comparison between data measured by the sensors and the pre-programmed instructions determines when the sampling criteria have been met. At this point, the operating system triggers the SCS. As an example, at Kelly, a storm water event is identified when the rainfall in a 24-hour period exceeds 0.1 inches and when the subsequent discharge at an outfall exceeds 100 gallons per minute (gpm). The combination of parameters that can be measured by the FMS and the user programming options available through the operating system provide a wide degree of flexibility for defining sampling requirements based on permit provisions.

Once the pre-programmed conditions have been satisfied, the microprocessor-controlled circuitry of the SCS is enabled. The SCS can begin a sampling event as soon as the FMS enables it, at an interval or multiple intervals designated from the time of enablement. Sample types are characterized by sample pacing. There are two types of sample pacing: time-pacing and flow pacing. In time-paced sampling, the interval between samples is a

specified time interval. In flow-paced sampling, the interval between samples is determined by a specified volume of liquid which has passed a measuring point in a flow stream.

No sample pacing is required when collecting a single discrete sample, but pacing is required when collecting composite samples. Kelly's permits require collection of a discrete sample within the first hour of a recognized storm event. Composite samples consist of a collection of multiple discrete samples over a permit-specified time period (i.e., 24-hour composite). Kelly's permits require collection of both discrete and composite samples, depending on the specific outfall.

The actual sample collection process takes place within the SCS. The distributor arm of the SCS moves to the bottle which is to receive the sample, the pump rotates in the reverse direction for the pre-sample purge, then the pump rotates in the forward direction to fill the suction line up to the liquid detector. After the suction line has been filled to the liquid detector and liquid has been detected, the sample volume measuring begins until the programmed volume of liquid has been delivered to the appropriate sample bottle. The distributor arm advances and the pump then rotates again in the reverse direction for the post-sample purge. The cycle continues if a time or flow paced sample is to be taken in either a sequential or composite form.

If desired, the OS can be a primary component of the programming for the FMS and SCS through the Flowlink software. The operating conditions can be entered via Flowlink, as well as the data acquisition and storage parameters for archiving blocks of data. Flowlink allows for storage, downloading, and interpretation of the flow meter data. Reports can be generated in table or graph format, and the historical data can be exported in ASCII format. A copy of a Flowlink graph and report are provided as Figure 3 and Figure 4, respectively.

If a CTS is used in conjunction with the OS, most primary functions of the FMS, as well as the interface between the OS and FMS, can be manipulated remotely. An internal modem in the FMS is relayed by a modem line to a personal computer, as opposed to a direct connection interface with a portable computer taken to the field. Considering the time involved in traveling to and directly manipulating the FMS and SCS at each outfall, made additionally inconvenient if there is a simultaneous storm event occurring, the capability for remote access is a significant time saving function. Additionally, since many storm events are borderline with respect to meeting the predetermined conditions, it is convenient to be able to retrieve real-time status readings from the FMS to determine if sampling has been initiated. An additional feature of the CTS is one that calls a pre-programmed telephone number when the SCS is enabled. This informs the system operator that the sample condition has been met by the storm event and the sampling routine has begun.

Electricity is provided at each storm water monitoring station to power the FMS, SCS, and CTS. Where practical, power is supplied through a direct A/C line run from a breaker box connected to a live main on Kelly. When this approach is not feasible, such as at remote locations, a SPS is utilized to collect and provide electricity. The constant power requirements of the FMS and the interval power draw of the CTS can be provided directly from the SPS with mostly cloudy to clear conditions. A trickle charge is employed to keep a deep cycle marine battery charged for night conditions and when a larger power draw is required.

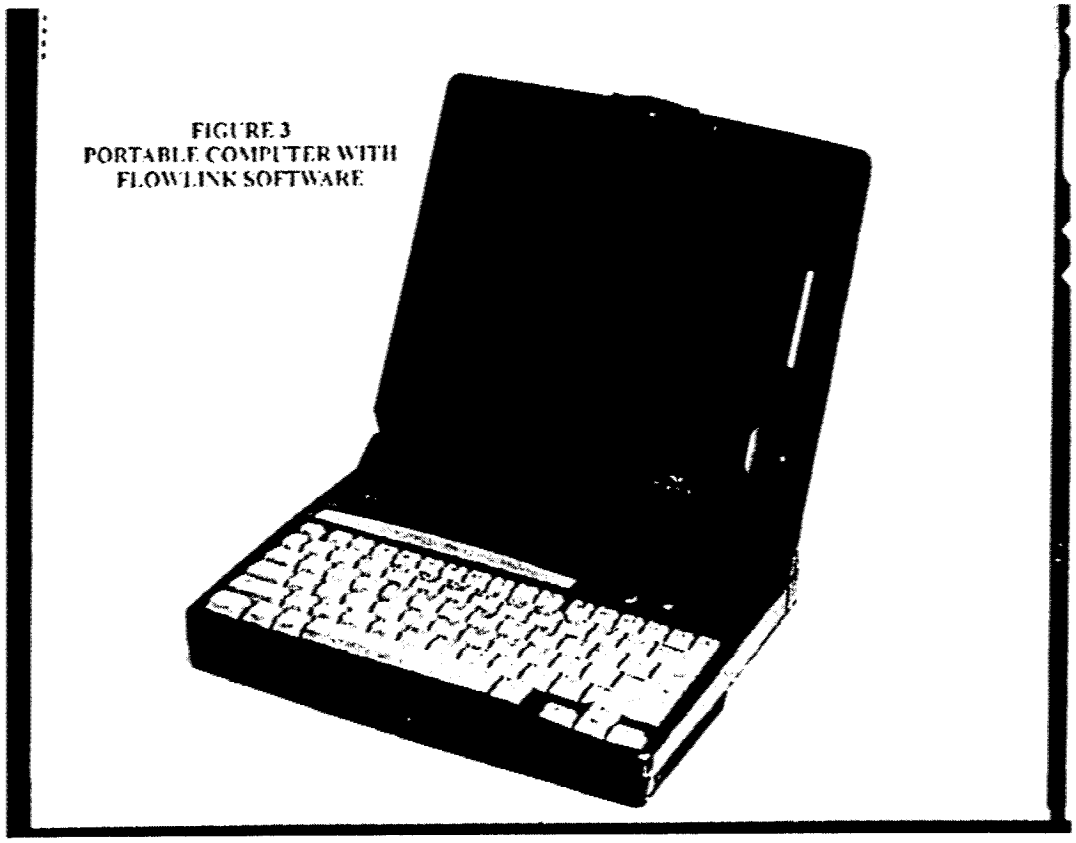


Figure 3 – Flowlink Graph on Portable Computer

MONTHLY SUMMARY Site 8789544093 Outfall 008

Wed 01 Apr 1998 00:00 - Thu 30 Apr 1998 00:00

Part D Flow

Date	Minimum Flow Rate (gpm)	Maximum Flow Rate (gpm)	Average Flow Rate (gpm)	Total Flow (Mgal)
Wed 01 Apr 1998	0.00 @ 00:10	0.03 @ 16:00	0.00	0.00
Thu 02 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Fri 03 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Sat 04 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Sun 05 Apr 1998	0.00 @ 00:10	0.07 @ 17:00	0.01	0.00
Mon 06 Apr 1998	0.00 @ 00:10	0.02 @ 10:00	0.00	0.00
Tue 07 Apr 1998	0.00 @ 00:10	0.01 @ 07:50	0.00	0.00
Wed 08 Apr 1998	0.00 @ 00:10	0.03 @ 15:50	0.00	0.00
Thu 09 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Fri 10 Apr 1998	0.00 @ 00:10	0.02 @ 12:20	0.00	0.00
Sat 11 Apr 1998	0.00 @ 00:10	0.85 @ 17:30	0.10	0.00
Sun 12 Apr 1998	0.00 @ 00:10	0.96 @ 17:10	0.15	0.00
Mon 13 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Tue 14 Apr 1998	0.00 @ 00:10	0.13 @ 17:10	0.00	0.00
Wed 15 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Thu 16 Apr 1998	0.00 @ 00:10	0.03 @ 14:10	0.00	0.00
Fri 17 Apr 1998	0.00 @ 00:10	0.04 @ 12:00	0.00	0.00
Sat 18 Apr 1998	0.00 @ 00:10	320.73 @ 05:20	10.07	0.01
Sun 19 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Mon 20 Apr 1998	0.00 @ 00:10	0.04 @ 12:20	0.00	0.00
Tue 21 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Wed 22 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Thu 23 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Fri 24 Apr 1998	0.00 @ 00:10	0.22 @ 20:30	0.02	0.00
Sat 25 Apr 1998	0.00 @ 00:10	0.54 @ 16:00	0.05	0.00
Sun 26 Apr 1998	0.00 @ 00:30	0.07 @ 00:10	0.00	0.00
Mon 27 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Tue 28 Apr 1998	0.00 @ 00:10	0.00 @ 00:10	0.00	0.00
Wed 29 Apr 1998	0.00 @ 00:10	0.01 @ 16:20	0.00	0.00
Thu 30 Apr 1998	0.00 @ 00:10	0.01 @ 12:20	0.00	0.00
Monthly results	0.00 @ 00:10 Wed 01 Apr	320.73 @ 05:20 Sat 18 Apr	0.35	0.02

Figure 4 – Flowlink Report printed in Table Format

CONCLUSIONS

With the advent of the NPDES storm water permit program, and subsequent State regulated discharge permit programs, the monitoring and controlling of storm water runoff at industrial facilities has become a requirement as well as a necessity. Implementation of these new storm water monitoring requirements posed a logistics and manpower problem to industrial facilities, like Kelly, that have multiple storm water outfalls and complex discharge permits. The casual approach to monitoring storm water was no longer a viable option. Kelly responded to the storm water monitoring regulations by installing an automated storm water collection system at each of the base's eight regulated storm water outfalls. Since Kelly's installation of this system, the base has been able to meet all of its storm water discharge monitoring permit requirements and has freed limited manpower resources for other important program tasks. An added benefit to using the automatic samplers has been that Kelly is now able to identify contaminated discharge problems closer to the source and in a timely manner, rather than after the contaminant reaches the receiving waters.

Asbestos Management in Buildings

FAA Southern Region Asbestos Control Program

Ronald R. Nelson
MEM SMO Environmental Compliance Manager
Safety Officer

What will be Covered

- Synopsis of FAA Structure
- Overview of FAA Facilities
- Asbestos Control Program (ACP)
- Outline of How to Develop an ACP

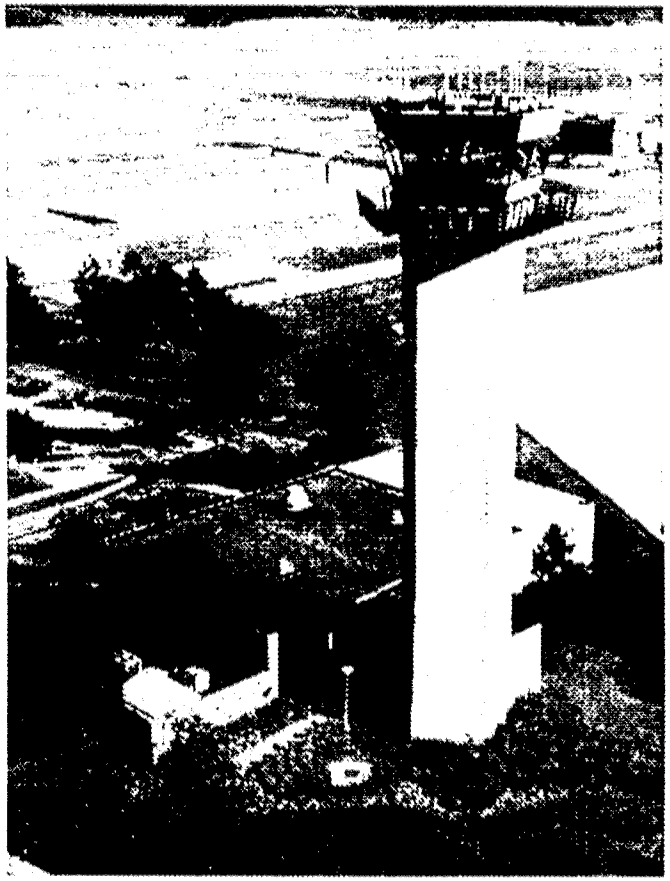
FAA Structure

- Air Traffic (AT)
  - Control Aircraft
- Airway Facilities
  - Regional
    - Facilities & Equipment (F&E)
      - Design
      - Construction
    - Operations Support
  - Field
    - Operations (OPS)
      - Facility Maintenance

FAA Facilities

FAA Facilities

- Air Traffic Control Tower (ATCT)



FAA Facilities

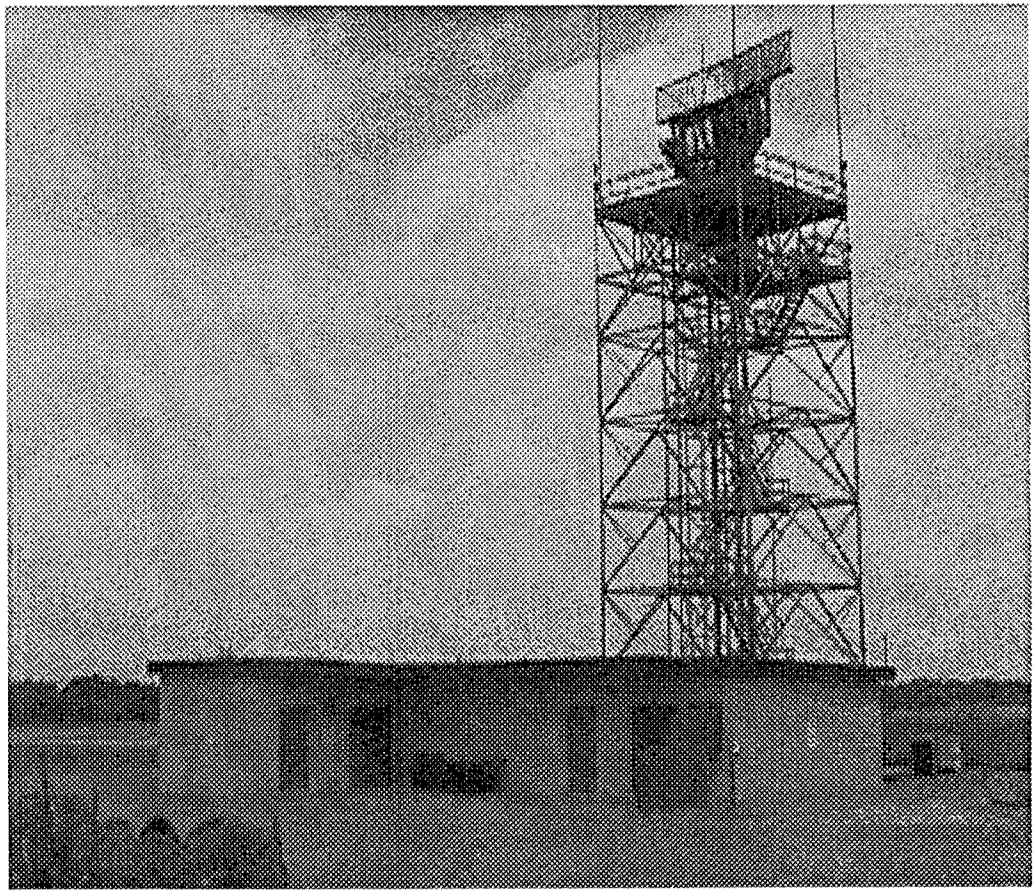
- Air Route Traffic Control Center (ARTCC)

FAA Facilities

- Automated Flight Service Station (AFSS)

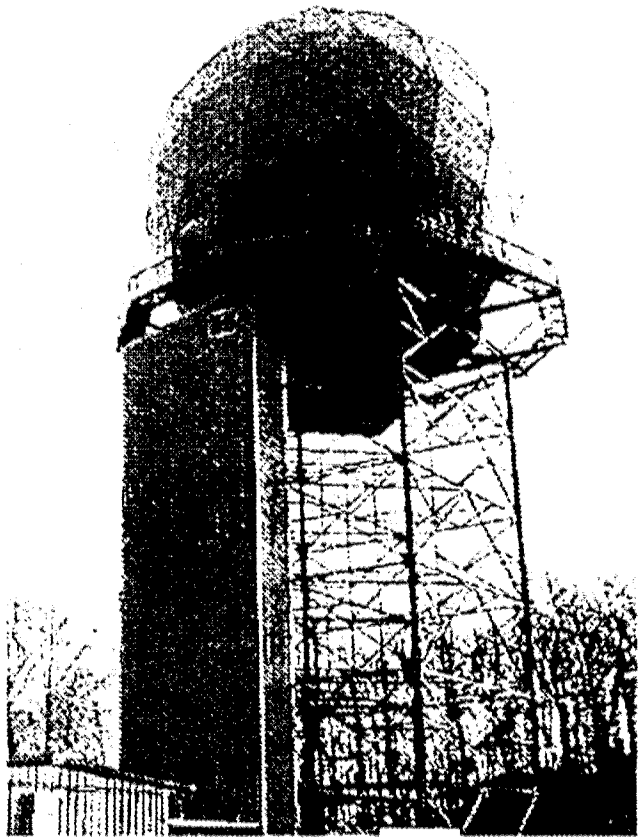
FAA Facilities

- Airport Surveillance Radar (ASR)



FAA Facilities

- Air Route Surveillance Radar (ARSR)

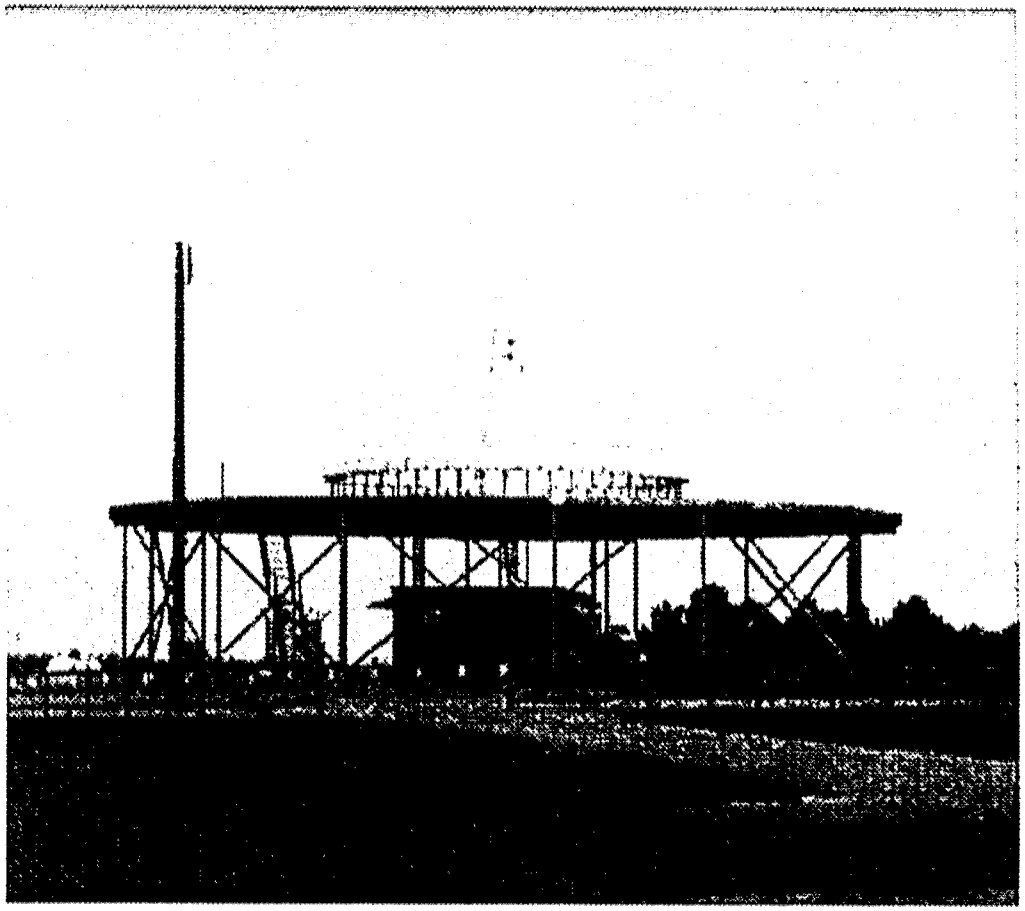


FAA Facilities

- Terminal Doppler Weather Radar (TDWR)

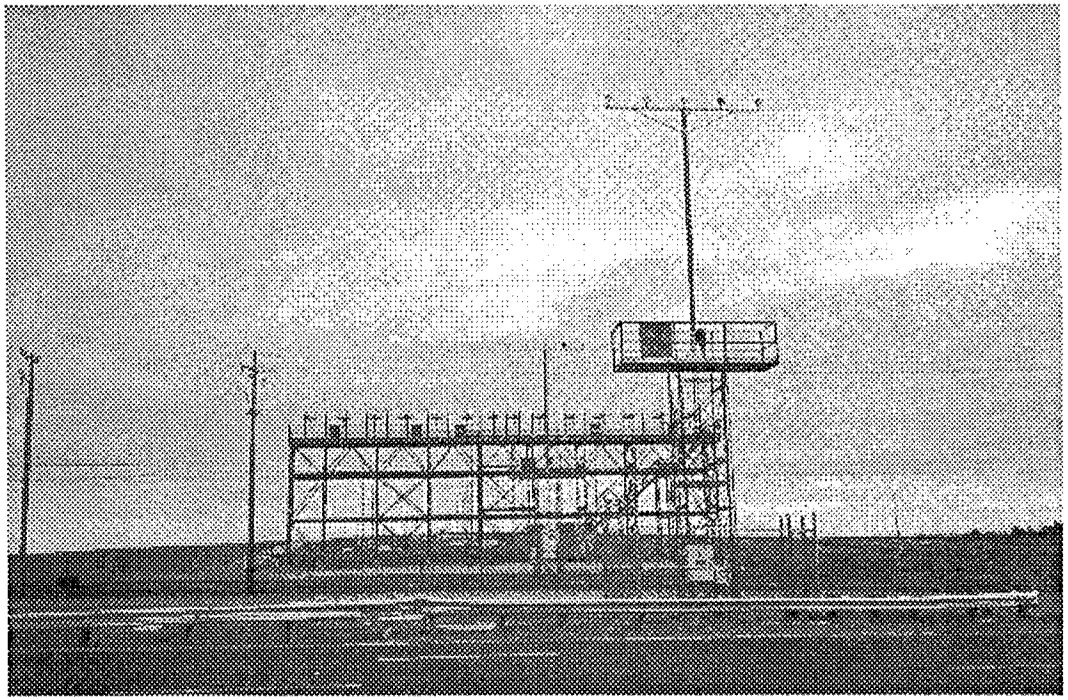
FAA Facilities

- Very High Frequency Omnidirectional Range (VOR)



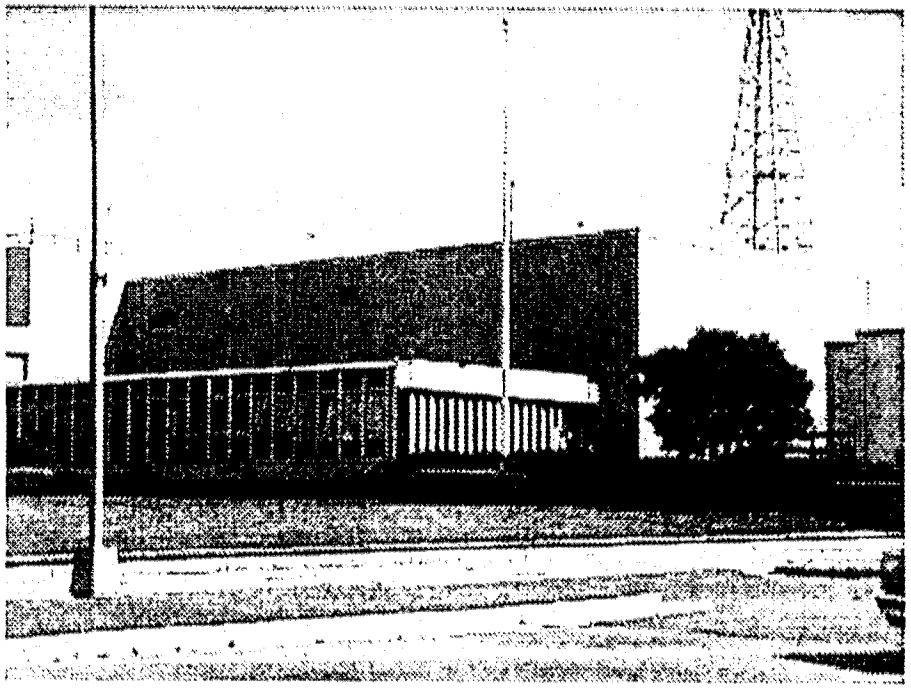
FAA Facilities

- Navigational Aids (NAVAIDS)



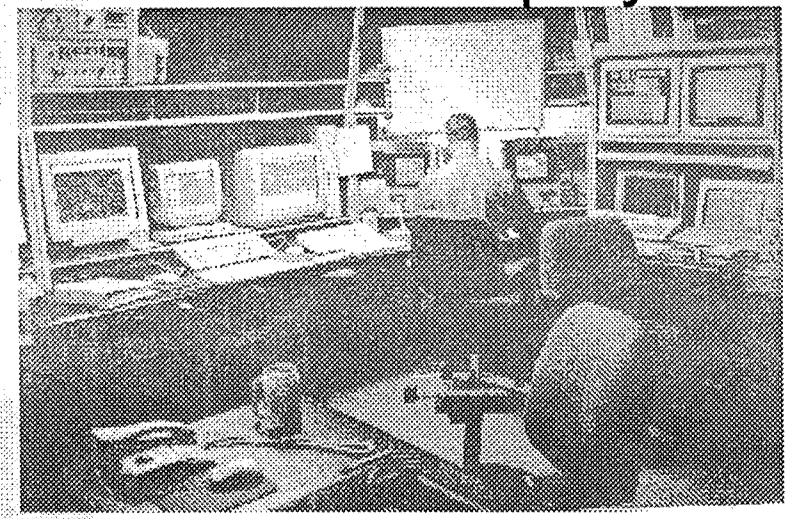
ARTCC Physical Structure

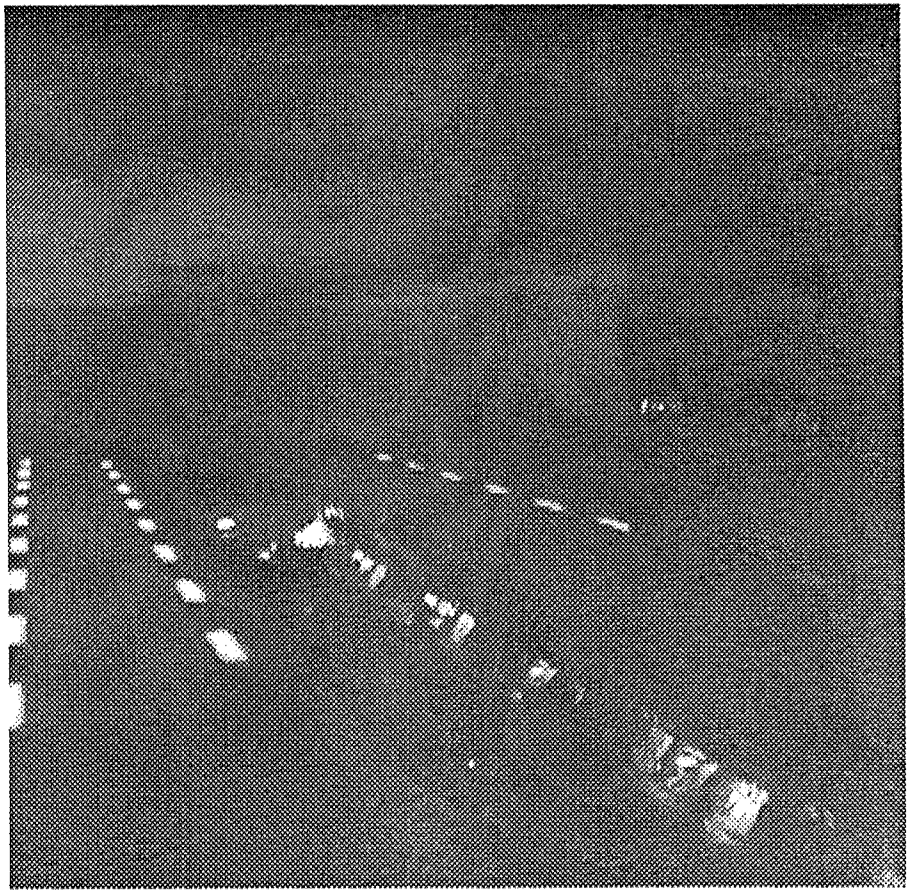
- 150,800 sq. ft. Total
  - Floor Tile
    - 41, 184 sq. ft.
  - Spray Applied Fire Proofing
    - 84,000 sq. ft.
    - 10,000 sq. ft. abated
- 5 ARTCCs in Southern Region
- 32 Nationwide



ARTCC Operation/Personnel

- 24 hrs/day
- 365 days/yr.
- 90-100 AT Employees
- 4-10 AF Employees





Asbestos Control Program (ACP)

Asbestos Control Program (ACP)

- Why Developed
- How Developed
- Program Elements

ACP-Why Developed

- Management Tool to Satisfy Asbestos Requirements
- Manage Asbestos In Place
- Minimize Employee Exposure
- Coordinate Abatement

ACP-How Developed

- Polled Employees
  - Facility Managers
  - Maintenance Personnel
  - Design/Construction Engineers
  - Equipment Installers

Responses

- All Materials Assumed Asbestos Containing Material (ACM)
- All Work Performed by Abatement Contractors
  - High Cost
  - Lack of Facility Familiarity
  - Time Consuming

Elements of our Asbestos Control Program (ACP)

ACP Elements

- Responsibilities & General Requirements
- Facility Surveys
- Asbestos Response Actions
- Medical Surveillance
- Training

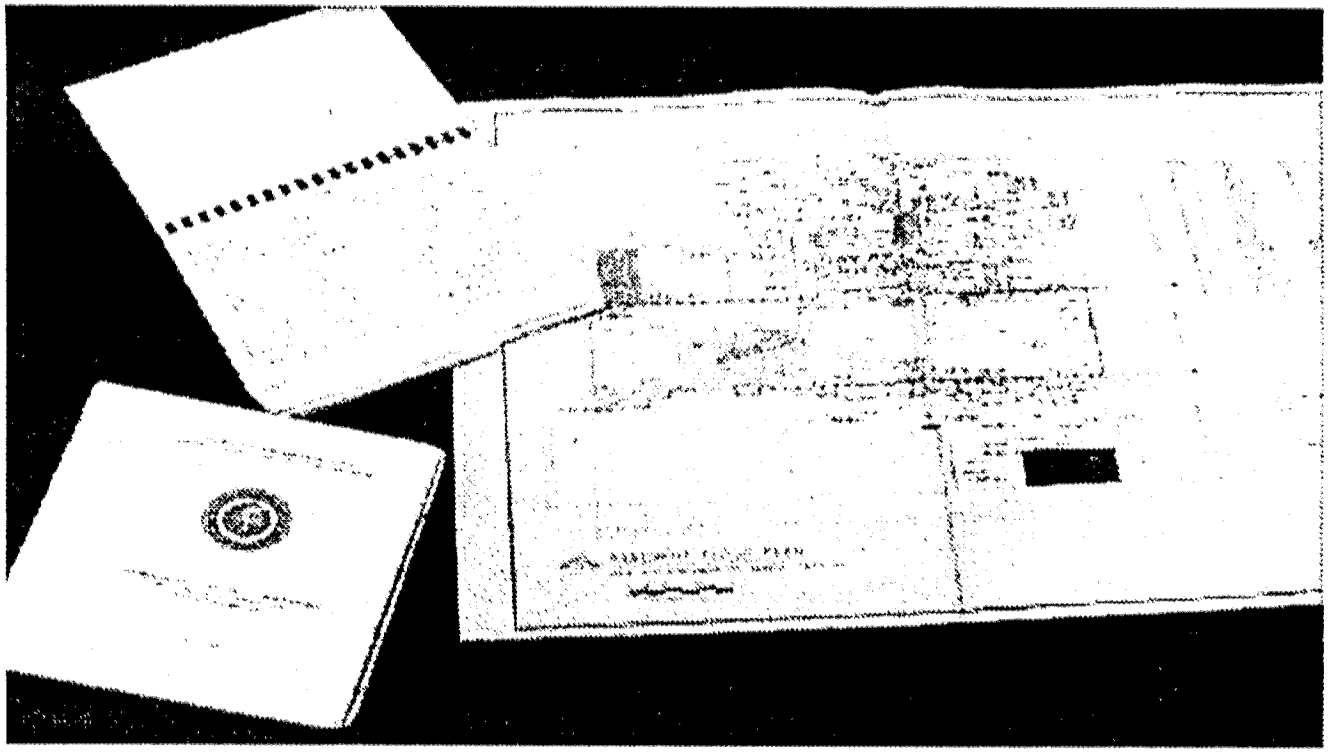
ACP Elements
1. Responsibilities

- Regional
  - Program Manager for Environment and Safety (RPMES)
  - Regional Occupational Safety/Health Manager (ROSHM)
- Systems Management Office (SMO)
  - SECM (SMO Environmental Compliance Manager)
- Systems Service Center (SSC)
  - FAC (Facility Asbestos Coordinator)

ACP Elements

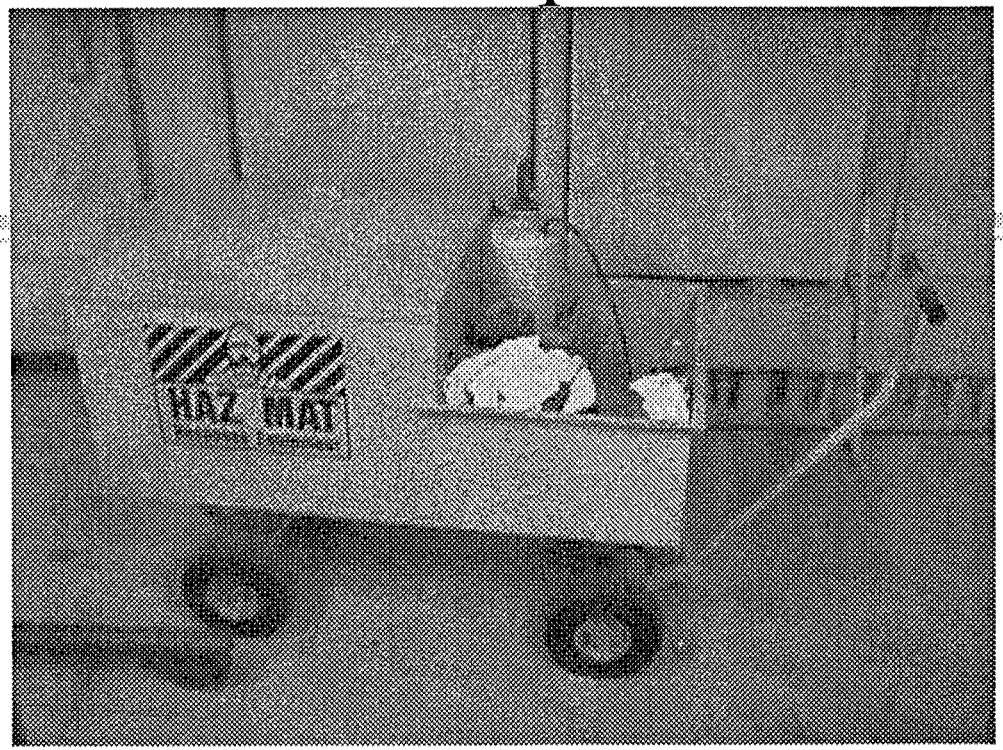
2. Facility Surveys

- All Manned Facilities Surveyed
  - Asbestos Survey Inventories Developed



ACP Elements

3. Asbestos Response Actions



Response Actions

a. Work Permit System

- Regional Project
  - Submitted with 90% Design Review Package
- Local Project
  - Submitted 45 Days Prior to Project Start

Microsoft Word Document

Response Actions (continued)

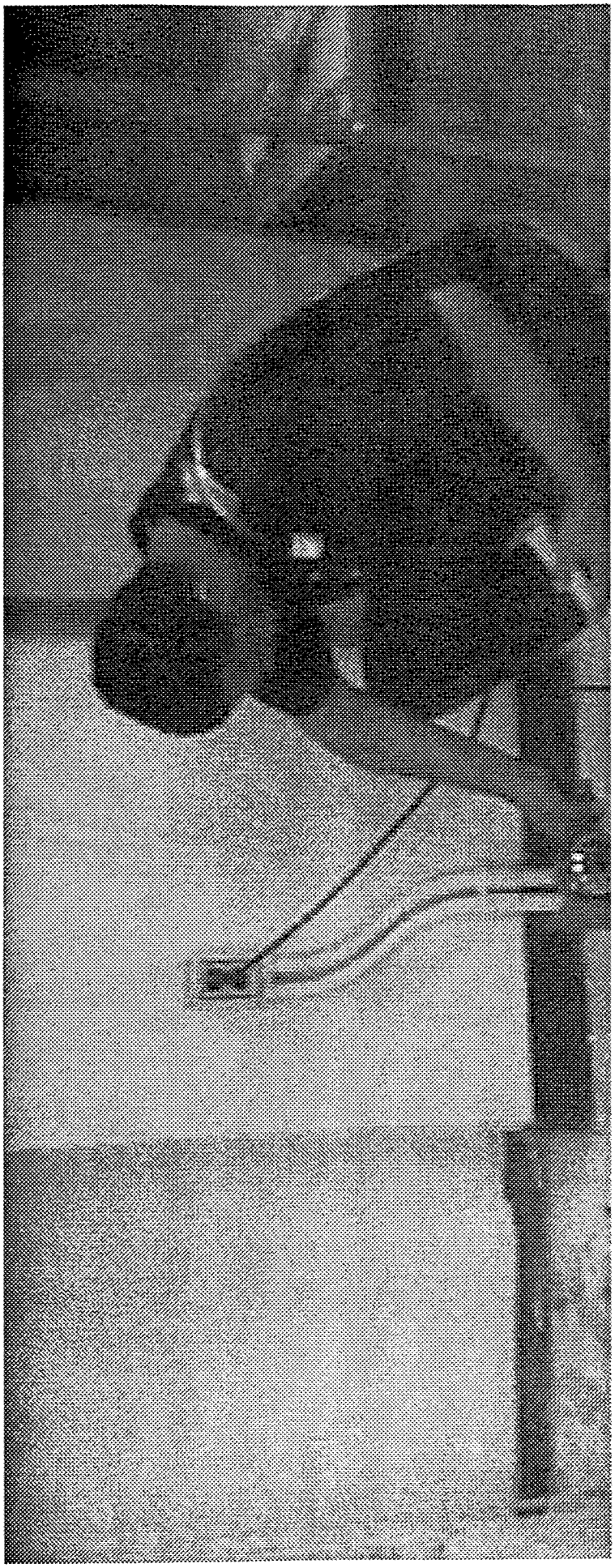
b. Operations and Maintenance (O&M)

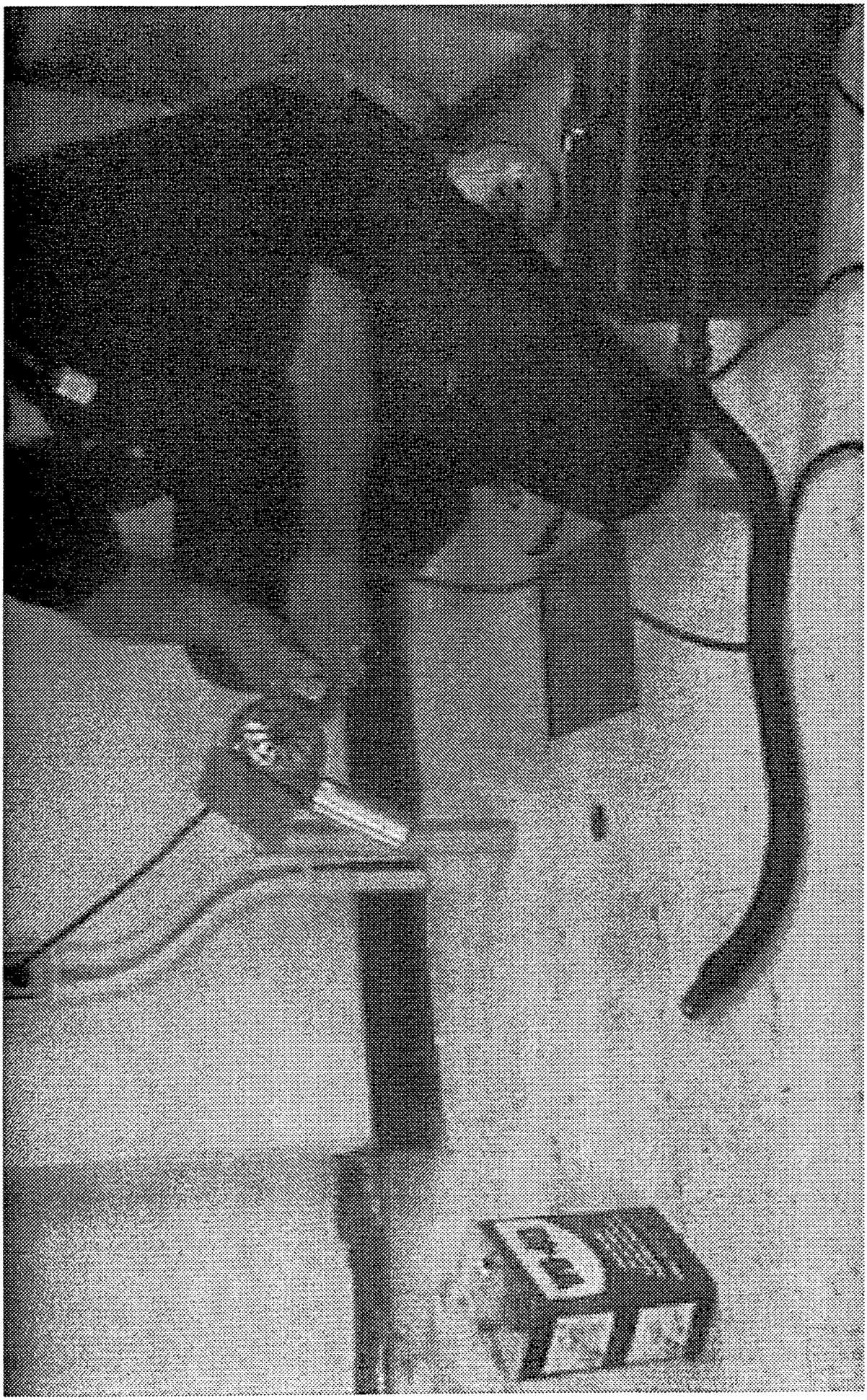
- O&M Activity
  - Resultant Waste of an Activity may be Contained in an Asbestos Disposal Bag (32"x48")
- Abatement
  - Resultant Waste may not be Contained in one Asbestos Disposal Bag

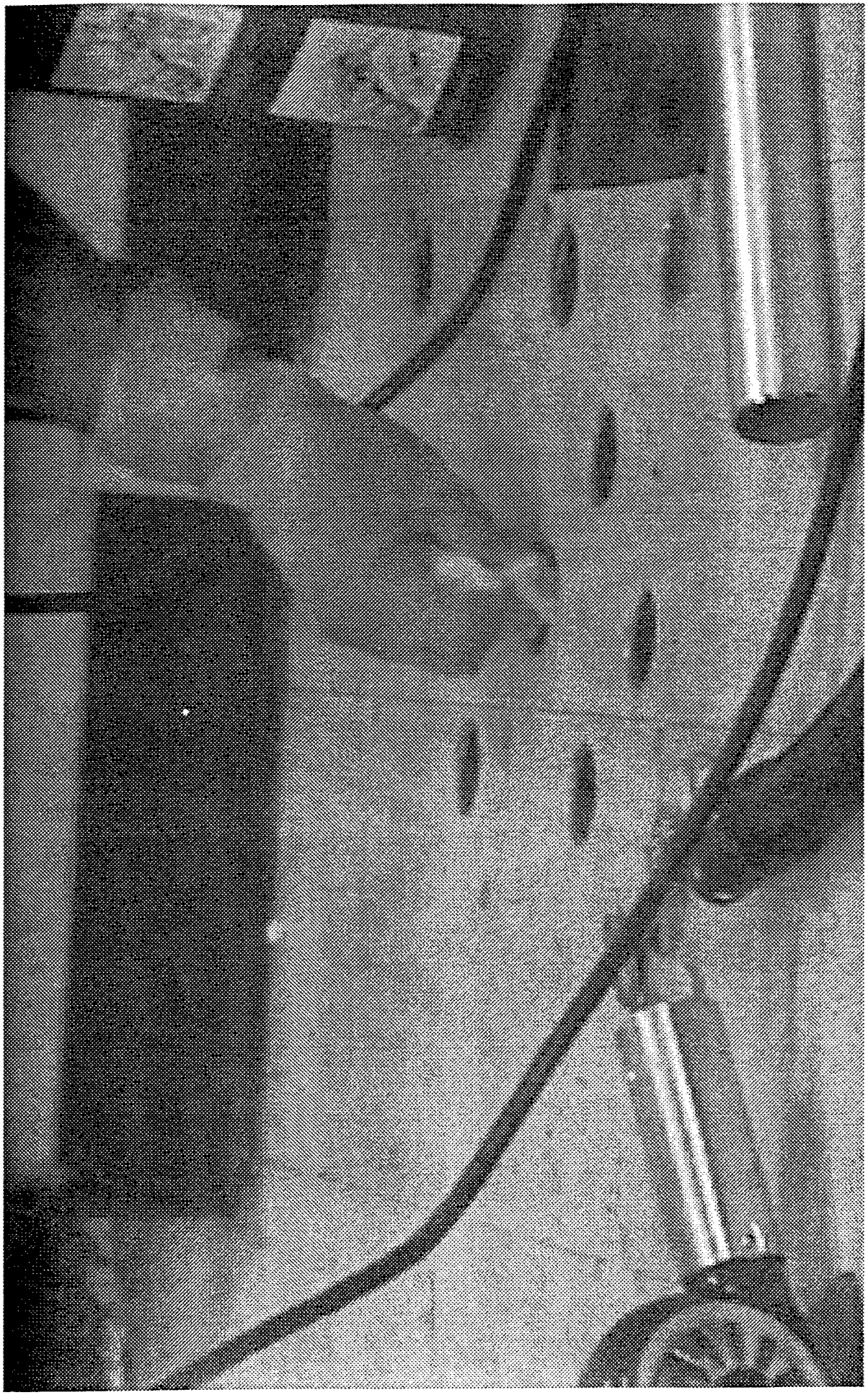
Response Actions (continued)

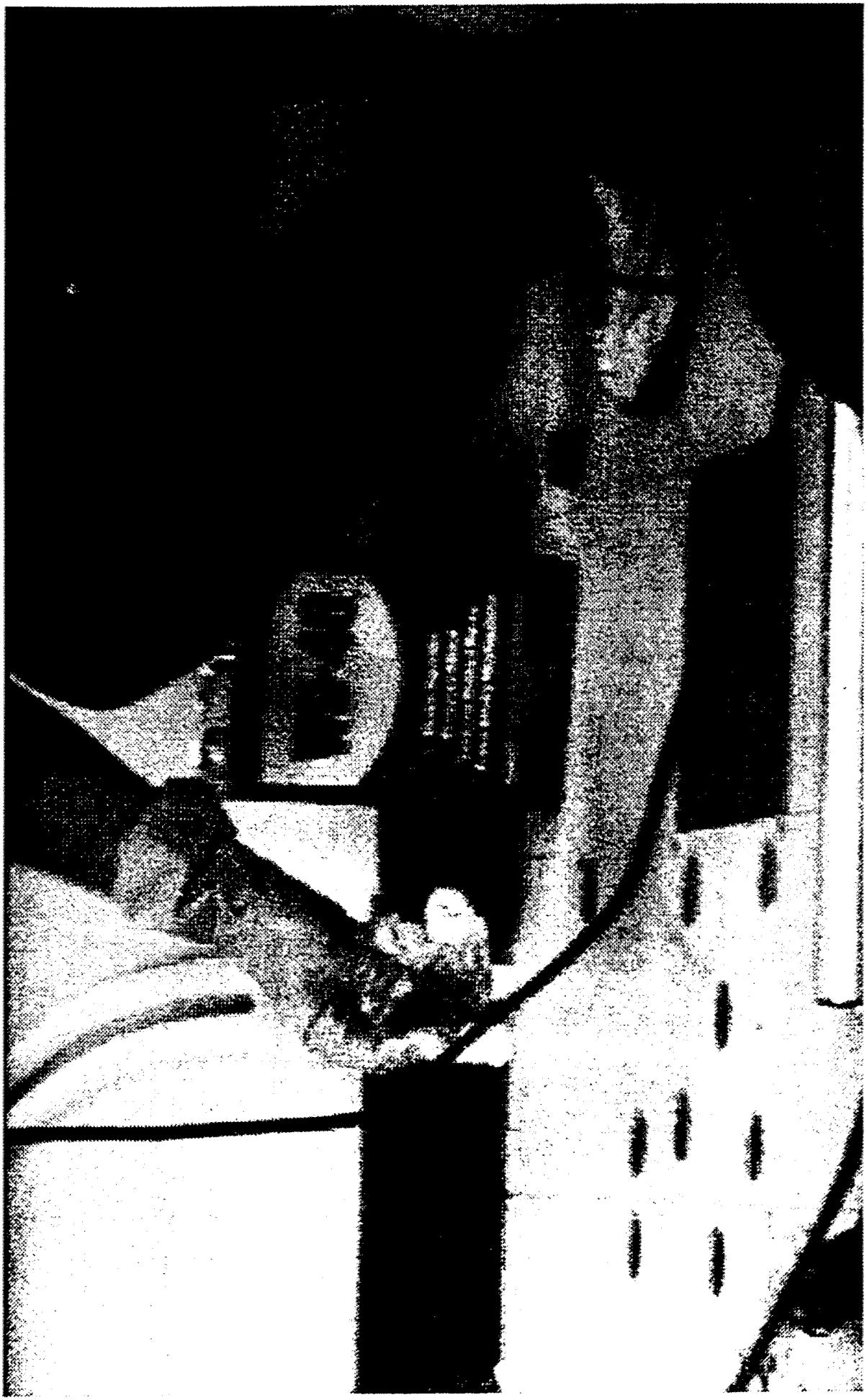
c. Standard Operating Procedures (SOPs)

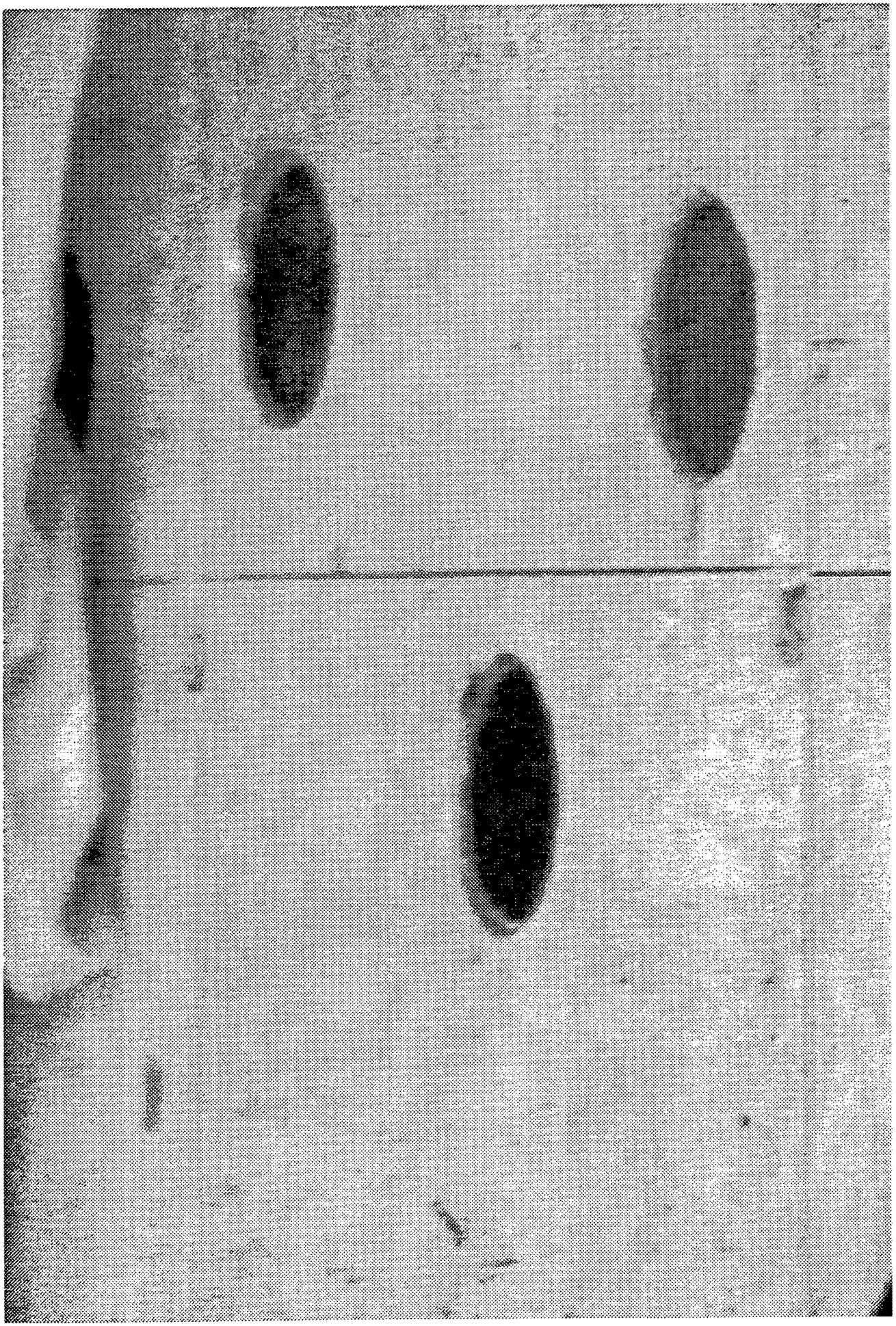
- Developed in Accordance with 29CFR1926.1101 Asbestos
- Performed Negative Exposure Assessments 29CFR1926.1101(f)(2)(iii)
  - Drilling Floor Tile
  - Removal of Floor Tile
  - Changing Light Bulbs/Ballasts
  - HEPA Vacuum Filter Replacement

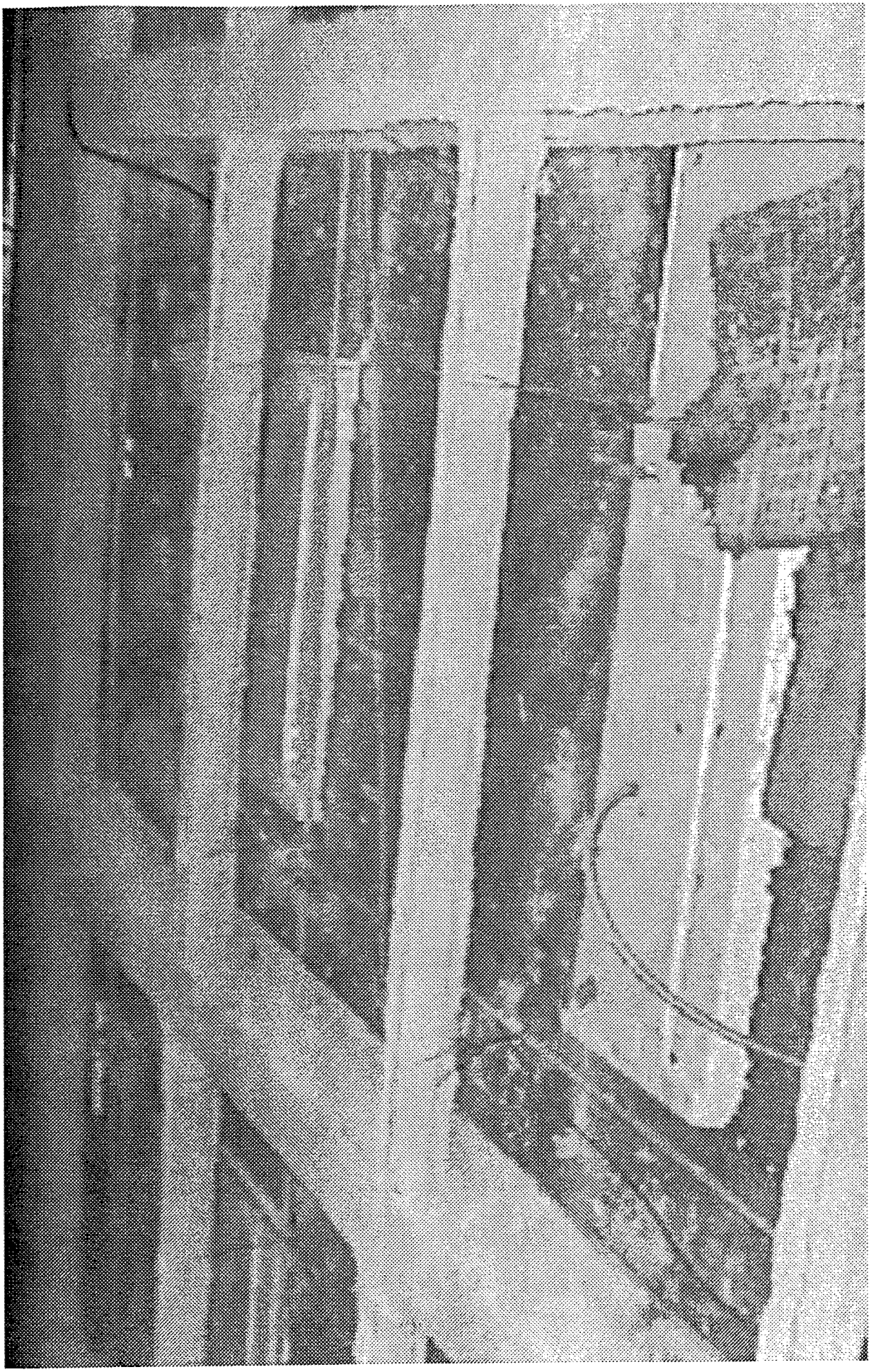


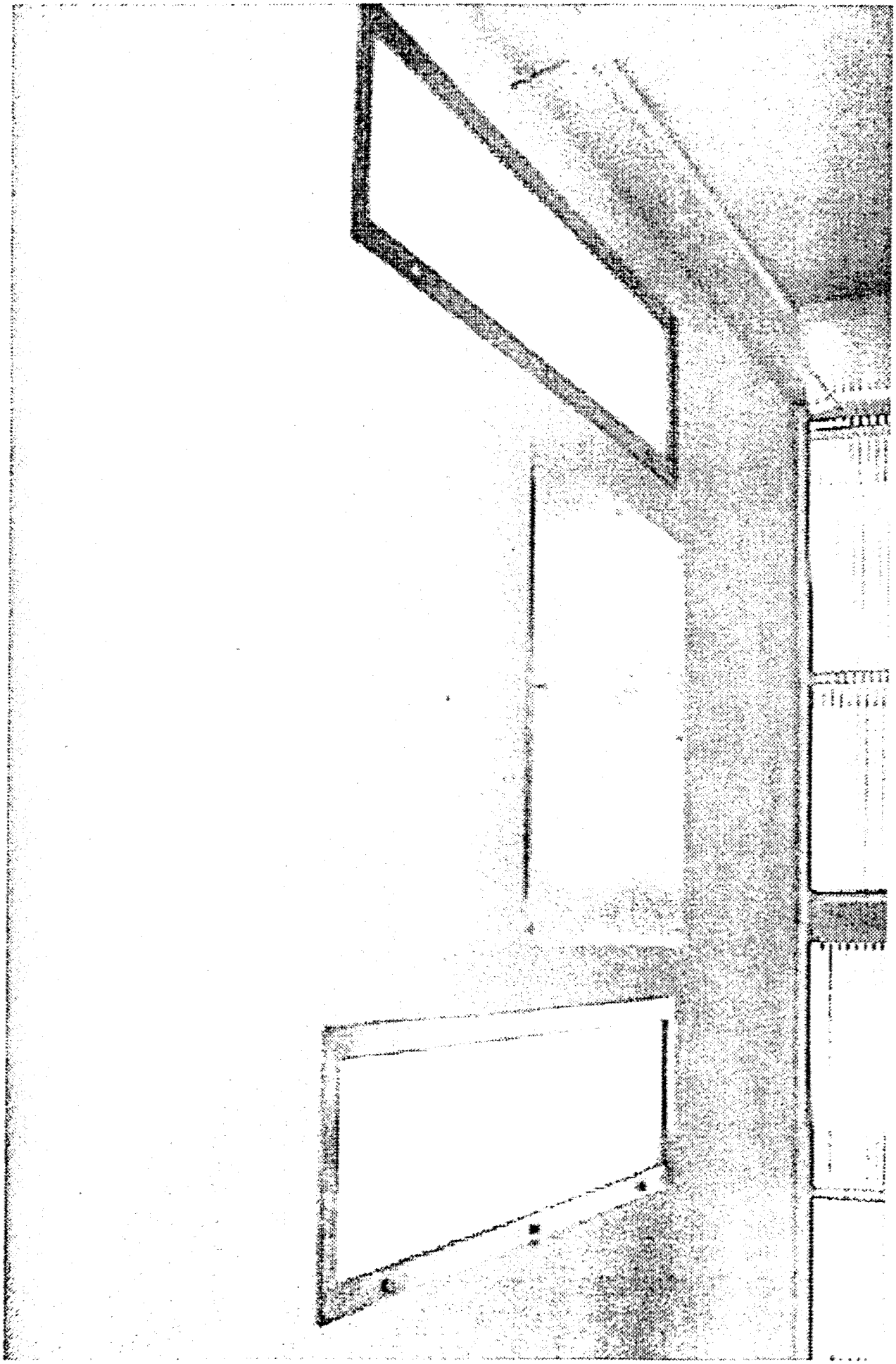


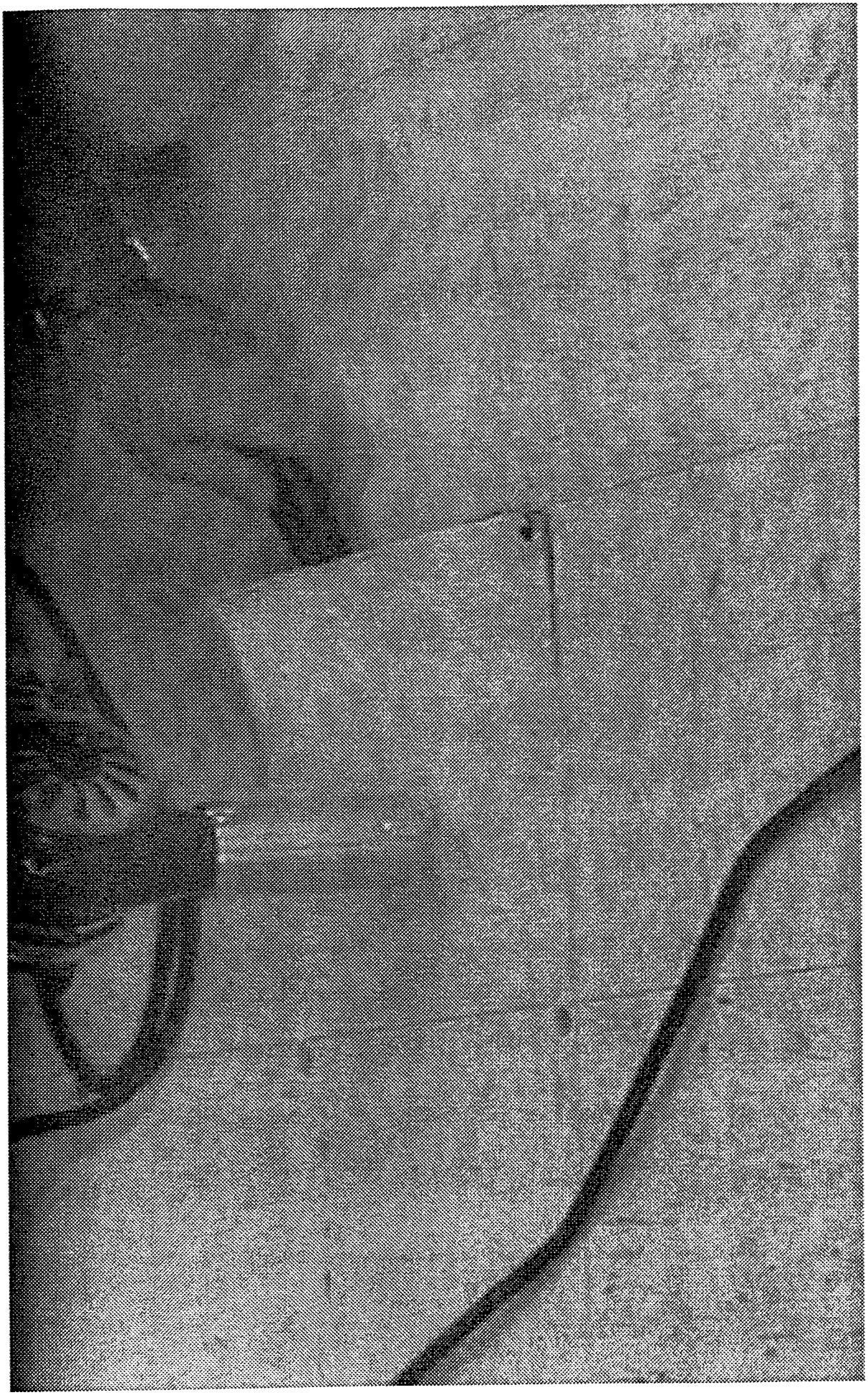


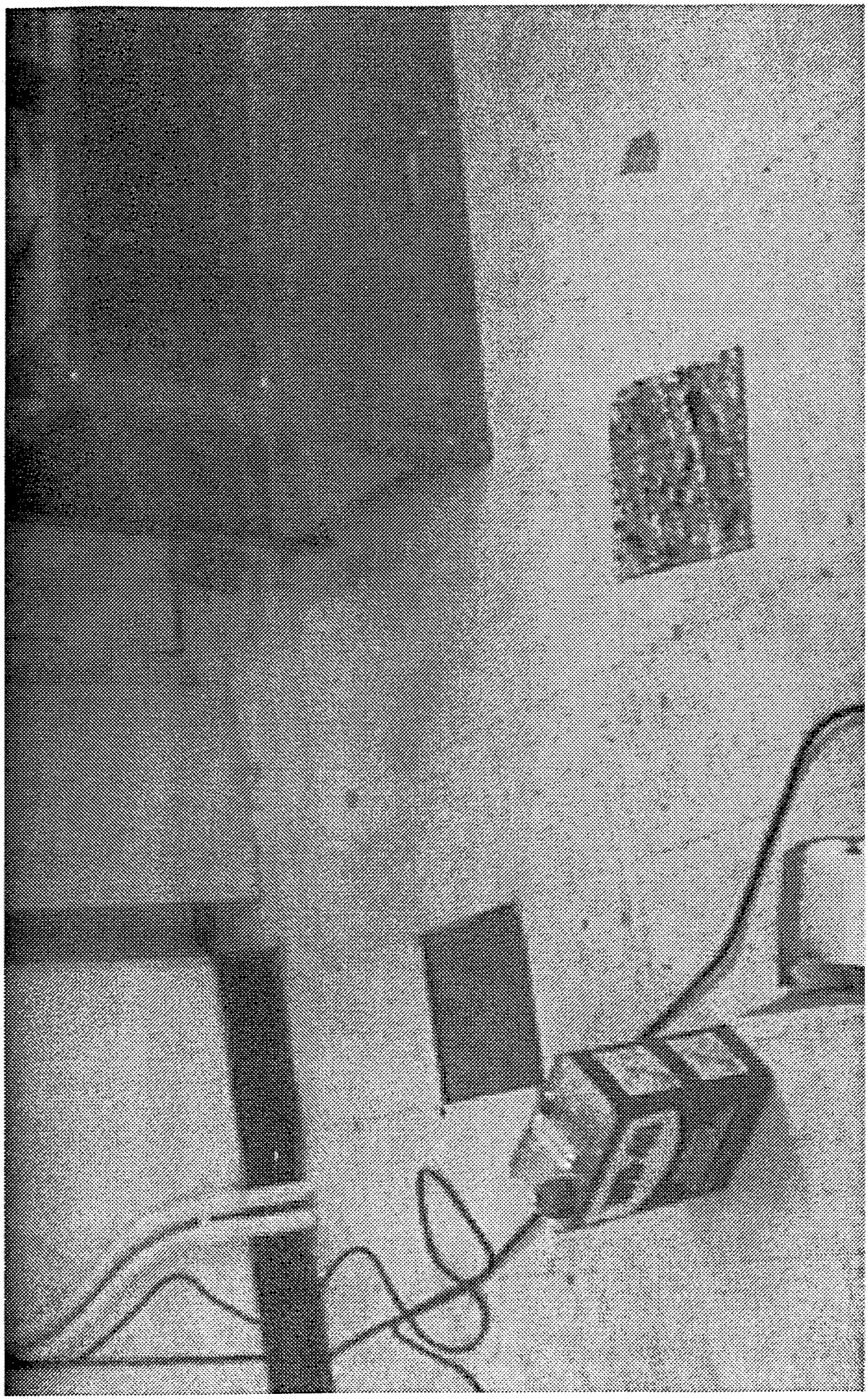












Response Actions (continued)

d. Transportation Storage and Disposal

- Use Small Sealed Containers for Transportation (5 gal. bucket)
- Small Container for Local Storage (30 gal. @ SSC)
- Disposal Arranged Through SECM
  - Waste Load Out
  - Manifesting

Response Actions (continued)

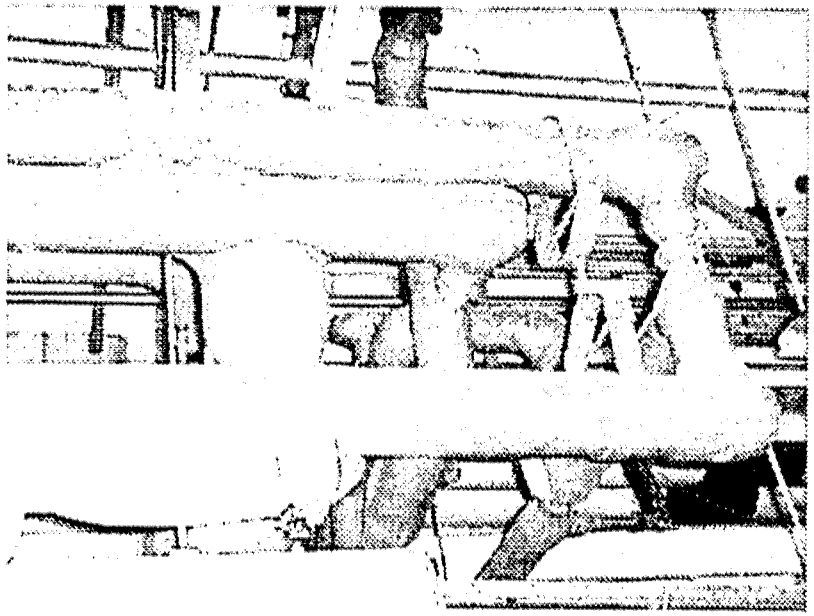
e. Recordkeeping

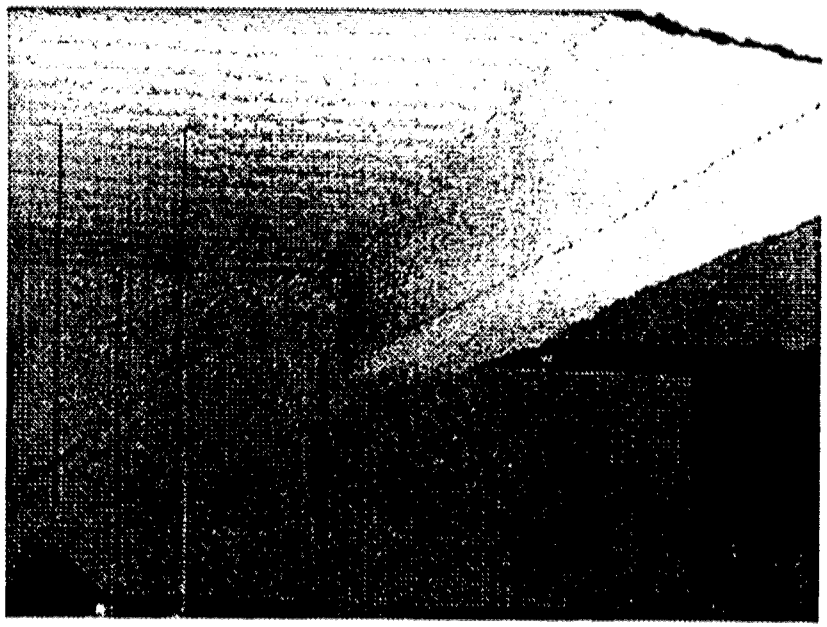
- Work Permits Filed and Maintained
- Air Monitoring Results Maintained
- Exposure Monitoring Records
- Respiratory Protection Program
  - Respirator Fit Test Records
  - Respirator Medical Clearances
  - Respirator Maintenance Documents
- Project Documents
- Incident Descriptions/Documents

Response Actions (continued)

f. Periodic Surveillance

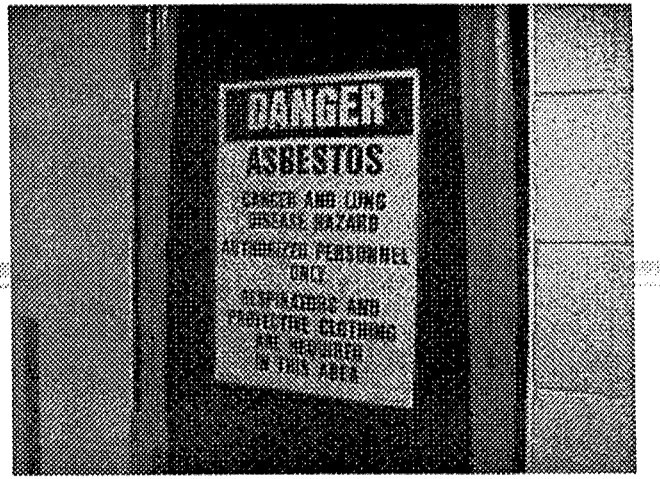
- Air Monitoring (6 month interval)
- Condition Assessment (annual)





ACP Elements

4. Medical Surveillance



- Maintenance Personnel
  - Enter Regulated Space (attic)
  - Full Face PAPRs
- Control Room Personnel
  - Hooded Respirators
  - Emergency Use Only
- Medical Clearance Required

ACP Elements

5. Training - Three Major Categories

- Awareness (2-4 hrs.)
  - Background
  - Health Effects
  - Regulations
  - Locations in Facility
  - Damage Recognition
  - Precautions
  - O&M Program
  - Response to Releases
- Basic O&M (FAC) (16 hrs.)
  - Respirator Use/Fit Testing
  - PPE
  - SOPs
  - Decontamination
- Worker (32 hrs.)

Reality and How we Address It

- ARTCCs Always Operational
  - Incidental Releases
- Project Designers are not Facility Residents
- Removal is Expensive
- Numerous Contractors
- Contingency Plan Developed
  - Hooded Respirators
- Work Permit System and Facility Surveys
- O&M and Training
- Coordination with a Facility Representative

What Makes it Interesting

- Bargaining Unit Personnel
  - Lack of Trust of Management
  - Not Knowledgeable of Regulations
    - Fearful and Emotional
- Maintenance Personnel
  - Previously worked w/o Respirators
  - Work Above Operational Areas
  - Feel Limited by the Permitting System
- Facilities in Constant Change

What Makes it Interesting

- FAA Installers
  - Work at Outlying Un-Manned Facilities
    - No One Monitors their Work
- Contractors
  - Numerous at any Time
    - Difficult to Manage
- Transportation/Storage

Elements of an Asbestos Control Program Revisited

What You Will Need to Develop an ACP for Your Facility

ACP Development

- Perform Facility Assessment
  - 29CFR1910.1001(j)(2)
- Determine Work Activities Required
- Develop a Work Permit System
- Perform Negative Exposure Assessments
  - 29CFR1926.1101(f)(2)(iii)
- Develop SOPs
- Train Employees
  - 1910.1001(j)(7)
- Recordkeeping
- Remove ACM

Partnering for a Sustainable Working Relationship

Jennifer H. Hobbs
Florida Department of Environmental Protection
Orlando, Fl 32803
and
Charlie Venuto
USBI Co.
USBI-SF
Kennedy Space Center, Fl 32815

ABSTRACT

The State of Florida Department of Environmental Protection (FDEP), NASA and USBI Co. have embarked on a unique relationship. Together they have put substance into the term partnering. Traditional relationships between environmental agencies and industry have been based on regulatory requirements. USBI, NASA and the FDEP agreed to take an alternative approach through a partnering effort. A continuous improvement tool, Environment, Health and Safety (EHS) Kaizen was used. Results from the Kaizen event and insights will be discussed

Introduction

The traditional focus of the business community has been on producing goods and services for a customer and creating profit for themselves. The concern now is not just on these customers who purchase the goods and services but rather all stakeholders. This has expanded the realm of interested parties to include stockholders, employees, communities and regulatory agencies. In parallel, the role of government and its influence on industry increased with the advent of environmental regulations.

In the United States, regulations regarding environment, health and safety have often put industry and government at odds. This conflict resulted in the use of resources to oppose each other rather than creating a positive climate to resolve issues. Long term, sustainable relationships need to be based on trust and understanding. A foundation for a mutually beneficial relationship is to identify common goals and objectives. For businesses to survive, their current operations need to meet the needs of the present without compromising the ability of the future generations to meet their own needs. Government should assist in fostering an environment that promotes sustainability. There will of course be those businesses that demonstrate poor environmental performance. The command and control approach is most appropriate in these cases. However for those businesses that understand the strategic importance of environmental issues, working cooperatively with government may produce a synergy that benefits the business, the government, the environment and human health.

Historical Relationship Between Industry and Regulatory Agencies

The passage of environmental legislation mandated government agencies provide oversight to regulated entities in the form of compliance inspections. Many of the laws required the issuance of a permit for the discharge of pollutants into the environment. The permits are essentially specific requirements directed toward a process or facility. Inspections and permit negotiations brought industry and regulatory agencies together but hardly in a manner that fostered sustainable relationships. The complexity of the rules and regulations and the potential for fines and penalties, including potential jail time, often resulted in the inclusion of legal counsel in all compliance discussions between government and private businesses. The legal presence often added an element of contention to what could be best described as an uncomfortable situation.

Compliance Inspections

One of the most common encounters between industry and governmental regulatory agencies is during compliance inspections. Businesses that operate under environmental permits or use hazardous substances are subject to review and inspections due to notification of activities or citizen complaints.

Inspections are typically an adversarial situation. A regulatory agency enters a business unannounced to evaluate compliance with a law or perhaps many laws, if the inspection is multi-media. The complexity and particulars of most of the regulations often makes absolute compliance difficult. Some businesses have taken the view that the government approach is one of command and control. On the other hand, the regulatory agencies may feel that industry should know and understand the rules, especially those that have professional EHS staffs.

Evolution: Compliance to Beyond Compliance

Environmental management typically has transitioned through numerous phases; the most rudimentary program is purely reactive, responding to regulations. A more advanced approach involves participation and influence in rule development. However, in both cases the emphasis is on compliance with regulations. The next level of management addresses the reduction or elimination of the sources that generate pollutants. Part of this approach involves working with environmental agencies on programs to protect the environment.

Voluntary Programs (EPA)

Recognizing the potential benefits of collaborating with industry, especially in projects designed to prevent pollution, the EPA developed cooperative, voluntary programs. These programs are an alternative approach to regulations. In most cases they are non-binding agreements to venture into a project that has both environmental and cost saving benefits. EPA has also developed alternatives to fines and penalties. In place of fines, supplemental environmental projects may be negotiated where a business implements a pollution prevention project, sponsors environmental education programs, or other projects that may benefit the environment in place of fines.

These programs include the 33/50 program that was designed for industry to voluntarily reduce emissions of 17 targeted chemicals. Another initiative, WasteWi$e, focuses on a wide array of waste reduction efforts. This may be through pollution prevention initiatives or purchasing recycled items.

Project XL (eXcellence and Leadership) was initiated in 1995 as part of the "Reinventing Government Program." Rather than a prescriptive approach, this program establishes the goals and objectives (i.e. environmental protection, pollution prevention) to be achieved. The regulated community in conjunction with the EPA develops the methods to achieve the objectives. Participation in the program mandates a high level of performance by the business.

The voluntary programs offer another tool for EPA to use to achieve its goal of protecting human health and the environment. A Senate bill has been introduced that would essentially codify these programs. The bill, "Innovative Environmental Strategies Act of 1997" allows EPA to enter into non-traditional agreements with owners or operators of facilities subject to EPA regulations. This strategy is an attempt to achieve environmental compliance and pollution prevention outside of the normal regulatory scheme.

This partnering approach is now used by FDEP with the approach of non-traditional relationships and using common sense initiatives. Many of these initiatives are on an individual basis.

Case Study - EHS Kaizen (Continuous Improvement) Event

USBI Co. is a wholly owned subsidiary of United Technologies Corporation, part of Pratt & Whitney Space Propulsion, with operations primarily at the Kennedy Space Center in Florida. USBI performs the refurbishment, assembly and test of the non-rocket motor components of the Space Shuttle's solid rocket boosters. NASA is the owner of the facilities and most equipment that USBI operates.

Typical of the relationship between regulatory agencies and industry, USBI only dealt with the FDEP during inspections or permit negotiations. NASA, as the policy maker, was also involved in these dealings with FDEP.

In 1994 a hazardous waste inspection was conducted at Kennedy Space Center including USBI operations. There was one issue that FDEP and USBI could not agree upon. Rather than try to resolve this matter through the administrative process, USBI, NASA and FDEP agreed to work together on a pollution prevention event. USBI would take the lead and offer to have their manufacturing processes evaluated for pollution prevention opportunities. A continuous improvement process, "Kaizen" would be used. Kaizen, a Japanese term, is an accelerated continuous improvement process. "Kai" means to take apart and make anew, "Zen" refers to think and help others.

Total Quality Management (TQM) had been introduced to many American businesses during the 1980s. A helicopter manufacturer, Sikorsky, a subsidiary of United Technologies Corporation, used TQM to address problems in manufacturing processes. However, after some initial successes, the rate of improvement diminished. To continue the momentum generated by TQM, the Kaizen management approach was instituted.

A typical TQM team would meet on a periodic basis, perhaps once or twice a week, often for weeks or months. Recommendations would be presented to senior management who would decide on what suggestions to implement. Eventually (hopefully) changes would be made. In contrast, Kaizen is continuous improvement in fast forward. A team of employees such as technicians, engineers, supervisors and managers who understand a process are placed on a team. These teams are dedicated for the duration of an event (one to two weeks) to study, understand and implement improvements to the process. The teams are empowered to make changes to facilities, systems and processes. A multitude of improvement opportunities are discussed and the most feasible are implemented during the time frame of the event.

Empowerment of the teams gives employees a sense of accomplishment and ownership. Through Kaizen events, Sikorsky was able to achieve a 25-50% improvement in production efficiency. Kaizen was also applied to improve paperwork flows such as process engineering changes.

United Technologies Corporation and Pratt & Whitney in Berwick, Maine sponsored such an event. The Maine Department of Environmental Protection and employees of the facility participated in this Kaizen. The week long event resulted in two major accomplishments. The efficiency of production processes was increased through waste reduction and perhaps more importantly the relationship between the Maine Department of Environmental Protection, United Technologies Corporation/Pratt and Whitney improved.

USBI had similar experiences with TQM and Kaizen. While EHS issues had been addressed during their Kaizen events, it had never been the focus, nor had the involvement of an outside agency been critical to its success.

Sustainable Communications Meeting

Prior to collaborating on the pollution prevent Kaizen, it was decided to bring the groups together. This would give the organizations the opportunity to meet and develop a fundamental understanding of each other, creating a more congenial atmosphere. The charter, roles, polices and objectives of the groups must be articulated and understood. These core principles provide a starting point. The theme of this initial gathering would be communications and coordination.

Representatives from USBI, NASA, FDEP and other NASA contractors met at the FDEP's Orlando office to conduct the meeting. Senior managers from USBI and FDEP described the uniqueness of the event and the new direction the groups are headed. This was an opportunity to begin a new relationship.

To help initiate a mutual understanding, the Kennedy Space Center community and FDEP took turns at presenting an overview of their management systems, legal requirements, policies, goals and objectives. The meeting was lead by a facilitator experienced in bringing diverse groups together for continuous improvement events. The facilitator helped to maintain the participants' focus.

The group broke into small teams to discuss what each organization wanted from each other and what projects they wanted to work on together. No ideas were rejected initially. The ideas were discussed and, based on consensus, it was agreed that the following proposals would be pursued:

Regular Meetings

Although the prospect of adding additional meetings to anyone's schedule may not be desirable, it was determined regular meetings would keep communications open and would serve as a vehicle for exchanging information. Quarterly meetings involving NASA, the contractors and the FDEP were scheduled. In the two meetings that have taken place, open and honest discussions on issues ranging from policy to compliance issues have occurred. The charter of this meeting group is to function as a steering committee for Kaizen events, to address best management practices and review NASA Environmental Management Standards. The membership has been expanded to include representatives from the Cape Canaveral Air Station that is adjacent to the Kennedy Space Center.

Training Exchange

Both groups possessed training information, opportunities and resources desired by the other. NASA and its contractors offer numerous technical training courses for its work forces, including health and safety classes. The FDEP was interested in participating in confined space entry training to educate inspectors on the dangers they may encounter in confined spaces while conducting inspections. In turn, the FDEP would provide training to operators, engineers and supervisors in hazardous waste management, air emissions and water pollution.

FDEP conducted three, 3-hour sessions on Hazardous Waste Management, "What FDEP Inspectors Look For." There were approximately 180 attendees made up of Kennedy Space Center employees. After the third session, two site visits/mock inspections were conducted at USBI. This provided the opportunity for technicians, supervisors and management to experience the protocols of a FDEP hazardous waste field inspection. A FDEP and a USBI representative chose the inspection locations prior to the site visit and all questions and likely scenarios were reviewed. The exercise was intended to be a learning experience. The FDEP was not on site to perform an official review. The inspector would not cite any minor violations, but merely point them out if any were noted. During the mock inspection the inspector discussed container management, tested safety equipment and walked the group through what an inspector sees and thinks while inspecting.

This mock inspection demonstrates the high degree of trust that has developed between the regulatory agency and industry. Inviting regulatory inspectors to examine hazardous waste processing, holding and storage areas is a far cry from the days when inspectors were held at bay and discouraged from entering a facility.

The Air Section from FDEP also conducted a compliance course at Kennedy Space Center to discuss air permitting and compliance issues. This course was attended by 40 employees, again with representatives from the major contractors and NASA.

The FDEP has taken advantage of training offered by Kennedy Space Center, several FDEP employees have completed the Confined Space Entry Course.

The FDEP/Kennedy Space Center cross training is in its infancy but clearly has had positive results as exhibited by comments on course evaluations. This aspect of the partnering project has tremendous potential and is a win-win situation for all participants. The cooperation required to organize and conduct the training also added to the partnering process. The mutual benefits derived help to establish a climate of sustainability.

Monitoring Data

There are numerous environmental monitoring stations at Kennedy Space Center for surface water, ground water and air. The data collected is not required by permit conditions but rather to understand the environment and see what, if any, effect its operations may be having on the local environment. Kennedy Space

Center provided historical data and will continue to provide future reports to FDEP. This will expand the FDEP's database and allow for better scientific based decisions.

Pollution-Prevention Projects

The reduction of pollution is a goal common to industry and the regulatory community. Less pollution equates to reduced liability, more efficient operations, less expenses associated with waste disposal and emission fees, diminished regulatory burden and therefore establishing sustainable processes. It also supports the goal of environmental regulatory agencies to protect human health and the environment. Although joint participation in a continuous improvement event involving pollution prevention was an up front goal, the cooperation at this planning meeting helped to establish the atmosphere of trust that would be needed to successfully complete a pollution prevention project. The meeting broke down some barriers, and the group was ready to take it to the next level.

It was concluded from the session that protection of the environment was not just the aim of environmental regulatory agencies but was clearly an objective of all the participants. As the meeting concluded instead of various factions there was cohesiveness between the organizations.

EHS Kaizen

The EHS Kaizen was recognized as a critical component of establishing a meaningful partnership between industry and the government. To assist in making the event successful, help was brought in from organizations outside of USBI. This included employees from United Technologies Corporation EHS and Pratt & Whitney EHS who had either participated or led other EHS Kaizens. Technical assistance was also brought in from the United Technologies Research Center. NASA participants included an environmental representative from the Kennedy Space Center and a Materials and Process Engineer from the Marshall Space Flight Center. USBI employees included technicians, refurbishment engineers, supervisors, material and process engineers, and representatives from facilities, EHS and quality assurance. The FDEP had a contingent of eight including inspectors and pollution prevention experts. This was the largest group of regulatory agency personnel ever to participate in an EHS Kaizen within UTC.

On July 28, 1997 the pollution prevention event was initiated. A successful pollution prevention project needs the support of senior management. Senior management from USBI and FDEP launched the event providing general direction for the team and emphasizing the importance of this effort to all organizations. This was followed by some Kaizen training, discussing issues such as risk and hazard analysis, prioritization of EHS issues, financial considerations and understanding inputs and outputs of processes.

The group was divided into four process teams. The processes were selected prior to the event based on an analysis of risks and hazards. Team membership consisted of a team leader, FDEP employee, technician, engineer and supervisor. This broad based composition allowed for a wide range of perspectives and ideas. The four process teams were: metal treatment small parts, metal treatment large components, grit blasting, and painting.

The teams were instructed to examine the processes associated with their assigned areas. Observations of shop activities, interviews of shop personnel and review of work documents were performed. Inputs and outputs of the processes were documented. The majority of this review was conducted during the first day. This provided a fundamental understanding and allowed the teams to focus on items that could improve EHS.

As the week progressed ideas were discussed and, where it made sense and was possible, immediately implemented. Improvements made during the week of the event included replacing leaking hoses used to rinse off hazardous metal treatment solution. The leaks contributed to an increase in hazardous waste production. A high beam used for attaching lanyards was wrapped with foam rubber to minimize danger from head impact, a safety issue.

The ideas and suggestions produced by the teams were numerous and creative. A synopsis of the teams and their activities follows:

Metal Treatment Small Parts

The small parts metal treatment process consists of a series of tanks with solutions for cleaning and treating aluminum components. The team identified a potentially significant waste saving solution. With the current process, a part is immersed in a tank containing a metal treatment solution. The part is then transferred to another tank where the treatment solution is rinsed off with water from a hose. This rinse water was then transferred to a hazardous waste storage tank. The team suggested the rinse water could be reused for subsequent rinsings (based on analytical research). The rinse water could also be used to replenish evaporative losses from the process tank.

These changes would require physical modifications to the system. This modification could not be accomplished within the time frame of the Kaizen event. However, the project was funded, designed and scheduled for completion by mid 1998.

Some changes were made during or right after the event. Standard spray nozzles were replaced with low volume, high pressure units. This had an immediate impact on reducing waste. Controls were placed on the process tanks with the implementation of a bath maintenance program. This extended the life of the detergent bath from three months to one year and the metal treatment from one year to indefinite.

These improvements resulted in a reduction of 3000 gallons per year of hazardous waste and over $2,500 per year in cost savings.

Metal Treatment Large Components

The large components are handled in a manner similar to the small parts. However these parts are too large for dipping into tanks. Rather, detergent and metal treatment solutions are applied via a spray container and then rinsed with water. Wastes are directed to storage tanks.

While observing a metal treatment operation, the team discovered excess metal treatment solution was disposed of as hazardous waste rather than being saved for the next operation. This had been a standard shop practice as there was no approved location to store the solution in the spray can. The team immediately ordered a chemical locker so that the spray applicator with metal treatment solution could be stored in the shop.

As in the small parts area, new low volume, high pressure nozzles for the metal treatment applicator and rinse water hoses were ordered and installed. There were administrative changes made to the process including standardizing the work documents for metal treatment application and improvements in the training of operators.

Recycling of rinse water was proposed for this process. However, unlike the small parts tanks, the large components are processed in a large room without any environmental controls such as heat or air conditioning. Rinse water is applied to the structure and allowed to run off onto the transportation dolly holding the structure. The rinse water then falls onto the concrete floor and is finally routed into the waste drain. Contaminants such as oils and grease could be introduced into the process that could jeopardize the integrity of the flight hardware. The rinsing process would also become more complicated as the recycled rinse would have to be followed by a fresh water rinse. The recycling of the waste water was not pursued.

The Kaizen helped to raise awareness of the hazardous wasted generated. The metal treatment rinse is the largest waste stream produced by USBI. As a result of the Kaizen, another team was created to examine non-toxic alternatives to the metal treatment solution. The improvements that were implemented have reduced waste and improved the process.

These ideas saved 160 pounds per year of alodine solution and reduced wastes by an equal amount. Monetary savings exceeded $250.00 per year.

Painting Process Team

Structures are coated with a two part paint after the metal treatment process. The paint system was a recent replacement for a paint containing lead pigment. The new paint has a water based top coat and is low in volatile organic compounds. However, the paint wastes were among the top five wastes produced. After a thorough review of the operations, the team decided to focus on the wastes produced during spray gun cleaning as well as some ancillary issues. Paint spray guns were cleaned with a solvent that was transferred to a collection drum after each cleaning. It was determined that a gun cleaner that reuses solvent for cleaning would be preferable. The cleaner was ordered during the event. The FDEP member of the team pointed out that the solvent used for a gun cleaner would not be considered waste until removed from the gun cleaner and deposited into a waste drum. This provided some relief from the 90 day storage limit. During its evaluation of shop operations the team found that containers used to transport solvents were not safety approved. Proper containers were ordered immediately. The team also implemented some administrative changes, including the development of training aides to preserve the useful pot life of the paint and to provide training to standardize equipment prior to mixing.

The spray gun cleaner will reduce waste by 4,000 pounds per year, with the related reduction in chemical purchase and waste disposal resulting in a savings of over $6,000 per year.

Media Blasting Team

The process of blasting was broken down into three categories by media type: plastic, glass and mineral. Plastic media is used to remove paint from large components. The plastic media blasting is performed in a booth were the media can be reused until the particles are too small. Two immediate problems were noted by the team. First, plastic media was escaping from the blasting bay under a door and was coming into contact with the metal treatment solution, creating additional hazardous waste. This was quickly solved by taping the area between the lip of the door and the floor. The work documents were changed to have the integrity of the tape checked prior to blasting operations.

The other problem was a poorly operating pinch valve in the system. Once a week the valve would fail resulting in the loss of 100 pounds of media and four man-hours to clean up and dispose of the media. A system modification is under review.

Recycling of the plastic media was suggested by the team. Over 90,000 pounds of plastic media is disposed annually at the county landfill. There are companies that can accept the used media and convert it to household fixtures. Bids have been solicited to perform this task.

Glass media is used to remove corrosion from components. The recycling of spent glass media is also under investigation; however, since the glass media and mineral media blasting are performed in the same booth the co-mingling of these waste streams may prohibit recycling.

With the likelihood of recycling the plastic media, a significant solid waste stream will be put to beneficial reuse. The recycling will cost about $5,000 more per year than just disposal; however, it was deemed worth the extra cost. Recycling will lower the potential long term liability associated with solid waste disposal in landfills.

Insights

The partnering of industry and regulatory agencies may prove to be a more powerful means of protecting the environment than command and control. Partnering needs to be a selective process. Industries that have working environmental management systems and good compliance records should be considered for partnering. This approach could be used to encourage compliance by those businesses that have poor compliance records. This

is a case by case decision. Establishing partners with firms that can be trusted will allow the regulatory agencies to spend more of their efforts on companies that need additional oversight.

There is great risk for the regulatory agencies when they enter into a partnership, especially one that may involve granting some relief from regulations. Issues resulting from an industry partner could be highly visible and exploited in the media. A perception that a regulatory agency may have sanctioned behavior that led to a non-compliance situation could be very damaging to the publics' faith in government.

Partnering provides regulatory agencies with the opportunity to be proactive. Partnering requires an up front investment in time and resources. Like any investment, there is a risk that it will not pay off. However, the potential to save time and money in the long term makes this a risk worth taking.

The USBI, NASA and FDEP partnering demonstrated that the unthinkable is achievable. The regulatory and process expertise provided synergy for a creative process. The opportunity to work together on common problems went a long way in establishing trust. Partnering has often been discussed in lofty terms. The EHS Kaizen provided a mechanism to put substance into the term partnering. This process also showed how each entity can benefit from the other.

Partnering is a dynamic relationship that will always require nurturing. . Sustainable relationships benefit all parties involved. Considering how much energy was put into the traditional adversarial relationships of the past, the energy spent on developing and maintaining a partnership is well worth the effort

Hazardous Materials Elimination
A Management Perspective

Alan Brown
The Boeing Company
Rocketdyne Propulsion and Power
Canoga Park, California

Abstract

Rocketdyne conducted a very successful hazardous materials elimination program from 1989 through 1996. Goals for the program were established in accordance with regulatory constraints and a team was assembled to address the actions. Technological advances are seldom completed with respect to calendars or legislative decrees; however, this program accomplished the goals in a time frame that satisfied the regulatory activity. In reviewing the program, several critical factors were identified which were key to success. These elements are identified along with examples that demonstrate the contribution of each. They are valuable lessons learned and can be applied to any hazardous materials elimination activity to achieve success. This is a management perspective on conducting a successful Hazardous Materials Elimination program.

Introduction

In the mid-1980s, Rocketdyne Propulsion and Power recognized the need to increase its efforts in hazardous materials elimination due to impending regulations associated with the Montreal Protocol. As a result, a multidisciplinary Hazardous Materials Elimination Team was formed in 1989, to eliminate ozone-depleting substances and minimize the use of other hazardous materials. This proved to be a judicious decision as the 1990 Clean Air Act Amendments effected a ban on the production of many of these substances within the subsequent 10 years. To give a scope of such an undertaking, in 1989, Rocketdyne was gulping down 450,000 pounds of 1,1,1 - trichloroethane and 150,000 pounds of Freon 113 annually. The task was certainly formidable, but rather than settle for an easier goal, total elimination was established as the target. The atmosphere driving the technical challenge was constant change. Three years into the project, in 1992, President Bush announced that the U.S. would accelerate the schedule even more, to December 1995, thus significantly impacting the program in progress. The task was completed over the span of 7 years and resulted in the elimination or replacement of all of the solvent processes utilizing Class I ozone depleting chemicals, as well as minimizing the use of other solvents and hazardous materials such as cadmium and hexavalent chrome. Rocketdyne achieved success in meeting the goal and, as such, may be used as a case study in managing a successful Hazardous Materials Elimination Program.

Examining the reasons for success, one finds the following 7 key elements: acknowledgment of the problem, recognition of the impact, commitment to action, resource allocation, individual empowerment and integrated teams, active political involvement, and customer involvement.

Acknowledgment of the Problem

One of the first, most important steps in a successful program is understanding and acknowledging a problem exists. Regulations in the environmental area in particular are not always given serious attention in an industrial context. "Ozone holes", for example, are not very tangible, especially when compared to production problems, budgets, and schedules. They are often thought of as inventions of beaurocrats

down at City Hall out of touch with reality or as fatalistic dreams created by fanatical environmentalists. It can be difficult to see how any of it really has a bearing on how one conducts business. But when one comes to understand the issues at hand, and when one recognizes the attempts to protect either the individual or the environment, one begins to have an appreciation of the purpose of the legislation, even if one doesn't necessarily agree with the outcome. Nevertheless, once a regulation is legislated it can have a big affect! Violations often carry significant fines for as long as the infraction exists. The proper response is to attempt to understand the legislation and to respond appropriately. This is the step where it is acknowledged that a problem might exist, i.e. a regulation has been passed or has been brought to attention and that it might effect the way business is conducted.

Rocketdyne responded by proactively acknowledging that changes would be required to comply with the Clean Air Act Amendments, not ignoring their existence and hoping they would disappear. Recognizing and defining the impact of the regulation is the next step in the process.

Recognition of the Impact

Once the problem is acknowledged, the next step is to recognize the impact of the regulation on the organization. What affect does this have on the way things are performed here? Is it a simple substitution of one product for another? Does it require a new piece of equipment or does it require changes to existing processes, equipment or facilities? What are the costs involved? Often this step requires a study to understand the regulation, determine if action is required and usually produces an insight into the amount of effort that might be involved in taking that action. At this point comes the recognition that the organization is or is not impacted and that action is now required. Most regulations have fairly reasonable implementation schedules for compliance as long as they are acknowledged and the impact is recognized. Also at this juncture, a preliminary assessment of effort, cost and schedule is made to estimate the impact.

Obviously, Rocketdyne would be very much affected by the production ban on ozone-depleting chemicals. Many basic processes had used these materials for many years and were highly dependent on these materials as demonstrated by the large quantities used. The impact was large; no one was really certain of the amount of effort that would be required, or if alternative processes would even be possible, let alone achieve comparable results. Once the impact has been recognized, a commitment to action is required.

Commitment to Action

The third step involves commitment: real and honest commitment. This is where the successful organization begins to differentiate itself. Some organizations simply fall into denial. "The regulation doesn't really mean that." or "They can't really mean that." or "They don't know what they're talking about." Or "This certainly can not apply to us." The degree to which any of these responses are defended is usually in proportion to the perceived amount of effort or cost involved in the solution to the problem. Other organizations simply pay lip service to the solution because it's the thing to do, but never really take the effort seriously. "That needs to be fixed, but there's just never time." or "The budget won't permit it to be fixed right now." or " It's just too important for production right now, it can't possibly be fit in." or "We are implementing it, but on a non-interference basis (never)." None of these approaches will be successful in the long term. They risk the possibility of stiff penalties, fines, and even the possibility of ordered cessation of activity in some extreme cases. They also waste the time provided by the implementation schedule allocated for compliance. Therefore, when it is brought to light that the organization is not fulfilling its responsibility, the costs escalate due to hastened implementation schedules, technical risk due to uncertainty associated with the lack of time required to fully evaluate the alternatives, and a community public relations nightmare, often accompanied by litigation. The management of a successful organization avoids these problems by making a commitment to fully comply to the best of their ability with the regulations, as they understand them.

Often there can be extensions to the implementation schedule for compliance, or even waivers that can be granted in specific cases, but in order to be considered serious in requesting these, one must also demonstrate that an honest attempt has been made to comply. An honest attempt is not demonstrated by waiting until the last minute and then claiming the schedule is unrealistic nor is claiming there is not a technically acceptable alternative without demonstrating some effort has been spent looking for one. Also, the community seems to have plenty of suggested alternatives, which the authority is quick to point out. The problem is that those who identify these alternatives usually lack sufficient technical understanding of the process so that the applicability of these suggested alternatives is very often not of practical use. In addition, one must be extremely careful of hidden agendas on the part of those recommending the alternative. However, this demonstrates that several alternatives should be discussed and why the alternatives are not appropriate or are not yet developed sufficiently for implementation. In any event, these efforts require a commitment on the part of the organization in a timely manner.

Even though the total scope of the effort was unknown, Rocketdyne made the commitment that they would begin an attempt to comply. The problem was acknowledged and a commitment was made that action would be taken. Next, resources must be allocated to address the impact and resolve the problems associated with compliance.

Resource Allocation

Once the impact is recognized, and the commitment to proceed is made, resources to perform the required activities are necessary. People need to be selected to perform the tasks and their time needs to be allocated to the project. Response to the regulation may have several alternatives, including simple substitution of a material, elimination of a process that really was unnecessary, changes to existing facilities/equipment or a completely new process using new equipment/facilities. A change to existing equipment and/or facilities and procurement of new equipment most often requires capital expenditures. These funds need to be made available in order to accomplish the task. These costs may not be insignificant, but may ultimately be offset by lower operating costs of more efficient equipment and/or processes, or cost avoidance due to elimination of unnecessary operations and/or costly materials. However, due to the high penalties assessed for non-compliance, simply avoiding these fees can result in a significant return. A successful program will perform a cost/benefit analysis to determine the best approach to addressing the problem. For example, the entire cost of the Rocketdyne aqueous fine clean facility was recovered by avoiding the procurement cost of Freon 113 and 1,1,1 trichloroethane over a four (4) year period. This does not take into account the increased cost due to lack of supply or increased tax liability on purchases and inventories. Additionally, as supplies continue to dwindle, manufacturing schedules have the potential of being impacted. New contracts being issued have provisions that require the hardware to be processed without Class I ozone-depleting chemicals. Allocating proper resources ensures the ability to continue processing existing hardware and also helps ensure the future capability of the organization.

In the case of Rocketdyne, resources were allocated early during the technical evaluation stages, both personnel and financial which resulted in the successful outcome. In addition, the decision was made that those materials that faced a possible future elimination date would be avoided if possible, thus preventing a future repeat of this activity and minimizing future cost. After allocating the resources, the next step is to empower the employees, keep them motivated, and provide them with appropriate authority to implement the change.

Individual Empowerment and Integrated Teams

Another of the keys to a successful program is empowering individuals, conveying upon them responsibility and providing the authoritarian support when it is needed for authentication. One of the biggest problems was identifying all the various uses of the hazardous materials, especially the undocumented ones. Working together with the employees affected by the change, helping them to understand the reasons for change and providing them an opportunity to give feedback on the replacement

technology helped solidify the use of the alternative. One pitfall to this approach that must be avoided is the employees who are comfortable with the norm and who perceive all change as negative. Resolving this can be difficult, however, if the individual resisting is made a part of the solution, the process is usually successful. Like it or not, the alternative will not work if the employees who are tasked with using it refuse to use it. It can be rather enlightening in these cases to impose a rather rapid succession of changes and watch the employees latch onto each successive alternative as steadfastly as the original one when it comes time to change it as well.

This team approach was implemented at Rocketdyne with very successful results. The employees that were affected by the changes became part of the solution. The impact of some of the regulations and the design of some of the new equipment was driven by an active role in the legislative process. This aspect of the Rocketdyne Hazardous Materials Elimination Program had some important ramifications and can be a very useful tool. The next step is to become involved in the process of creating the legislation.

Active Political Involvement

Something can be done about the process of developing regulations. Becoming involved with the process assists the regulatory authority in understanding the affect of the legislation on the industrial community. Their goal, despite what some may think, is not to eliminate industry. They are simply attempting to match an environmental, health and/or safety concern with an appropriate requirement to ensure the continued benefit to all. Most agencies welcome the industry input and will try to consider the input provided. This does, however, require a relationship to be developed between the group and the industry as a whole, or as an individual company. This is key because the first assumption is that the company or industry has a hidden agenda, is self-serving and does not care about much else other than making a profit. Getting beyond this assumption requires building a trusting, professional relationship, which will create an atmosphere where respect and consideration will be given to honest input. It forms the foundation for mutual understanding of the issues and the goals for which the legislation is being proposed. It is in this fundamental formulation stage where the greatest impact can be made, either for good or bad. It can minimize the impact and cost of a regulation, but recognize that this must also maintain the spirit of the intended goal of the regulation. The approach should be honest and open while attempting a win-win situation. The converse situation is not to get involved and then complain that the legislative authority does not have any idea what it is talking about. This is clearly the wrong approach

In the case of Rocketdyne, there are many examples where getting involved has led to a greater understanding, as well as the effect of minimizing an impact of a regulation. One case involved the cleaning of ground support equipment. The applicable regulation prohibited solvent use on ground support equipment, but not on space flight hardware. This would have created a problem in that separate processes would be required and managing the two would be difficult and very confusing to the employees. The South Coast Air Quality Management District (SCAQMD) representatives were invited to Rocketdyne to observe the hardware and the process. The outcome was a change that allowed solvents to be used on space flight hardware and ground support equipment that is required to meet the same requirements as the flight hardware. The overall goal, which was to minimize the use of solvents, is still achieved, but the problem of two different processes has been avoided. In this example, as others, keeping involved with the regulatory authority has proven to be a wise approach. Rocketdyne has been recognized by the SCAQMD in their effort to minimize air pollution through the presentation of the Clean Air Award for the new aqueous precision process.

Many of the new processes implemented at Rocketdyne employ new equipment designs either conceived at Rocketdyne or by innovative suppliers. The design of much of the equipment or facilities took into consideration the applicable regulations and a conscious choice was made as to which regulation would be an easier management choice in the future. This took into consideration the purpose of the equipment, the anticipated amount of use and various other factors. Mixed requirements from an environmental standpoint, fire requirements, and health and safety requirements were considered. For

example, tanks were placed at an elevation that was covered by a trench definition, not an underground storage tank. Air quality rules were considered when designing a solvent cabinet to size the pan to drain ratio to avoid having to permit the unit. These options are available to drive design constraints, if they are considered early enough in the design process. Another important aspect of a successful program is the involvement of the customer in the elimination process.

Customer Involvement

Sometimes the changes required drive changes to significant customer requirements, as in the case of the elimination of Freon 113 and 1,1,1, trichloroethane. These solvents had been used for over 40 years, both for the cleaning and the verification of cleanliness of space hardware. Keeping the customers involved informs them of the direction in which the work is proceeding and provides early feedback on the data necessary for them to support the change. It also permits them to interact with multiple contractors with the same or similar problems. In this way they can function as a resource of information, disseminating the results in an effort to minimize duplication of effort and to prevent mistakes or dead end paths from being repeated. Frequent communication and status of the effort with the customer results in a faster approval process. It fosters understanding of the change and the proposal becomes a more cursory review of the change, rather than a complete technical review of something new and innovative that requires time to contemplate.

Further, the customer proved to be a source of support and encouragement. When these activities are in process, many negative attitudes prevail as has been explained. Sources of encouragement and positive attitudes are very welcome and appreciated by the people involved in attempting to make the changes. They recognize the changes are not optional, but must be achieved regardless of the opinions of those who claim it can not be done. Thus, a supportive voice and a positive attitude can mean the difference between success and failure. This is important to remember, even within the organization, but hearing it from your customers can have an even greater affect.

Conclusion

The success with which Rocketdyne conducted a Hazardous Materials Management Program is demonstrated by the complete elimination of Freon 113 and 1,1,1 trichloroethane in all precision cleaning processes. An examination of their program to identify key milestones, which contributed to their success, identified 7 elements. These elements were acknowledgment of the problem, recognition of the impact, commitment to action, resource allocation, individual empowerment and integrated teams, active political involvement, and customer involvement. These elements can be applied to any organization in the conduct of a Hazardous Materials Management Program and should result in a similar success.

ELECTROSTATIC HAZARD CONSIDERATIONS FOR ODC SOLVENT REPLACEMENT SELECTION TESTING

by

Brad Fairbourn

Thiokol Propulsion
P.O. Box 707 - M/S 244C
Brigham City, UT 84302

ABSTRACT

ODC solvents are used to clean many critical substrates during solid rocket motor production operations. Electrostatic charge generation incidental to these cleaning operations can pose a major safety issue. Therefore, while determining the acceptability of various ODC replacement cleaners, one aspect of the selection criteria included determining the extent of electric charge generation during a typical solvent cleaning operation. A total of six candidate replacement cleaners, sixteen critical substrates, and two types of cleaning swatch materials were studied in simulated cleaning operations. Charge generation and accumulation effects were investigated by measuring the peak voltage and brush discharging effects associated with each cleaning process combination. In some cases, charge generation was found to be very severe. Using the conductivity information for each cleaner, the peak voltage data could in some cases, be qualitatively predicted. Test results indicated that severe charging effects could result in brush discharges that could potentially result in flash fire hazards when occurring in close proximity to flammable vapor/air mixtures. Process controls to effectively mitigate these hazards are discussed.

INTRODUCTION

At the outset of the ODC program, a series of tests were devised to identify any electrostatic discharge (ESD) hazards that might result in solid rocket manufacturing operations coincidental to the introduction of different cleaners. Specifically, tests were performed to determine the electrostatic response of various solvents when used to clean a sundry variety of RSRM motor production "critical" substrates. These tests included cleaner conductivity, peak voltage, and brush discharge testing.

RESULTS AND DISCUSSION

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

Solvent Conductivity Testing

When measured, a solvent's conductivity value provides a qualitative indication of the solvent's polarity and the amount of charge that is likely to be generated during a cleaning operation using this solvent. When a cleaning operation using a solvent-soaked cleaning cloth is performed, the amount of charge generated is a function of 1) the relative speed of contact and separation action involved in the circular wiping motions, 2) the speed at which the cleaning cloth is ultimately removed from the surface being cleaned, and 3) the relative affinity/aversion for electrons exhibited by each of the intimately contacting media. A solvent's conductivity can dramatically affect the amount of charge accumulation on the materials by controlling whether charge—decoupled during the cleaning process—can migrate back and equalize with its counterpart before the separation process is ultimately complete.

The conductivity was measured for each of the following solvents:

- Reveille
- PF Degreaser
- Isopropyl Alcohol (IPA)
- Prime
- Ionox BC
- TCA

To effectively measure each solvent's conductivity, two conductivity meters were utilized. The first meter was a calibrated Emcee Electronics Model 1152 liquid conductivity meter. It was used to measure the conductivity of those solvents believed to non-polar because its range capability ranges from 0 to 2000 picosiemens per meter. This meter was used to measure the conductivity of both Reveille and PF Degreaser. The second meter employed was an Orion Model 140 conductivity meter. The Orion meter was used to measure the conductivity of those solvents believed to exhibit varying degrees of polarity. This included the remaining solvents IPA, Prime, Ionox BC, and TCA. The Orion meter was calibrated just prior to testing using the potassium chloride reference solutions delineated in the 1995 revision of ASTM D1125 entitled, "Standard Test Methods for Electrical Conductivity and Resistivity of Water." A calibration curve was then produced for the Orion meter by which the measured solvent conductivity values could be adjusted to their correct and true values.

After performing the conductivity tests described above, the following results were compiled:

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

Solvent Name	Conductivity (microsiemens/cm)	Temperature
Reveille	0.00000002	71.6° F
PF Degreaser	0.00000001	71.2° F
Isopropyl Alcohol (IPA)	0.24	71.2° F
Prime	5,810	71.6° F
Ionox BC	0.63	72.0° F
TCA	0.14	71.0° F

From these conductivity results, each of the tested solvents was essentially grouped into one of two categories: non-polar and polar. Specifically, Reveille and PF Degreaser are very non-polar while the rest of the solvents are relatively polar. What is implied by this categorization is that the non-polar solvents will be strongly inclined toward electrostatic charging and build up. This charge generation/build up inclination is primarily the result of the time constant for these two solvents is greater than the contact-break time involved in the cleaning operation itself. In contrast, the polar solvents will permit charge relaxation to occur and thereby resist charge accumulations on the substrate and swatch involved in the cleaning operation. Indeed, some of these trends can be seen in the test data obtained in the peak voltage/brush discharge testing test results.

Peak Voltage/Brush Discharge Testing

The other series of tests performed included peak voltage and brush discharge testing. The peak voltage measurements indicate, worst-case, how much electrical charge is generated by the cleaning action and ultimately accumulates on the cleaning cloth and critical substrate. A solvent's conductivity affects the amount of charge migration during the cleaning process—as noted above—and in this way, solvent conductivity does influence the peak voltage data resulting from a cleaning operation.

The peak voltage testing was conducted by performing the following steps:

1. Neutralize the electric charge on all candidate cleaning cloth and substrate surfaces
2. Soak the cleaning cloth swatch with the candidate solvent—not to dripping wet
3. Zero adjust the electrostatic voltmeter and measuring the zero volt level on the solvent-soaked cloth, dry-wipe cloth, and critical substrate surface

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

4. Performing the simulated wet-wipe and dry-wipe cleaning operations measuring the potentials resulting on each cleaning cloth and substrate surfaces versus time
5. If a surface potential exceeds 5,000 volts, then attempt to produce a brush discharge

The peak voltage tests essentially consist of measuring the results of a simulated critical substrate cleaning contact-electrification process. This cleaning process involves a number of parameters that can give rise to wide variability in the measured surface voltage variable. For this reason, the measured voltages resulting from the simulated cleaning operation were confirmed by performing each operation twice using both Rymple cloth and Poly Wipes for each solvent candidate and critical substrate combination.

All surface voltage measurements—including zero volt levels—were digitized and stored. Further, following each test, the zero volt levels were used to determine the peak voltage points for each simulated cleaning operation and these peak voltage data points were then recorded in data tables.

During the peak voltage testing, if the peak surface potentials were sufficiently high, it was considered possible to produce a brush discharge from the highly charged, non-conductive surface. (Electric charge is generated on conductive substrates but since these substrates are typically grounded in use, the charge build up and resulting spark discharge potentials were not considered in this study.) Therefore, the second part of this test involved checking for the advent of a brush discharge following the solvent cleaning process, if the surface voltage exceeded 5,000 volts. The actual brush discharge testing consists of approaching the charged substrate with a grounded, ½" diameter metal probe with a ¼" radius on the end while monitoring for electromagnetic radiation using a heterodyne receiver. If as the probe approaches the charged surface, a sudden discharge of the surface electric charge occurs, the receiver will detect a time-varying magnetic field and convert it into an audio signal that is recognized by the test technician.

If the critical substrate being tested was non-conductive, it was positioned atop a non-conductive table top that was physically located at least 18" away from the nearest earth ground. If the substrate was conductive, it was placed atop a conductive and grounded stainless steel panel.

All peak voltage measurements were performed with a calibrated Monroe Model 175 electrostatic voltmeter using an 1017 HV high voltage probe positioned on a non-conductive mechanical arm. (This mechanical arm was fastened to the top of the non-conductive table top noted above.) This meter has a rated precision of +/- .1 percent of full scale which equates to +/-20 volts for a calibrated surface potential measurement. This meter achieves this precision by making the surface potential measurement using a field-nullling principle. This simple means that at the controlled 1-cm standoff, the

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

probe is driven to the voltage of the surface under measurement and therefore, does not reduce the surface potential via capacitive loading. Since when performing the testing, the length of the mechanical arm resulted in minute probe-to-surface standoff changes, the author felt the surface voltage could realistically be resolved to the nearest +/- 100 volts. Therefore, the peak voltage data recorded in the noted data tables is reported with a tolerance of +/- 100 volts.

The list of critical substrates—with their physical dimensions–that were run through the peak voltage/brush discharge testing in combination with the previously mentioned solvents includes the following:

- Aluminum Witness Panel: 12" X 8" X ½" thick
- D6AC Steel Witness Panel: 12" X 8" X ½" thick
- Dexter Crown 6656 Primer/6611 Topcoat-Painted Aluminum: (see above)
- Rustoleum 5690 Primer/5691 Topcoat-Painted Steel: (see above)
- Cured EA 913NA Adhesive: 10" X 13" X ¼" thick
- Cork : 12" X 12" X ¼" thick
- Cured PR1122 B2 PolySulfide: 10" X 13" X ¼" thick
- Cured RTV (DC 90-006): 10" X 12" X ¼"
- Cured EA 946 Adhesive: 10" X 13" X ¼"
- Cured Carbon-Filled EPDM Rubber: 8" X 12" X ½" thick
- Cured ASNBR Rubber: 8" X 12" X ½" thick
- Dupont Primer/Topcoat Teflon®-Coated Steel: 8" X 12" X ½" thick
- Cured DC 732 RTV: 10.5" X 13" X 125 mils thick
- Glass-Cloth Phenolic: 12" X 8" X 640 mils thick
- Carbon-Cloth Phenolic: 12" X 8" X 640 mils thick
- Cured RSRM Main Grain Propellant: 12" X 8" X ½" thick

The conductivity values for each of the critical substrates tested was either known previously or was discovered indirectly via the peak voltage test results. Specifically, if the conductive/nonconductive nature of a specific substrate was not known, the surface voltage produced through contact-electrification was monitored. If the voltage was non-zero and additionally exhibited no decay, the substrate was considered to be non-conductive. Using this newly gained information and that known from prior testing, the substrates were appropriately grouped into the following conductive/dissipative/non-conductive categories:

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

Conductive: Aluminum Witness Panel

D6AC Steel Witness Panel

Cured Carbon-Filled EPDM Rubber

Carbon-Cloth Phenolic

Dissipative: Cured ASNBR Rubber

Cured RSRM Main Grain Propellant

Non-Conductive: Cured EA 913NA Adhesive

Cork

Cured PR1122 B2 PolySulfide

Cured RTV (DC 90-006)

Cured EA 946 Adhesive

Cured DC 732 RTV

Glass-Cloth Phenolic

According to these groupings, the substrates identified as conductive and dissipative were grounded during testing while the non-conductive substrates were not grounded. Those substrates that essentially consisted of a thin non-conductive film or coating applied to a conductive material were considered conductive because the underlying material was grounded during testing. These included Dexter Crown 6656 primer/6611 topcoat, Rustoleum 5690 primer/5691 topcoat, and Dupont primer/topcoat Teflon©.

Examples of some of the voltage versus time traces recorded during the peak voltage testing are included in Figures 1, 2, and 3 below.

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

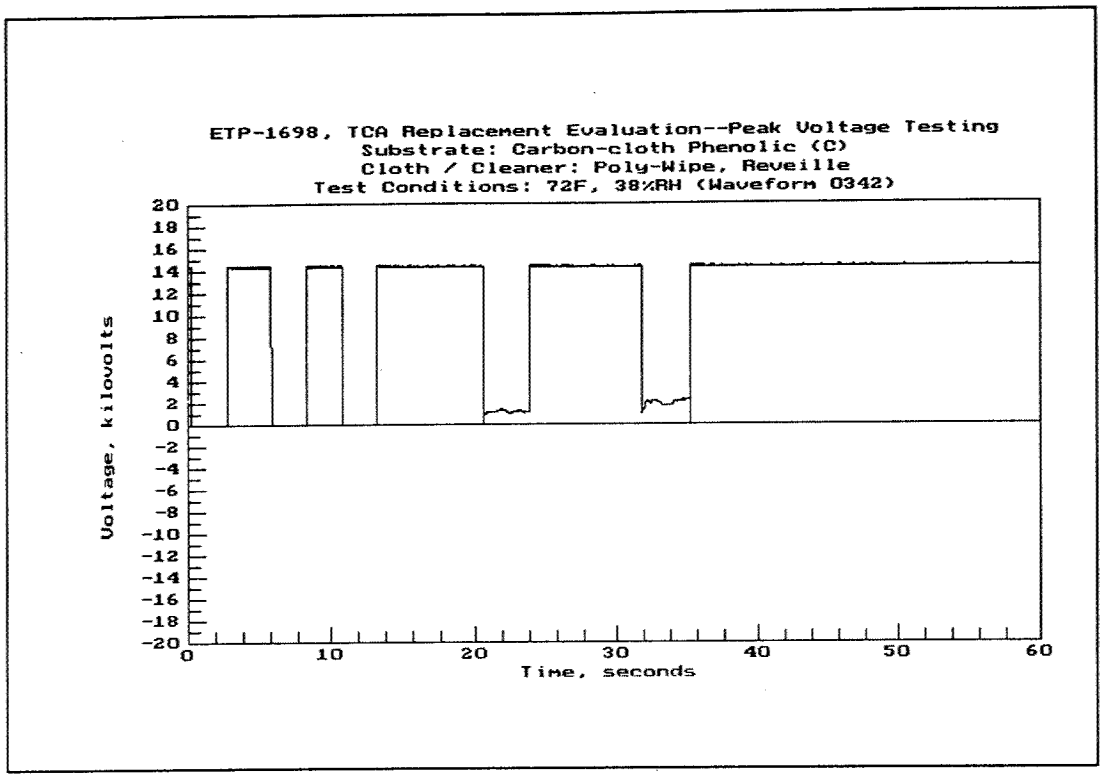


Figure 1. Carbon-Cloth Phenolic & Poly Wipe Surface Voltages: Reveille Cleaning Solvent

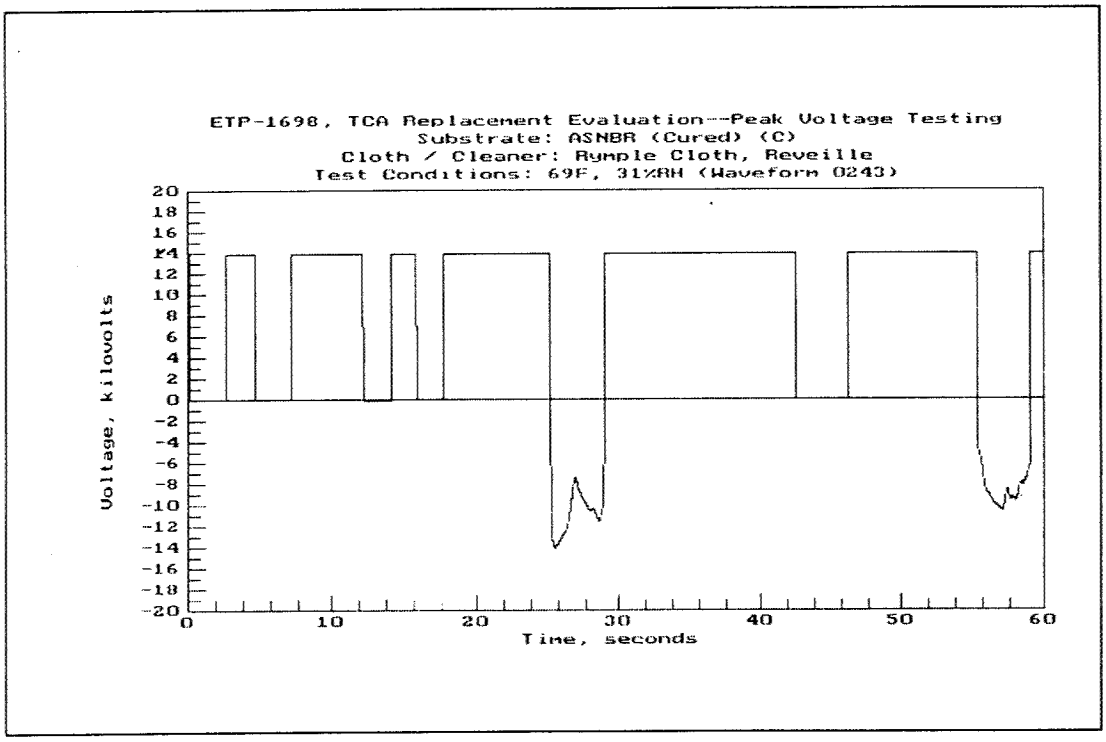


Figure 2. Cured ASNBR & Rymple Cloth Surface Voltages: Reveille Cleaning Solvent

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

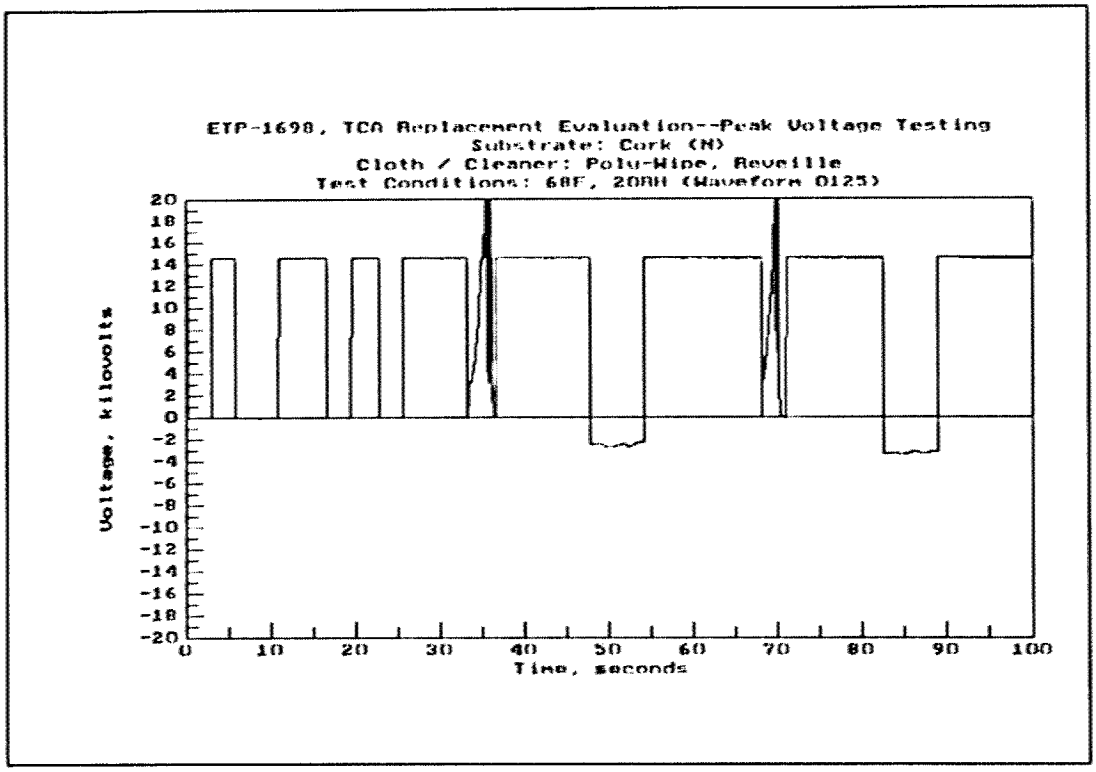


Figure 3. Cork & Poly Wipe Surface Voltages: Reveille Cleaning Solvent

All of the surface voltage test results were resolved into figure plots similar to those shown above. In fact, a total of 386 such figure plots were generated to support this testing campaign.

The peak voltage data for all of the cleaning solvent and critical substrate combinations using both rymple cloth and poly wipes in wet- and dry-wipe cleaning processes were compiled into a number of data tables. These peak voltage data tables are provided in the attached Tables I through XXXII.

The testing procedure utilized to resolve all of the peak voltage data onto a single figure plot will now be discussed while referring to Figure 3 above.

The time base of the above figure plot is 100 seconds. To effectively complete this particular test, a number of voltage measurements had to be taken using a method by which one test could be discerned from the next. To accomplish this task, the analog output of the electrostatic voltmeter was connected to the digital storage oscilloscope (DSO) via a relay. When a voltage measurement was not being taken, the voltmeter was disconnected from the DSO and a 7.25 volt signal was inserted in its place. The result is that in between each measurement, a +14,500 volt marker was recorded. Using

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

this scheme, a total of eight separate/distinct and consecutive voltage measurements were recorded in Figure 3. In order, they were:

Prior to Testing (zero-voltage confirmations)

1. Ground plate (baseline reference)
2. Critical Substrate
3. Wet-wipe solvent swatch
4. Dry-wipe swatch

Following Wet-Wipe Test

1. Solvent swatch
2. Critical Substrate

Following Dry-Wipe Test

1. Swatch
2. Critical Substrate

In this particular case, the substrate was non-conductive. However, when the substrate is conductive as shown in Figure 1 above, only five voltage measurements were recorded. This is because with a grounded conductive substrate, the substrate's voltage was known to be zero and therefore three of the eight measurements were not necessary.

When comparing the results of these tests to those obtained previously, it was noted that there was a significant magnitude increase in the data obtained in this present testing effort. To ensure that these differences were real, the test methods used in both cases were closely reviewed.

The first data obtained was non-ETP data performed simply as a screening test. For this testing, a hand-held Monroe model 255 electric field meter was utilized. In contrast, the test results presented in this study were obtained using a carefully configured laboratory setup using a Monroe model 175 electrostatic voltmeter. As stated earlier, this model 175 meter was used for reasons of precision and repeatability. However, the model 175 meter would automatically provide higher voltage values than the model 255 meter simply because of the way it functions. Specifically, the model 255 meter is a ground-referenced electric field meter and would therefore, capacitively load and thereby diminish the surface voltage being measured. The model 175 meter does not do this and would provide results that are more representative of what actual voltage conditions are.

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

Knowing this fact, why was the model 255 meter used then? Because it is a small, hand-held meter that is used for live process static voltage monitoring and our tests were simply screening tests that were intended to be related back to measurements made during an actual process. In comparison, the model 175 meter is a large laboratory type instrument that weighs about 40 pounds. However, because the results of this study were performed in an ETP setting, the author felt that the model 175 meter was the better choice—given the testing requirements and desired accuracy.

When the results of the peak voltage testing were discussed, a question was asked regarding whether increased humidity might be expected to reduce the measured peak voltage values. The answer to this question is as follows. Since water is not miscible with the non-polar solvents, a wet-wipe using a non-polar solvent would not be expected to benefit by increased humidity and thereby exhibit a corresponding voltage reduction. In fact, moisture with a non-polar solvent may actually aggravate electric charge generation due to the presence of a two-phase system. In contrast, if the cleaning swatch and/or the substrate being cleaned is hygroscopic, some voltage diminution could result provided the operation was using a polar solvent or simply utilized a dry-wipe.

The peak voltage testing was performed over many days and the relative humidity varied from one day to the next. In fact, the relative humidity conditions at the time of testing ranged from 12 to 42 percent—as can be seen in the attached data tables. According to the description given above, this varying humidity most certainly affects the measured test data and thereby added some confounding to test results. However, since Thiokol does not have a humidity controlled room wherein this testing could be performed, the testing was performed and the humidity conditions at the time of testing were recorded.

How do these peak voltage data and brush discharge occurrence information relate to ESD hazards in rocket manufacturing processes? The answer to this question is multifaceted.

Since it can be shown that in some worst case scenarios, there is sufficient energy in a brush-type discharge to ignite flammable solvent vapors, cleaning operations where brush discharges are expected to occur (e.g., non-polar solvent wet-wiping or dry-wiping), should not be performed around flammable solvents. When one looks at the number of factors that need to coexist in order to enable a brush discharge to successfully ignite a flammable vapor/air mixture, the probability of such an event occurring is very low. This statement is certainly corroborated by the fact that we have performed many dry-wiping operations without having experienced a flash fire mishap. However, the possibility does exist and therefore warrants prudence in how cleaning operations are performed.

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

It should be noted here that if the charge generated by either a wet-wipe using a non-polar solvent or simply a dry-wipe were to accumulate on an ungrounded conductor, a spark-type discharge could result. Further, the probability of this type of discharge successfully igniting a flammable vapor/air mixture is relatively high. For this reason, the cautionary measure of grounding of all conductive objects during these type of cleaning operations is critically important.

When reviewing the likelihood of igniting solid rocket propellants via a brush type of discharge event, the ESD ignition sensitivity data suggests that such a scenario is very unlikely –except perhaps with some severe cases involving ferrocene- or catocene-filled propellants. It should be understood that there are qualifiers to this statement. For example, equivalent energy amounts imparted to the propellant in a pressurized environment can easily result in the propellant transitioning to a sustained ignition event. Further, if the same amount of electric charge generated by the wiping operations physically resided on a solid nonconductive propellant, the electric field strength inside the propellant medium would be very close to the propellant's dielectric breakdown strength.

CONCLUSIONS

After reviewing all the solvent conductivity, peak voltage, and brush discharge test results collectively, the following conclusions/observations were made:

- Voltages on the substrate and opposing cleaning swatch, have opposite polarities (e.g., charge is conserved)

- Voltages on substrates are generally less than on the cleaning swatch. (This is most likely due to voltage suppression associated with the substrate)

- Comparatively, when used in a wet-wipe cleaning operation, the non-polar solvents generate much higher surface voltages than observed with the solvents that exhibit some degree of polarity. However, work function differences—relative affinity for electrons—can also dominate the amount of charging that can occur (see Prime data in Table XVI)

- Of all the combinations tested, the highest peak voltages were observed with cleaning operations involving the following critical substrates:

    - Rustoleum 5690 Primer/5691 Topcoat-Painted Steel

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

- Cured EA 913NA Adhesive
- Cork (Stock #6566)
- Cured RTV (DC 90-006)
- Cured Carbon-Filled EPDM Rubber
- Cured ASNBR Rubber
- Dupont Primer/Topcoat Teflon®-Coated Steel

- Voltages on the cleaning swatch are not necessarily less when cleaning a conductive versus a non-conductive substrate

- Generally speaking, Poly wipes do not in all cases, charge more aggressively than does rymple cloth nor visa versa

- When using the polar solvents, the dry-wiping operation comparatively generates higher surface voltages than observed with a wet-wipe operation. This trend is especially aggravated with the higher vapor pressure solvents IPA and TCA

- Discharging effects can be exhibited during cleaning operations where either non-polar solvents or dry-wiping is utilized. In other words, depending upon the specific substrate being cleaned, when performing either a wet-wipe with non-polar solvents or a dry-wipe with either rymple cloth or poly wipes, sufficiently high surface voltages can be produced to give rise to brush discharging effects

- Depending upon the solvent, swatch type, and substrate involved in the cleaning process, brush discharges can be observed off both the cleaning swatch and the substrate itself

RECOMMENDATIONS

The following recommendations are made with regard to how the test results reported in this study potentially affect process safety:

1. Where possible, separate operations involving flammable vapors and cleaning operations that use either non-polar solvents or dry-wiping. Where these type of cleaning operations are still necessary, ensure that all component and personnel grounding practices are followed

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

2. The necessity and implementation of non-polar solvents or dry-wiping cleaning in rocket motor manufacturing operations should be carefully reviewed for potential ESD hazard effects

ACKNOWLEDGMENTS

The author of this paper wish to thanks NASA and Thiokol RSRM Program Management and Engineering for their funding and sponsorship of this study.

Copyright '98 Cordant Technology, Inc. All Rights Reserved.

Chrysotile Asbestos Behavior During Burning of Waste Solid Rocket Propellant

James M. Dietz
Thiokol Corporation
Brigham City, Utah

Abstract

Topic Areas: Asbestos management, Chemical propulsion: environmental effects, Propellant waste disposal

Washout of solid rocket propellant from missile cases results in some insulation being removed with the propellant. Normal disposal of the propellant waste is done by combustion. Since insulation from the case may contain chrysotile asbestos, some concern exists that these fibers may be liberated during the burning of the propellant. Results of a laboratory study show that heat sufficient to liberate free fibers from the insulation dehydrates the fibers to form non-asbestos magnesium silicates. The study was conducted on fibers heated in the laboratory as well as samples taken from actual burning pits. Microscopic techniques of polarized light and dispersion staining were used to characterize the fibers.

Introduction

Chrysotile asbestos is used as a filler material in many liner and insulation formulations for solid rocket motors. Asbestos has some unique properties that make it ideal for this application. However, due to its physiological activity coupled with irresponsible handling practices dating back to World War II, asbestos use is highly regulated and human exposure is limited by law.

Solid rocket propellant is routinely disposed of by open pit burning, where permitted by State Environmental Agencies. This propellant, by its very nature, burns rapidly and hot, and generally consumes any organics and transforms or heat affects any asbestos that is mixed or otherwise in contact with it. However, demilitarization of solid rocket motors, and subsequent reclamation of the propellant ingredients has produced reactive asbestos containing material (RACM) waste from the inert liners and insulation. Disposal of this waste can be difficult and expensive. It has been shown by many studies, that chrysotile asbestos can be converted to forsterite, enstatite and other non-asbestos silicates if it is exposed to high temperatures for sufficient time.

In 1994, the Demilitarization group, in concert with the Environmental group at Thiokol, Wasatch Division, requested approval from the State of Utah to conduct experiments to use open burning to thermally destroy these materials. The State granted an Experimental Approval Order to allow experimentation; the key operating parameters to achieve this goal were determined and published during the subsequent two years. (5)

These experiments required laboratory support both prior to the start of the experiments to determine feasibility, and post experiment to evaluate effectiveness. This paper reports the laboratory efforts associated with these experiments.

Discussion

Copyright 1998 Cordant Technologies Inc. All rights reserved

Chrysotile is a silicate. Silicate structures are based on the silica tetrahedron, that is one silicon atom in the center and one oxygen in each corner. The negative charge on the oxygen combines with positive charged metal ions and can be arranged into chains, sheets, cyclic and non-cyclic discrete formations. Chrysotile belongs to the serpentine group of silicate minerals and consists of layers curled up into tiny cylindrical rolls. The layers consist of two "half" layers of silicate divided by a layer of magnesium hydroxide (brucite). (3,4) The idealized chemical formula for chrysotile is $Mg_3Si_2O_5(OH)_4$. An idealized structure of the silicate half layer is found in Fig. 1.

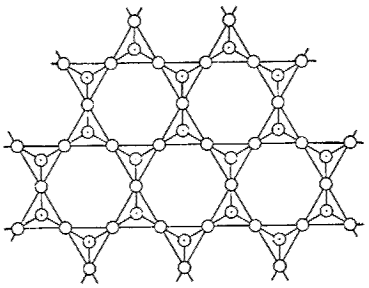


Figure 1
Idealized 2-dimensional drawing of silicate layer

Several studies have been conducted to determine what physical changes occur in chrysotile as it is heated. Most of these studies involved heating for several hours or even days, followed by x-ray diffraction examination to determine the form of the resulting material. Some of these studies are summarized in Table I.

Table I
Reported Changes in Chrysotile at Elevated Temperatures for Long Durations

Temp.° C	Duration	Description of Change	Ref.
< 500	1-7 days	No Change	(1)
500-700	1-7 days	Mostly forsterite, some chrysotile remains. Birefringence increases. Complete dehydration.	(1)(6) (3)
640-750	4 hours	Step wise exotherms, converting to forsterite	(3)
800-900	4 hours	Starting to show enstatite, (-) sign of elongation. Under hydrothermal conditions, Talc is formed.	(3)(6) (1)
985	10 minutes	Mostly converted to enstatite	(4)

All of the studies indicate that dehydration occurs up to about 750°C, probably in steps. At temperatures above approximately 800°C, rearrangement of the Mg and Si occurs, and forsterite is formed. At higher temperatures, ~1100°C, the products appear to be forsterite and enstatite. Forsterite is an *ortho*silicate of magnesium having a formula of Mg_2SiO_4 and enstatite is a long chained pyroxene having a general formula $Mg_2Si_2O_6$ and an idealized structure similar to Fig. 2.

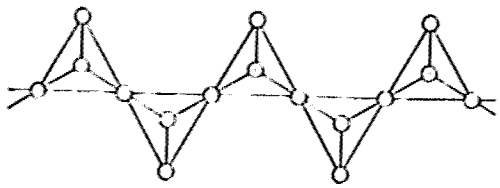


Fig. 2
Idealized drawing of silica arrangement of enstatite

The microscope laboratory at Thiokol has examined hundreds of samples of rocket insulation taken from the open pit burning grounds. In all most every case, the chrysotile asbestos is bound harmlessly within the insulation matrix and those fibers which are found on the charred, friable surface, have been thermally transformed into forsterite and enstatite. It was obvious that the surface of the insulation had burned very hot for a significant amount of time to convert exposed chrysotile to its breakdown products. Solid rocket propellant burns vigorously, and some concern existed that some surface asbestos could be released during the burn without being exposed to sufficient heat and time to convert it.

Since the literature did not show any studies involving heating periods any shorter than 10 minutes, we set up a method to investigate the conversion at high temperatures for very short durations. A graphite furnace used on an old II.550 AA Spectrometer was used to heat small quantities of chrysotile asbestos floats. The asbestos floats were placed in the furnace boat. The furnace heated the samples via induction to a preset temperature in about 5 seconds. The sample could then be held at that temperature for a preset length of time. After exposure to the heat, the asbestos was removed and examined using polarized light and dispersion staining microscope techniques. Fresh samples were used for each temperature and time sequence. The temperatures and corresponding microscopic examination is found in Table II. The study showed that even momentary exposure to temperatures above 1100°C, completed the conversion. Figures 3 to 8 are photomicrographs of the samples after exposure to heat.

Table II
Microscopic Appearance of Chrysotile Asbestos at Elevated Temperatures for Short Durations

Temp. °C	Duration, sec.	Microscopic Appearance
900	0	Fibers show dispersion colors, elongation sign of chrysotile.
900	5	Smaller fibers are converted; most large fibers still show dispersion colors.
900	45	Dispersion colors visible on a few large fibers; all others maintain morphology, but do not dispersion stain.
900	135	No dispersion staining at all. Fibers still retain structure.
1000	0	Very slight dispersion staining on large fibers. All others show none. Fibers are intact.
1100	0	No dispersion staining observed. Only large fibers even react to polarized light.
1200	0	No dispersion staining. Fibers beginning to break apart. Still some anisotropic fibers.
1400	0	No anisotropic fibers. No dispersion staining. Only a few fibers remain.
1600	0	Most fiber characteristics are absent.
2000	0	Vitreous conversion. Particles are opaque.

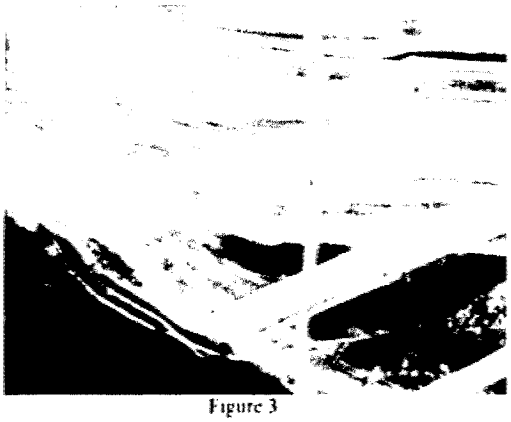


Figure 3
Chrysotile Starting Material
125X - Nomarski

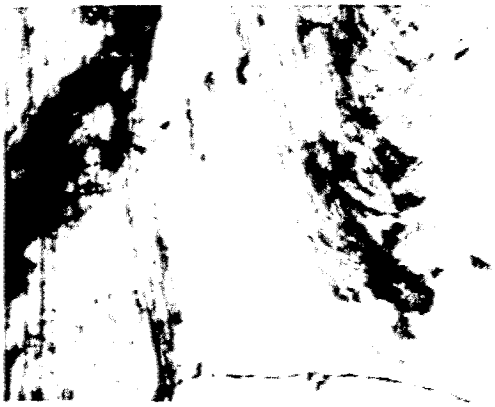


Figure 4
Chrysotile after 900°C for 5 seconds
125X - Nomarski

Figure 5
Chrysotile after 1500°C for 5 seconds
125X - Nomarski

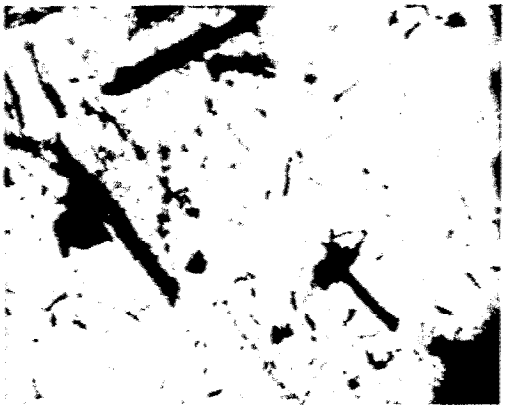


Figure 6
Chrysotile after 1500°C for 0 seconds
125X - Nomarski

Figure 7
Chrysotile after 900°C for 5 seconds
100X Dispersion Staining - Central Stop
1 550 R 1

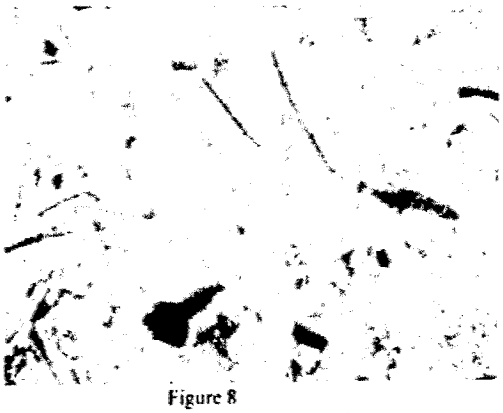


Figure 8
Chrysotile after 1500°C for 5 seconds
100X Dispersion Staining - Central Stop
1 550 R 1

Other studies (2) have shown that solid rocket propellant, even with reduced oxidizer content, will reach a minimum temperature of 1900°C, as long as combustion is sustained. Therefore, solid rocket propellant mixed with some asbestos containing insulation should be able to be burned in open air without creating an environmental hazard.

The State of Utah granted approval to develop an acceptable method for the open air incineration of asbestos containing materials. As part of this study, a method was devised to capture any airborne particles generated by the burning propellant. These samples were then analyzed in the laboratory to see if any unconverted chrysotile had been liberated by the burn. Insulation residue remaining in the burn pit was also analyzed. Using microscopic and infra-red spectroscopy, the temperature at which the residue was exposed could be estimated. This laboratory support was used to successfully develop an incineration method that was approved by the State of Utah.

Conclusions

Chrysotile asbestos is converted to other forms for durations of <5 seconds at 1100°C and above, based on small samples exposed to induction heating. Standard microscopic methods used for identification and quantitation of chrysotile asbestos can be used to estimate temperatures at which individual fibers were exposed.

Acknowledgments

The author expresses thanks to Jeff Lindsay and M. Dean Howard for all the microscopy and sample preparation involved with this study. They have demonstrated a special ability to identify the various asbestos forms based on optical parameters and were uncanny in their ability to find fibers hidden amongst quantities of burn pit residue. Thanks also goes to Chad Saunders, who did all the graphite furnace work for this study and to Doug Merrill who worked closely with the laboratory during all the burn pit studies.

References

1. Ball, M. C., Taylor, H. F. W., "The Dehydration of Chrysotile in Air and Under Hydrothermal Conditions", *Journal of the Mineralogical Society*, No. 33, 1963, pp. 467-482

2. Bennett, R. R., Thiokol Internal Memo, 16 Feb. 1994

3. Datta, A. K., Samantaray, B. D. , Bhattacherjee, S., "Thermal Transformation in Chrysotile Asbestos", *Bull. Mater. Sci.*, Vol. 8, No. 4, October 1986, pp.497-501

4. Goymer, P., MacDonald H. S., "The Effects of High Temperature Over Short Periods on Chrysotile and Amosite Varieties of Asbestos", *Microscope*, Vol. 43:4 pp. 177-178 (1995)

5. Merrill, D. C. "Open Burning of Reactive Asbestos Containing Material (RACM)", Internal Report, Thiokol Corp. Brigham City, Utah 84302-0707, 1996

6. Rodriguez, J. "INTER/MICRO-88"; *Microscope* 1985, 33, 213-214

High Pressure Water Stripping Using Multi-Orifice Nozzles

David Hoppe
NASA/MSFC
Mailstop: EH33
Huntsville, AL 35812
(256) 544-8836

Abstract

The use of multi-orifice rotary nozzles greatly increases the speed and stripping effectiveness of high pressure water blasting systems, but also greatly increases the complexity of selecting and optimizing the operating parameters. The rotational speed of the nozzle must be coupled with its transverse velocity as it passes across the surface of the substrate being stripped. The radial and angular positions of each orifice must be included in the analysis of the nozzle configuration. Orifices at the outer edge of the nozzle head move at a faster rate than the orifices located near the center. The energy transmitted to the surface from the impact force of the water stream from an outer orifice is therefore spread over a larger area than energy from an inner orifice. Utilizing a larger diameter orifice in the outer radial positions increases the total energy transmitted from the outer orifice to compensate for the wider distribution of energy. The total flow rate from the combination of all orifices must be monitored and should be kept below the pump capacity while choosing orifice to insert in each position. The energy distribution from the orifice pattern is further complicated since the rotary path of all the orifices in the nozzle head pass through the center section. All orifices contribute to the stripping in the center of the path while only the outer most orifice contributes to the stripping at the edge of the nozzle. Additional orifices contribute to the stripping from the outer edge toward the center section. With all these parameters to configure and each parameter change affecting the others, a computer model was developed to track and coordinate these parameters. The computer simulation graphically indicates the cumulative affect from each parameter selected. The result from the proper choices in parameters is a well designed, highly efficient stripping system. A poorly chosen set of parameters will cause the nozzle to strip aggressively in some areas while leaving the coating untouched in adjacent sections. The high pressure water stripping system can be set to extremely aggressive conditions allowing stripping of hard to remove adhesives, paint systems, and even cladding and chromate conversion coatings. The energy force can also be reduced to strip coatings from thin aluminum substrates without causing any damage or deterioration to the substrate's surface. High pressure water stripping of aerospace components has thus proven to be an efficient and cost effective method for cleaning and removing coatings.

Standard Operational Parameters Effects

There are several basic operating parameters which determine the stripping effectiveness for any high pressure water blast system. The pressure and the flow rate determine the energy potential available for removing coatings. The quantity and combination of orifice size affects the pressure and flow rate. The orifice configuration must be calculated to ensure that full pressure is available at the pump run out point.

The type and design of the orifices are also an important consideration. The energy potential of the water stream is reduced as it passes through the restriction of the orifice. This reduction is dependent upon the nozzle material and the internal structural design of the flow path. The selection of different orifice designs and different materials can give a wide range of efficiencies. Material type must also be taken into consideration to allow the restriction to be strong enough to prevent excessive wearing. A quickly wearing orifice will change the flow characteristics of the nozzle and reduce the maximum pressure obtainable.

At high operating pressures, water velocities are above the sonic level. The water emerges from the nozzle as a very coherent unidirectional stream. As the stream passes through the air, the water molecules interact with the air and cause turbulence to be introduced into the outer layer of the stream. As the water stream continues to interact with the air, more of the water molecules break away from the solid cohesive flow until the solid core of the water stream no longer exists. As the water flow becomes turbulent its motion becomes more random and the velocity slows down the longer it interacts with the air. This causes the energy potential of the water stream to be reduced the further away the water has traveled from the exit of the orifice until the water streams are just a mist.

The distance between the nozzle exit and the substrate (stand-off distance) is therefore another critical parameter which must be carefully selected. If the exit of the nozzle's orifice is too close to the surface of the object to be stripped, the water stream impacts the surface as an extremely cohesive stream basically, the diameter of the exit of the orifice. This results in a very aggressive stripping at the point of impact but only a fine line of coating removed as the water stream passes across the surface. If the exit of the nozzle's orifice is too far from the surface of the object being stripped, the water stream has dispersed into a wide random mist and lacks sufficient energy to remove most tightly adhering coatings. With a properly selected standoff distance, the water stream maintains enough of its coherent flow to transfer sufficient energy to the surface of the substrate while having sufficient interaction with the air to cause just enough turbulence to expand the width of the stream into a larger impact area without greatly reducing the energy potential of the water stream. This optimized standoff distance allows the water stream to strip a path across the substrate wider than the diameter of the orifice.

When a coating is removed by the mechanical impact of water striking the surface, the coating travels away from the impact point dependent upon the characteristics of the

coating. A thick coating with poor adhesion quality but strong tensile strength will more than likely fly off the substrate in large chunks. As the water stream cuts through the coating and impacts the hard substrate underneath, the water velocity vector changes tangentially to the substrate, slicing through the bond between the coating and the substrate and dissipating the rest of its energy as it recoils from the surface trying to cut back through the coating. The water then is able to penetrate the coating, cut tangentially through the bond surface for a short distance and randomly dissipate back through the coating cutting and lifting off a large piece of the coating around the area of impact. A stream running perpendicular to the surface will give a somewhat symmetrical stripping of the coating following the path of water impact. An angled water stream attack will skew the removal of the coating in the direction of the attack angle. Since the water stream no longer is required to make a perpendicular change in direction, but will mostly turn in the direction of the angle of attack, less energy is loss during the direction change. This allows more energy to be available to dissipate into the coating as it cuts through the bond line and back up through the coating. The result is a larger amount of coating removed than from a perpendicular impact.

For thin, tightly adhering coatings, there is no sympathetic stripping as can happen with the thicker less tightly adhering coatings. The area of removal of the coating is basically the same as the area of impact of the water stream. The coating then is reduced to extremely small bits as if it were dissolved in the water. The angle of attack then is not of any great consideration.

In the case of soft, tacky coatings, such as thick grease, the removed material could reattach itself after the water stream moves away from it impact position, loses energy and slows down. The water stream again cuts through the coating but as it makes its directional change, it pushes the coating away from the point of impact rather than cutting through a bond line. As the water slows, it looses energy allowing the bonding strength of the material to reattach to the surface of the substrate in a different location. Skewing the direction of water flow after its impact by adjusting the angle of attack will aid in the removal of the coating by pushing most of the coating in one direction. By adjusting the next pass across the surface to be in the same direction of the angle of attack, the coating can be essentially washed toward the edge and pushed off the surface. Gravity also plays a small role resulting in a downward angle aiding in the removal of this type of coating.

The water stream must be kept moving across the surface at all times. Prolonged dwelling of the water at any one spot will cause damage to the substrate. Even low pressure, low flow rates that dwell in the same location will eventually erode the hardest materials. The faster the stream passes across the surface, the quicker an area can be covered during stripping. The quicker the area covered during stripping, the wider the area over which the energy is spread. The wider the area over which the energy is spread, the lower the capability the system has to strip. The transverse velocity must therefore be optimized to balance moving as quickly as possible to cover the largest area possible in the shortest amount of time while moving slowly enough to ensure that the water stream removes the coating.

Two other factors can be selected to help in the balancing of the transverse velocity. The water stream can be set to overlap the previous stripping pass by a certain amount or the exact same path can be repeated multiple times. Since the outer part of the water stream breaks up and losses energy to the air it passes through while the center core may remain mostly intact all the way to the surface, the center of the impact receives more energy than the outer edges of the impact area. This invariably results in a well-stripped center section with tapering of the coating removal toward the edges of the strip path. By selecting an overlap such that the tapered edge of the next pass across the surface coincides with the opposite tapered edge of the previous pass, the energy imparted to the surface from the combination of two outer reduced energy areas can be sufficient to match the energy in the center of the strip path and therefore fully strip the coating evenly. The overlap can be adjusted as determined to be most effective. At a 50% overlap, the outer edge of the nozzle, passes across the center of the stripped path of the previous pass and the center core of water will pass over the outer edge.

Some times it is necessary to slow the transverse velocity to a small value in order to ensure that complete stripping of the surface occurs in one pass. This can result in slower than necessary stripping rates. Faster stripping rates may be possible by speeding the transverse velocity while planning to pass over the entire surface more than once. A double impact to a coating can be more efficient than one single blow. A coating to be removed must be tested to determine the transverse velocity necessary to fully remove the coating in one pass compared to stripping the coating in two or more passes. If the transverse velocity can be more than double using a two pass method, quicker stripping times will be achieved than with a single pass over the surface. When using double pass stripping parameters, it may be best to stagger the starting position of the water stream by at least half the difference between the stripping width less the amount of overlap. This keeps the most energetic part of the water stream from passing over the exact same spots on the substrate giving a better distribution of energy over the entire surface. For hard to remove coatings, operating with a 50% overlap between passes across the surface will cause the least energetic part of the water stream to pass over the path of the previous path's most energetic part of the water stream.

The effects from utilizing double passes can be combined with the overlap parameter by moving the nozzle only half of the nozzle strip width between passes. This would be identical to the 50 %overlap process. This not only causes the outer edge of the nozzle to pass across the center of the strip path on succeeding passes, but also results in water streams covering the substrate twice in a single run.

Some nozzles are designed to mix abrasive materials with the water stream. Abrasive material can increase the stripping capability of a high pressure water stream by several orders of magnitude. Care must be taken when operating under these conditions since this more energetic stream can quickly start cutting into the substrate. With all the different types of abrasives available, a type to suit each purpose can be selected. Crushed walnut shells are soft enough to minimize the danger of cutting into substrates

while garnet can be sufficiently aggressive to cut through several inches of hardened steel. Most nozzles designed for the mixing of abrasives use the vacuum from a venturi to pull the media into a mixing chamber and a second focusing nozzle to control the stream at the outlet. While greatly speeding up the stripping process, the use of solid additives to the water stream will add a large amount of material which must be cleaned up and dispose of after completion of the stripping process.

Special Operational Parameters Effects for Multi-Orifice Rotary Nozzles

Using multi-orifice rotary nozzles greatly complicates the choosing of operational parameters. With multi-orifice nozzles, the number of orifices, their positions within the nozzle head and the size of each orifice must be selected. The rotational speed of the head must be matched to the transverse velocity. Changes in the angle of attack give different stand-off distances between each orifice and the substrate at different times. The total tangential velocity of each nozzle will be different and variable as the head spins. The overlap between passes is more complex due to the different tangential velocities and the combination effect caused by more than one orifice passing across certain sections of the substrate.

The first consideration in choosing the orifices to be placed in the rotary nozzle head is to determine the inside diameter of each orifice. The total flow rate from all the orifices selected must not exceed the capacity of the pump at its rated pressure. If orifices are chosen which allow a larger flow rate than the pump is capable of delivering at its rated pressure, the system will operate at a lower pressure than normally achieved at the pump's rated flow rate. Different operating pressure and flow rate combinations can be chosen in this way. Operating the pump at its maximum flow rate and pressure will provide the maximum potential energy for stripping. Operating a positive displacement pump at its rated pressure, but at a reduced flow, can cause excessive heating of the pump. The pump still adds energy to the water by increasing the pressure, but the flow is lower which reduces the amount of water passing through the pump for cooling. The size and combination of the different orifice sizes must be selected to spread the energy distribution from the orifices evenly over the area be stripped. The total speed of each orifice is a combination of the transverse velocity of the head moving across the substrate and the tangential velocity from the rotation of the head. Since each orifice is located on a different radius for many nozzle heads, the speed of each orifice will be different. The rotation of the head causes the orifice's tangential velocity from the rotating head to be in the same direction of the transverse velocity some times and in the opposite direction at other times, the total velocity of each orifice will change sinusoidally with a magnitude equal to twice the transverse velocity as the nozzle head rotates and moves across the surface. If the nozzle moves in the same direction on the next pass across the surface directly below the previous path with a small overlap, the faster orifice speeds will overlap the areas with the slower speeds. If the next pass is in the opposite direction, the tangential component of the orifice velocity will cause the slower speeds to overlap the same lower speeds and the faster speeds to overlap the same faster speeds at successive

passes. If the tangential component of the velocity vector is much greater than the transverse velocity component the difference between the velocity of the orifice while the head moves one direction may be close enough to the velocity of the orifice when the head moves in the opposite direction to minimize this effect so that it need not even be considered. The velocity components should be checked before making this assumption.

The spray pattern across the surface of the substrate from multi-orifice rotary heads is trigonometrically dependent upon the transverse velocity, rotational velocity of the head, radial location of the orifice, and the angular location of the orifice in relation to other orifices. Since the orifice are fixed on the nozzle head, the only two operational parameters which can be modified are the rotational velocity and the transverse velocity. These parameters must be chosen to complement each other in order to spread the spray pattern evenly across the substrate. (See figure 1) All orifice move perpendicular to the transverse direction through the center section of the substrate. A high transverse velocity can spread those perpendicular paths far apart making it impossible to evenly cover the surface. The wrong combination of rotational and transverse velocities can cause individual orifice to spray directly at the same exact position that other orifice spray through the center section while leaving adjacent sections of the substrates with gaps where no spray comes in direct contact. This results in areas where too much energy has been applied to the surface causing the removal of underlying coatings which were not meant to be removed or damage to the substrate itself while leaving the adjacent areas with the coating intact and untouched. (See figure 2)

Since the tangential velocity of a rotating object increases proportionally with the radius, the orifice in the outer areas of the rotary head will move at a much quick speed than the orifices located nearer the center of the head. Water jets from orifice moving at a quicker pace will spread the potential energy of the water stream over a larger area than orifice moving slower. This causes an imbalance in the stripping ability of the nozzle from the outer areas across the center of the nozzle. In order to compensate for the difference in potential energy imparted to the substrate per linear inch of orifice travel, larger orifices are placed in the outer locations with incrementally smaller orifice diameters placed in subsequently closer locations to the center of the head. The force that the water exerts across the surface is inversely proportional to the square of the total velocity of the orifice. These calculations must be taken and included when specifying the size of orifice to be placed in each location of the rotary head. To further complicate the selection of orifice size and locations, every orifice on the head will pass through the center area of the nozzle path while only the outer most orifice will pass across the outside edge of the path. The energy imparted to the center of the nozzle path will be a combination of the energy imparted from the passes of all the orifices while the energy imparted to the substrate at the edges is due only to the one orifice at the extreme edge of the nozzle head. This is further complicated but at the same time minimized, by the direction the water stream travels over the surface at these two locations. The water stream at the radius of each orifice from the transverse motion path moves in the direction or opposite to the direction of the transverse velocity while the water stream at the center of the nozzle path moves perpendicular to the transverse direction. This causes the water stream at the

radius to cover a small strip along the path of the transverse velocity. The water streams at the center then cut a line perpendicular to the transverse velocity and with the correct combination of rotational speed and transverse velocity, each orifice will pass over a separate section of the substrate minimizing the number of multiple hits each spot on the substrate receives.

The wider the nozzle head, the more severe is the effect of changing the angle of attack. A perpendicular face to the substrate will maintain all orifice an equal distance from the substrate as it passes across the surface. Even nozzle heads with divergent flows from the different orifice will maintain the same stand-off distance as the head rotates. When the nozzle head is canted even a few degrees it causes each orifice to pass closer to the surface as the nozzle head rotates past the point where the nozzle is inclined toward the substrate and to pass further from the substrate 180° around. Since the range of most orifice inserts in these nozzles have a small effective stand-off distance, (between 1 and 3 inches), a small inclination can easily move the orifice outside of its most efficient operating range.

Since the geometry of the orifice is fixed with reference to its radial and axial positions for each orifice, the size and type of each orifice must be tailored designed for optimal stripping. Based on the location of each orifice, the relationship between the rotational velocity of the nozzle head and the transverse velocity can be calculated and graphically shown to determine the effectiveness of the spray pattern coverage. Additional problems setting the operating parameters for optimal stripping can then be smoothed out by selecting a proper overlap parameter.

Conclusion

A proper set of operating parameters will allow for a high pressure water stripping system to operate quickly and cleanly with a high level of efficiency. A failure to understand and select the proper parameters can result in a frustrating system which fails to perform satisfactorily either by allowing gaps in the stripping process or by over stripping and thus causing damage to the substrate. High pressure water stripping systems utilizing multi-jet orifice nozzle heads have been used to strip a wide variety of materials with great success.

Figure 1
Correct set of operating parameters.

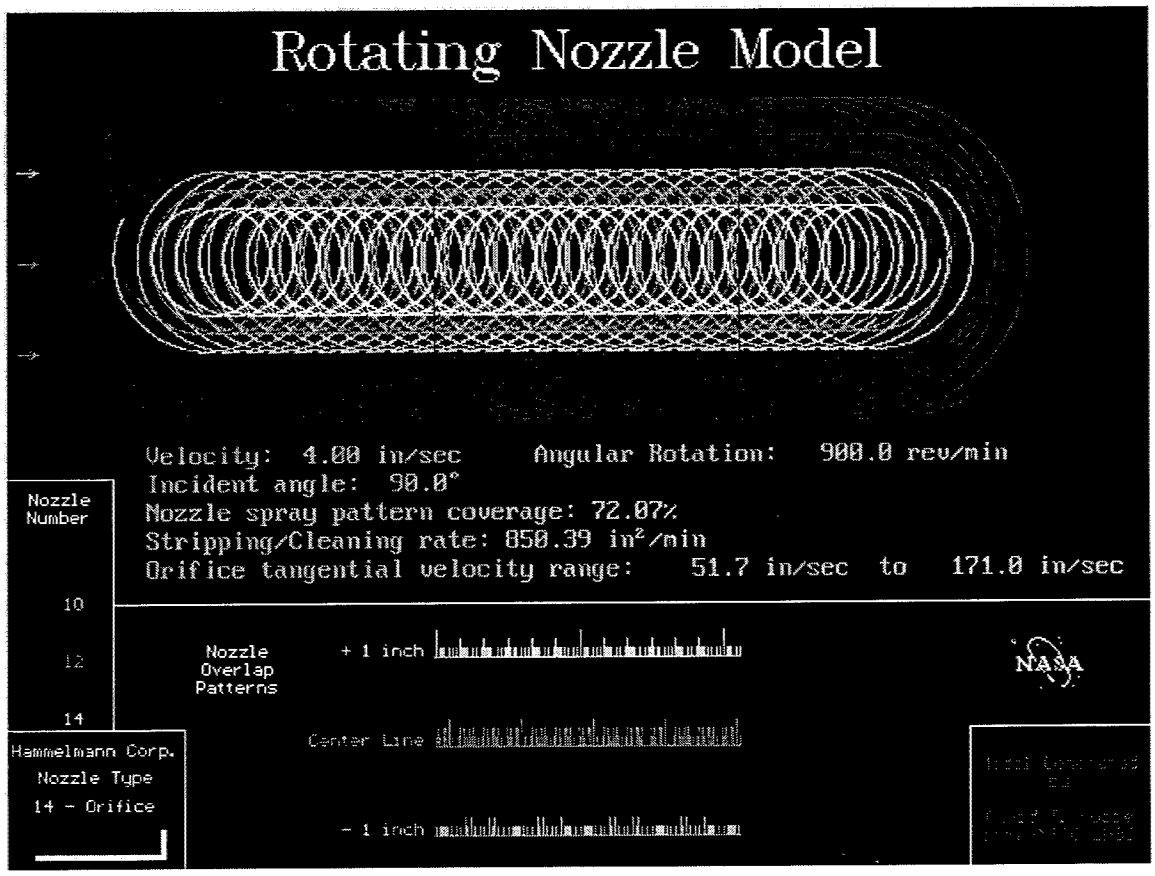
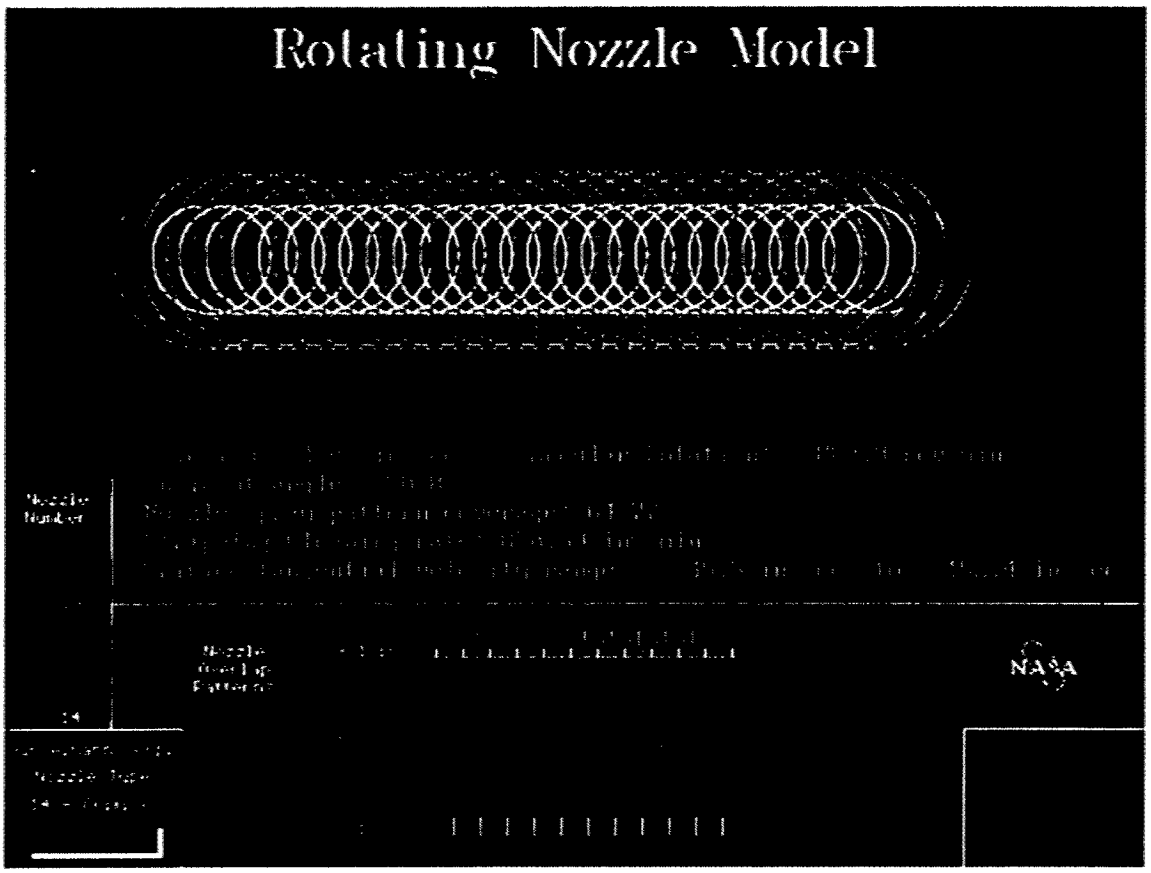


Figure 2
Incorrect set of operating parameters.



ODC-FREE CLEANING EXPERIENCES ON SOLID ROCKET MOTORS

Prepared by
Neil Sagers
Kurt Evans, Chad Saunders, Brice Betenson, Alan Rader
P.O. Box 707, Mailstop LC0, Brigham City, Utah 84302-0707

Abstract

An aqueous cleaning system has proven effective to clean cases for the Reusable Solid Rocket Motor (RSRM). Contaminants included oil & grease, dust and incidental contamination. The bath life was extended to over four months by the addition of potassium hydroxide. Occasional stains left on metal surfaces were greatly reduced by maintaining the rinse water conductivity at 275 micromhos or less.

A replacement cleaner was investigated for removal of silicone release agents from paint brushes. The silicones are a part of the brush manufacturing process and must be removed before the brushes are used to apply adhesive, primer and paint to the RSRM. An initial screening showed four cleaners removed silicone well from brushes, three were aqueous. Detailed follow-on tests are in work to implement the brush cleaning process with a new cleaner.

Introduction

Thiokol Corporation manufactures the Reusable Solid Rocket Motor (RSRM) at its Promontory, Utah plant and past processes used 1,1,1-trichloroethane (TCA) in many of the operations. RSRM manufacture now has almost completely been converted to non-Ozone Depleting Chemicals (ODC). Areas are discussed in this paper are aqueous cleaning for bond preparation and removal of silicone from paint brushes.

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. Many other parts include dome-shaped components and conical nozzle parts. Clean surfaces are essential to adhesive bonds such as the insulation-to-case, phenolic-to-metal and many other bondlines that hold the insulation and instrumentation to the case and nozzle components. Aqueous cleaning is preparatory to a grit blast and adhesive bonds. Only adhesive bond surfaces are grit blasted; the seal surfaces where the parts mate are not grit blasted.

TCA vapor degreasing was previously used to clean large metal parts, but vapor degreasing has been replaced with an aqueous wash process. Hand-wipe cleaning is performed to clean smaller areas of RSRM components but now non-ODC cleaners are being selected to replace the TCA

Several types of paint brushes are used to apply adhesives, primers and paints to the RSRM during the manufacturing process. All paint brushes are cleaned to remove silicone before they enter the manufacturing process. The silicone release agent on the bristles is a part of the brush-manufacturing process. Thiokol previously washed paint brushes in TCA to remove silicone. With the phase out of TCA, alternative cleaners are being investigated to remove silicone from the brushes.

Corporation 1998, All Rights Reserved

Aqueous Cleaning for Bond Preparation

Aqueous cleaning is used on large steel and aluminum RSRM components. Thiokol has two large washers which can accommodate the RSRM cases which are12 ft. in diameter and 13.5 ft. high. The first washer is located in Thiokol's RSRM Refurbishment Work Center and the second in the Insulation Work Center.

In the Refurbishment Work Center, the fired RSRM cases are broken down into individual components and the components are refurbished in preparation for succeeding manufacturing operations. RSRM components as well as tooling and support equipment are cleaned in the Refurbishment Center's washer. Soils in the Refurbishment work center include HD-2 preservative grease, Diala oil and residues from magnetic particle inspection. Cleanliness criteria are black light and water-break free.

The wash in the Insulation Work Center is a bond preparation step. Flight components only with very little soil go into the Insulation washer. The wash is followed by a grit blast for surface preparation of adhesive-bond surfaces. Seal surfaces are not grit blasted.

The Wash Process

The wash solution is a 10% Brulin 1990GD in deionized water at 170 °F. The first rinse is deionized water at 170 °F which typically contains a small amount of detergent which has been dragged out from the wash cycle. The second rinse is also heated to 170 °F; but the purity is controlled by allowing a maximum conductivity of 275 micromhos. In practice, the second rinse is changed when the conductivity exceeds 225 micromhos. Parts are allowed to drain for three minutes before the washer is opened and the parts are removed and wiped dry.

Brulin 1990 GD includes four surfactants, a phosphate and sodium metasilicate. The sodium tripolyphosphate (STPP) acts as a builder, deflocculant and a buffer. The sodium metasilicate acts as a corrosion inhibitor for aluminum. Table I lists the components of Brulin 1990GD. Code names only are given for the surfactants to protect Brulin Corporation's proprietary information.

Table I. Brulin 1990GD Components.

Constituent	Function
ANIONIC SURFACTANT (D-8)	DETERGENT
ANIONIC SURFACTANT (D-22)	DETERGENT
NONIONIC SURFACTANT (D-26)	DETERGENT
NONIONIC SURFACTANT (D-30)	DETERGENT
SODIUM TRIPOLYPHOSPHATE (STPP)	BUILDER, DEFLOCCULANT, BUFFER
SODIUM METASILICATE (SM)	CORROSION INHIBITOR, AND DEFLOCCULANT
POTASSIUM HYDROXIDE (KOH)	pH ADJUSTMENT

Bath Life

Initial tests showed that the Brulin 1990GD cleaned soils of interest best at about 180 °F, and the set temperature on the full-size washer is controlled to 170 °F due to facility considerations. It should be noted that 170 °F is higher than what Brulin Corporation normally recommends for 1990GD.

Full-scale runs with the Brulin 1990GD showed that the STPP hydrolyzes quickly at the higher temperature. The hydrolysis reaction releases an H+ ion that accelerates the breakdown of remaining STPP. The STPP is converted first to sodium pyrophosphate and finally to sodium orthophosphate as H+ ions are lost. The rate of STPP hydrolysis increases with temperature and is much slower below 150 °F.

Solubility of the sodium metasilicate is a function of pH. The H+ ions released from the STPP hydrolysis lower the pH of the bath and cause the sodium metasilicate to form an insoluble residue. Limits had been set for the minimum amounts of STPP and sodium metasilicate, but the hydrolysis at the higher temperatures limited the bath life to about one week. Surfactant concentrations remained stable throughout Thiokol's tests.

It was found that potassium hydroxide (KOH), a component of Brulin 1990GD, can be added to control the solution pH and maintain sodium metasilicate concentration. KOH addition can even help to redissolve sodium metasilicate that has precipitated. Stabilization of the pH also slows the hydrolysis of the STPP as excess H+ ions are neutralized. With KOH addition and relaxed limits on the STPP, the bath life was extended to over four months. The bath was changed only when it was necessary to have a fresh solution to implement the washer for RSRM production.

Stain and Corrosion Elimination

Some stains and corrosion have been found on the cleaned hardware after the wash process. The stains are one of these types:

1. A watermark is formed that encircles a drop of water that has dried.

2. A dark gray powder sometimes found in areas where water is allowed to stand after the wash.

3. A yellow powder that is also sometimes found where water is allowed to stand after the wash.

4. Red corrosion.

At least two mechanisms were suspected in the formation of stains on RSRM hardware: 1. Accelerated oxidation at the edge of a water droplet as it evaporates can be caused by the locally higher oxygen concentration. 2. Heavier deposits of a non-volatile residue can be formed by excess solids in the rinse water or excess solids carried through from the wash cycle. In addition to the stains, some occasional red rust has been found, primarily in threaded holes.

The yellow powder and dark gray stains from RSRM hardware were sampled to determine their composition. IR analysis confirmed that the dark gray and yellow stains contained detergent residue. The watermark stains could not be tested because there was not enough material available on the surface to analyze.

A test was conducted where samples from the rinse solutions were placed on steel coupons and allowed to dry. Stains produced were mostly from the residual detergent in the rinse solutions and similar to those on RSRM hardware. A wipe with deionized water removed most of the stains and left a faint but acceptable watermark. The test coupons with stains from the rinse solutions were held for one week at 70 °F and 70 %RH to determine if accelerated corrosion occurred due to the stains. No accelerated corrosion was found from the detergent stains, but the control sample with no detergent residue did corrode. ESCA analysis confirmed that corrosion had not accelerated due to the detergent residue on the metal surface. ESCA also confirmed that the detergent residue had been removed with a water wipe.

Heavier gray and yellow stains can also occur where water is trapped and cannot drain after the rinse cycle. Two of the surfactant components of Brulin 1990GD become insoluble and float on the surface of the solution above 110 °F then redissolve when the solution cools. Samples from gray and yellow stains indicate that the surfactants that float on top of the solution are present in the solid material.

Excess water is removed from such areas with a shop vacuum and compressed air, then the area is quickly wiped dry. Compressed air is also used to blow water out of small holes. If minor stains do occur, a water wipe soon after the wash can remove most of the stains. Some rework is still required to remove stains and improved methods are being worked on.

Corrosion can be formed when water without a corrosion inhibitor is allowed to remain on the steel. Such corrosion is most often associated with threaded holes where it is difficult to quickly dry the area after a wash. The Refurbishment washer uses a corrosion inhibitor in the rinse water to prevent corrosion, but that inhibitor is not yet approved for the wash process just before the bonding process.

In the implementation of the washer, the conductivity of the second rinse was allowed to be as high as 350 micromhos; however, it was found that less staining from residual detergent occurred with the conductivity limited to 275 micromhos. In practice, the second rinse is changed whenever the conductivity exceeds 225 micromhos.

Removal of Silicone from Paint Brushes

Contamination-control tests showed that paint brushes with Tynex bristles contain a silicone release agent. Other types of paint brushes occasionally have been found to contain silicone. The silicones are applied to the bristles to control static electricity as part of the brush manufacturing process and the silicones must be removed before the brushes are used to apply adhesive, primer and paint to the RSRM. It was not possible to obtain brushes of the required type without silicone and, for several years, all brushes were washed with TCA to remove silicones and then tested for any residual silicones before they were used in RSRM manufacture.

Tests are underway to determine if the amount of silicone on the paint brushes can affect adhesive bonds, but the tests are not complete. Preliminary data suggest that bond sensitivity to silicones varies according to the type of bondline and some bondlines are not affected by the amount of silicone available in a paint brush where others may be affected. The brushes are washed not because there is evidence that the amount of silicone on the brushes affected the bondlines, but to ensure that there is no possibility of weakening an adhesive bond.

The bondlines that appear to be most affected are Rustoleum primer/steel, Chemlok 205 primer/steel and EA-913NA/steel bonds. Bondlines that do not appear to be particularly sensitive are propellant/liner and NBR/Chemlok 233 bonds.

A replacement cleaner for TCA was investigated for removal of silicone release agents from paint brushes. Detailed follow-on tests are now being conducted to implement the brush cleaning process with a new cleaner. An initial screening of 31 cleaners showed four cleaners removed silicone well from brushes; three were aqueous and the other organic. Tests were performed on brushes with DuPont Tynex bristles because DuPont is known to use silicone release agents in the manufacturing process. DuPont, was contacted and stated that it is impossible for them to manufacture the bristles without silicone lubricants in their extruding machines.

The silicone-removal tests are being accomplished by repeating earlier laboratory-scale tests in a repetitive manner to statistically verify the results. The cleaners to be tested are listed in Table II. The two best cleaners will then be selected for full-scale tests based on results of the laboratory tests. Brushes washed in the full-scale equipment will be tested for residual silicone and cleaner to determine if the full-scale process was successful. Bond tests will also be conducted with Hysol EA913 NA® adhesive as that adhesive has been found to be sensitive to contamination. The bond tests will verify that there is no effect from the brush-wash process on the adhesive bonding process.

Table II. Candidate Cleaners.

No.	Code	Cleaner	Description	Process parameters
1	AC3	AmberClean Q3	Aqueous, non-terpene citrus base	25% solution, 70±10 °F
2	HS9	Hurrisafe 9575	Aqueous	25% solution, 70±10 °F
3	IC4	InproClean 4000	Aqueous with terpenes	25% solution, 70±10 °F
4	VER	Vertrel MCA Plus	Decafluoropentane 85%, acetone 10%, cyclohexane 5%	Neat
5	TSP	Trisodium phosphate	Trisodium phosphate	Mfg. Recommendation
6	BR8	Brulin 815GD	Surfactants, sodium tripolyphosphate	10±2%, 120±10 °F

Laboratory Study

New brushes will be tested by TCA extraction to verify the presence of silicone on the bristles. Once silicone had been verified on the new brushes, sample sets of brushes will be suspended in a container with enough solvent to cover the exposed top of the bristles for 15±1 minutes. The solvent will be agitated with a magnetic stir bar. The brushes will then be analyzed for silicone. This procedure will be repeated seven times in each cleaner for a statistically significant sample.

The full-scale tests will be conducted to assess the performance of the two best cleaners from the laboratory study. One batch of brushes will be washed for each cleaner in the full-scale washer. The brushes will then be tested for residual silicone and cleaner.

Bath-life tests will be conducted to determine how long a cleaner will effectively remove silicone from brushes. Several lots of brushes will be washed in one lot of cleaner and tested for silicone concentration. When it is found that the silicone is not removed from the brushes, the bath will be considered to be beyond the useful life.

Tapered Double Cantilever Beam (TCDB) tests will determine if adhesive bond strength is affected by brushes which have been cleaned with the new process. Bond samples will be constructed using Chemlok 205/ D6AC Steel and Rustoleum primer/D6AC steel with normal laboratory procedures. Paint brushes cleaned with the best cleaners in full-scale equipment will be used to apply the primers to the bond specimens. Paint brushes cleaned with TCA will be used as the control samples. Five TDCB samples per set were used so that the mean bonding fracture toughness and critical load can be compared between sample sets.

Conclusions

1. Wash chemistry definition and control are critical to effective aqueous cleaning.

2. Aqueous cleaning is effective for RSRM metal part bond preparation.

3. KOH add back can extend the bath life of Brulin 1990GD to over four months.

4. The final rinse conductivity is limited to below 275 micromhos.

5. Four cleaners removed silicone well from paint brushes.

Acronyms and Abbreviations

AmberClean 03®	Innovative Organics trademark
Brulin 815GD®	Brulin Corp. trademark
Chemlok®	Lord Corp. trademark
D6ac	Steel alloy
Diala®	Shell Diala® Oil
EA913 NA®	Hysol® Adhesive
°F	Degrees Fahrenheit
HD-2®	Conoco HD-2® grease
Hurrisafe 9575®	PCI of America trademark
InproClean 4000®	Oakite trademark
NBR	Nitrile butadiene rubber
ODC	Ozone-depleting chemicals
RSRM	Reusable Solid Rocket Motor
Rustoleum®	Rustoleum trademark
TCA	1,1,1-trichloroethane
TDCB	Tapered double-cantilever beams
Tynex®	DuPont trademark
Vertrel MCA Plus®	DuPont trademark

REPLACEMENT OF A HAZARDOUS SOLVENT DEGREASING OPERATION WITH AN AUTOMATED AQUEOUS PRECISION CLEAN LINE

Mal Privett
Pratt & Whitney
P.O. Box 109600, M/S 706-10
West Palm Beach, FL 33410
(561) 796-6173

Abstract

Pratt & Whitney has developed alternatives to trichloroethlyene used in precision cleaning operations for the manufacture of high pressure turbopumps for the Space Shuttle Main Engine program. Trichloroethylene has been traditionally used in a degreaser as the method for precision cleaning of components. Several methods were investigated to replace the degreasing operation. The aqueous ultrasonic method chosen to replace the degreasing operation was developed using the contaminants found in the manufacturing and assembly process. The process was validated using pilot scale ultrasonic equipment. Significant lessons were learned during the pilot scale trials, especially in the area of equipment design and optimization. Also, lessons learned from the implementation of a cleaning system used prior to fluorescent penetrant inspection were incorporated into the design of this system. The system chosen for implementation into the production environment was a customized, but cost effective, fully automated five station clean line. The system was designed to minimize both energy and water consumption and also to minimize process waste. In addition, this new process eliminates the use of all degreasers at the Pratt & Whitney - Florida facility.

Aqueous Precision Cleaning at Pratt & Whitney

Mal Privett
AETC - June 2, 1998

Precision Cleaning

- Removal of all contamination which could lead to initiation or propagation of an oxygen reaction or component/system damage
- Traditionally performed with non-flammable halogenated hydrocarbons such as CFC (Freon) 113, 1,1,1-trichloroethane, or trichloroethylene

P&W Problem Summary

- Use of Trichloroethylene (TCE) Degreasing
  - Marginally compliant degreasers (NESHAP)
  - Company halogenated solvent elimination policy
  - Safety/Health issues with toxic solvents

Program Background

- Previous Cleaning Methods
  - Majority of parts in TCE Degreaser
  - Some large parts (housing, shaft) flushed in TCE recirculating rig
  - Isopropyl alcohol wipe for certain surfaces
    - titanium alloys
    - carbon seals
    - some non-metallic materials

Cleaning Requirements

- Precision Cleaning to MSFC-SPEC-164
  - Non volatile residue less than:
    - 1 milligram per 0.1 square meter of part surface for components in LOX/GOX system
  - Particle size limits:
    - All particles must be less than 800/400 microns
      - (P&W requirement less than 300 microns)

System Approach

- Cleaner / Rinse Selection & Development
- System Hardware / Physical Requirements
- System Integration / Process Assurance

Project Methodology

- Selection of cleaner candidates
- Identification of candidate processes
- Down-select cleaner/general process
- Preliminary Trials
- Pilot scale trials/process development
- Demonstration/Validation
- Equipment Specification/Purchase

Cleaner Selection

- Three cleaners chosen for pilot scale testing:
  - Brulin 815 GD
  - Turco 3878 LF-NC
  - Turco 4215 NC-LT
- Final Cleaner Chosen : Turco 4215 NC-LT
  - Superior cleaning capability, consistency, and rinsing characteristics (29 of 30 NVR trials passed)
  - Uses Turco 4215 additive

Pilot Scale Trials

- Pilot scale testing performed:
  - National Defense Center for Environmental Excellence (NDCEE)
  - Dedicated system to project
  - No capital investment required
  - P&W personnel performed cleaning trials
  - Rapid data generation and process modifications permitted

Soiling Compounds

- Braycote 640 AC-MS
- Halocarbon 25-5S
- Safe-Tap
- P6F4
- ZL-60D
- ZP4B
- Fingerprints
- Light Machining Oil
- Kool Tool Cutting Fluid

Parts/Surfaces

- Initially worked with peened and grit blasted panels to determine overall effects
- Parts used in Pilot Scale Testing:
  - Bellows
  - Prebumer Housing
  - Turbine Turnaround Duct
  - Bearing Support
  - Inducer
  - Sales-M Bearing Cage
  - Prebumer Impeller
  - Turbine Vane Segment
  - Bore Tube
  - Turbine Blade (2)
  - Volute
  - Tubing
  - Armalon Bearing cage
  - Lift-off Seal Nut

Testing Methodology

- Begin testing using most conservative parameters: high ultrasonic power, long immersion times, etc
- Determine critical process factors: narrow down times, power levels, etc.
- Bound process
- Validation, Documentation
- All cleanliness verified by NVR using TCE

Critical Process Factors

- Ultrasonic cleaning inadequate without supplemental solution agitation
- Clean followed by minimum of two rinses
- Spray rinsing with DI water at several points in the process (critical improvement)
  - For automated system an SUI takes the place of the manual rinse

Material Compatibility

- Cleaning solution will not attack most metallic materials during immersion
  - some materials discolor when ultrasonics used
- Appears to be compatible with many non-metallic materials: PTFE, Salox-M, Armalon
- Will <u>not</u> remove some marking materials

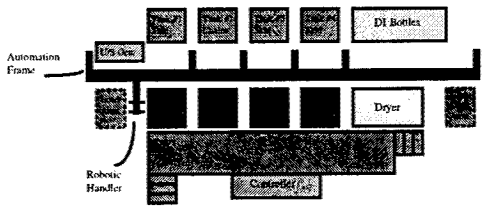
Material Compatibility

- Surfaces which can NOT be cleaned in the aqueous ultrasonic system:
  - silver plate
  - sputtered MoS_2
  - fuel housing insulation
  - carbon seals
  - certain bearing components

Cleaning System

- Five station cleaning system
  - Cleaning Tank
  - Spray in air rinse
  - Immersion Rinse #1
  - Immersion Rinse #2
  - Recirculating Dryer
- 500 lb. work rack in bottom of each tank
- Manual DI water spray rinse at all stations
  - DI water quality at least 1 megaohm-cm

System Layout



Immersion Tanks

- Clean tank and two rinse tanks
  - sloped tank bottom
  - double spargers (top and bottom)
  - Pause and resume buttons
    - Powerflush tooling port
    - Manual spray rinse
  - Sound absorbing design and materials
    - Keeps sound below 85 dB

Cleaning Tank

- 450 Gallons; 3 oz/gal Turco 4215 NC-LT with 4215 additive; 120°F
- pH sensor to monitor cleaning solution
- Coalescing tower to remove traces of oil
- Redundant filter housings

Spray In Air Tank

- 11 spray bars on four sides, tank corners, and bottom
  - 66 fan and cone low flow nozzles
  - adjustable to optimize coverage
- Source of water is first immersion rinse
  - this permits clean, heated water to be used
- Only location where fluid is discarded

Rinse Tanks

- Recirculating de-ionized water supply
  - regenerative heat exchanger allows high temperature operation in final rinse tank
  - redundant series of DI bottles
- Rinse #1 - 500,000 ohms/cm - 145°F
- Rinse #2 - 1,000,000 ohms/cm - 160°F
- Redundant filter housings
- Flush port

Recirculating Dryer

- Dual plenum design
  - permits dryer to be on standby
- Thermal distribution optimized
  - Blower → Heater → Filter
- Air knives in lid
- Nominal Temperature - 225°F
- Uses oil free compressed air supply

Spray Under Immersion (SUI)

- Tanks 1, 3, and 4 have SUI agitation
  - 10 spray bars, 66 nozzles
    - Sides, corners, and bottom
  - centerline eductor on tank bottom (adj. flow)
    - maximizes efficiency for hollow parts
  - 375 gallons per minute (switchable strainers)

Ultrasonics

- Ultrasonics in Tanks 1, 3, and 4
- 40 kHz center frequency with sweep
- 30 watts per gallon
- Adjustable power and sweep rate
  - Single controller for each tank
- Immersibles mounted on 4 sides + bottom
- Ultrasonics interlocked with SUI
  - Filtration, Coalescer, and DI loops always on

Transport Features

- Fully automated system
  - robotic parts handler (up to 500 lb)
  - multiple loads simultaneously
  - most functions centrally controlled
- Semi-automatic and manual operation are optional (has centerline "find" in S/A mode)
- Opposing sliding lids
  - improved safety over hinged lids

Automation

- Automatic parts pickup and delivery
  - sensors/gate to ensure no human or part injury
- Process Assurance
  - self diagnostic controls
  - multiple alarm conditions (G/Y/R)
  - process will not finish if conditions out of limits (STAMP WARRANTY)

Miscellaneous Features

- System is modular (skidded and able to be moved without major teardown
  - flexible lines between pumps and tank
- System is in a "portable" clean room
  - Class 100,000
- "Smart" utility design
  - 24h/7d timers for heat
  - optimum power distribution
  - very low water consumption

System Procurement

- Extreme detail in quote requirements
  - Assume nothing
  - Meet with potential suppliers before quote
- But, permit suppliers to be "creative"
  - Performance requirements
  - Have supplier propose solutions
- Allow LOTS of extra time in schedule

WASH SOLUTION BATH LIFE EXTENSION FOR THE SPACE SHUTTLE ROCKET MOTOR AQUEOUS CLEANING SYSTEM

by

Chad Saunders
Kurt Evans
Neil Sagers

Thiokol Propulsion
P.O. Box 707 - M/S 245
Brigham City, UT 84302

ABSTRACT

A spray-in-air aqueous cleaning system, which replaced 1,1,1 trichloroethane (TCA) vapor degreasing, is used for critical cleaning of Space Shuttle Redesigned Solid Rocket Motor (RSRM) metal parts. Small-scale testing demonstrated that the alkaline-based wash solution possesses adequate soil loading and cleaning properties. However, full-scale testing exhibited unexpected depletion of some primary components of the wash solution. Specifically, there was a significant decrease in the concentration of sodium metasilicate which forced change-out of the wash solution after eight days. Extension of wash solution bath life was necessary to ease the burden of frequent change-out on manufacturing. A laboratory study supports a depletion mechanism that is initiated by the hydrolysis of sodium tripolyphosphate (STPP) lowering the pH of the solution. The decrease in pH causes polymerization and subsequent precipitation of sodium metasilicate (SM). Further investigation showed that maintaining the pH was the key to preventing the precipitation of the sodium metasilicate. Implementation to the full scale operation demonstrated that periodic additions of potassium hydroxide (KOH) extended the useful bath life to more than four months.

INTRODUCTION

The Thiokol Corporation Clearfield Utah facility refurbishes reusable post flight Space Shuttle solid rocket motor metal hardware. Several processes are employed to strip the paint, insulation, and charred material down to a virgin metal surface. After refurbishment, the hardware is shipped 75 miles north by rail to the primary manufacturing area and undergoes a final surface preparation process (aqueous clean and grit blast) prior to bond assembly. Previously, TCA vapor degreasing was used to clean the metal surface at both locations. Recently, aqueous cleaning replaced vapor degreasing because of the ozone depleting properties of TCA. The aqueous cleaning process, which consists of three phases (wash, rinse 1, and rinse 2) is conducted in a Proceco Incorporated spray-in-air system. Sub-scale testing was used to optimize process parameters which included determination of the ideal concentration and temperature of the cleaner.

Copyright '98 Cordant Technologies, Inc. All rights reserved.

The full-scale process demonstrated a 20°F reduction in wash solution temperature after circulation from the heated holding tank to the spray in air nozzle. This reduction compromised cleaning efficiency and increased foaming in the cleaning chamber. Apparently, the foam suppression mechanism of the nonionic surfactants was inadequate at the lower temperature. The wash solution set temperature was increased from 150 to 170°F to compensate for the heat loss.

Analysis of the cleaning solution showed depletion of several primary components of the alkaline cleaner. Specifically, the rate of depletion of SM and STPP was greater than initially predicted. This depletion was unacceptable because violation of concentration-based acceptance limits for the primary components of the alkaline cleaner were established to ensure the cleanliness and condition of the hardware. Violation of these limits burdens manufacturing operations with frequent change-out of the wash solution. Cursory review of the chemistry data linked the depletion of STPP to the increase in wash solution temperature from 150 to 170°F and localized heating in excess of 170°F in the heating tank.

A laboratory study confirmed that the depletion of STPP is dependent upon the temperature of the wash solution. It also determined that STPP depletion reduces pH which jeopardizes the SM solubility which is a function of pH. A subsequent laboratory study demonstrated that additions of potassium hydroxide (KOH) to the wash solution controls pH above levels which circumvent SM precipitation, thereby extending the useful bath life of the wash solution. This KOH add-back method was successfully demonstrated in the full-scale system through a bath life study which extended the bath life to at least 120 days.

RESULTS AND DISCUSSION OF THE TEMPERATURE STUDY

The objective of this study was to determine the effect of exposure of the wash solution to a range of production representative temperatures on the pH and cleaner constituent concentrations.

General Outline of Procedure

Three distillation apparatuses were configured to maintain 10-percent solutions of the alkaline cleaner at temperatures of 150°F, 175°F and 200°F for five twenty-hour cycles. The three temperatures replicated the range of temperatures of the wash solution in the full-scale production process. General observations of the physical state of the solutions were recorded throughout cycling. At the end of each 20-hour cycle an aliquot of the solution was removed and the primary components of the cleaner were determined for these samples. The following table lists the primary components of the cleaner (excluding water and potassium hydroxide) and the analytical techniques used for measurement. Alkalinity and pH were also determined.

Table 1. Analytical Methods

Alkaline Cleaner Component	Method of Analysis
Sodium Tripolyphosphate	Ion Chromatography
Sodium Metasilicate	ICP-AES UV/Vis Colorimetric
D-08 (Anionic Detergent)	HPLC
D-22 (Anionic Detergent)	HPLC
D-26 (Nonionic Detergent)	HPLC
D-30 (Nonionic Detergent)	HPLC

Sixteen samples were collected during the study. The samples consisted of one control of the initial cleaner solution and 15 samples collected from five intervals of 20 hours for three temperatures (150°F, 175°F and 200°F). A cycle refers to the heating of a sample from ambient to the controlled temperature (150°F, 175°F, or 200°F) maintaining the sample at that temperature for 20 hours, then cooling back to ambient temperature. No external cooling was applied. A reference to "Cycle 3" indicates that the sample was collected after the third cycle and was exposed to the controlled temperature for a total of 60 hours. A 20-hour cycle simulated the time duration to complete a single production wash cycle if the cleaning solution is initially at ambient temperature.

Figures 1, 2 and 3 illustrate the behavior of the cleaner components during cycling at each temperature in terms of percent of initial concentration. In figure 3, the last three data points for D-30 were not included because the actual concentration was lower than the detection limit of the method. The relative detection limit is 40 percent of the initial concentration. The concentration of the each component at time zero was determined from the control sample.

The plots show that temperature significantly affects the concentrations of STPP, SM and pH. The effect on the surfactants is less marked except at 200°F. A more detailed discussion of the effect of temperature on each cleaner constituent follows.

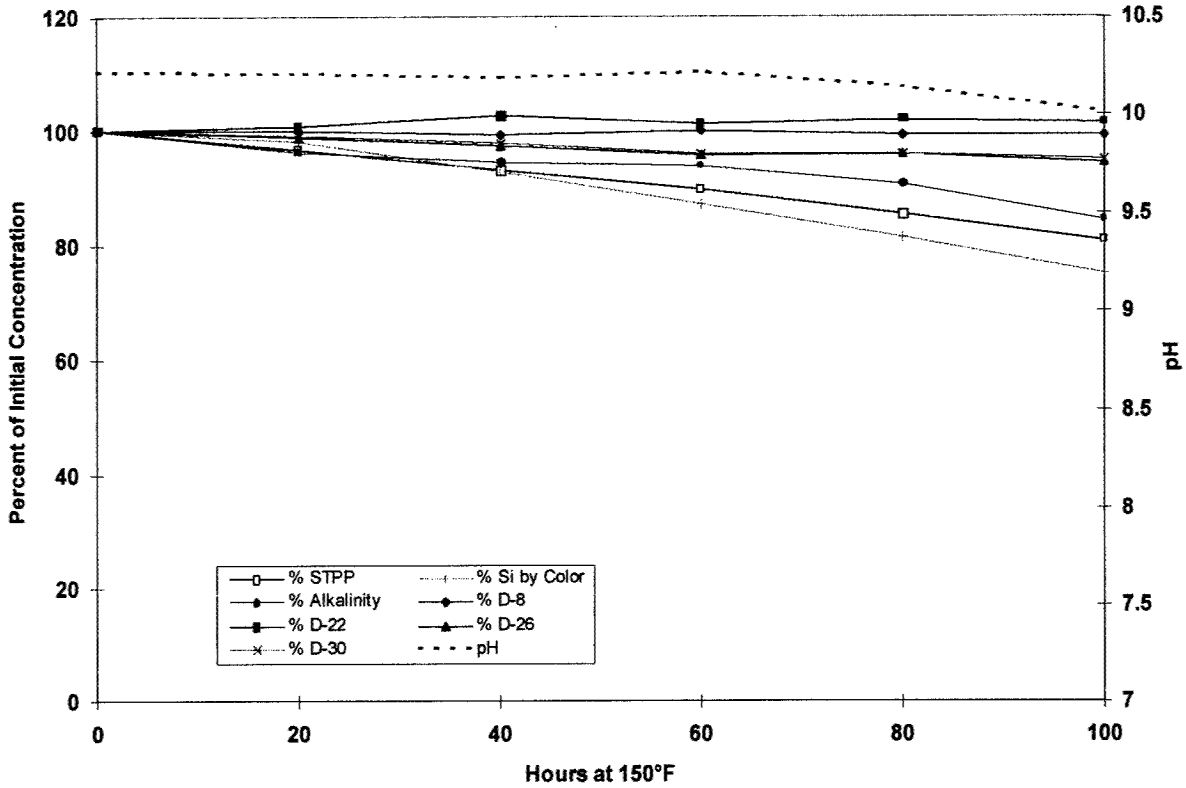


Figure 1. Percent Depletion of All Components at 150°F

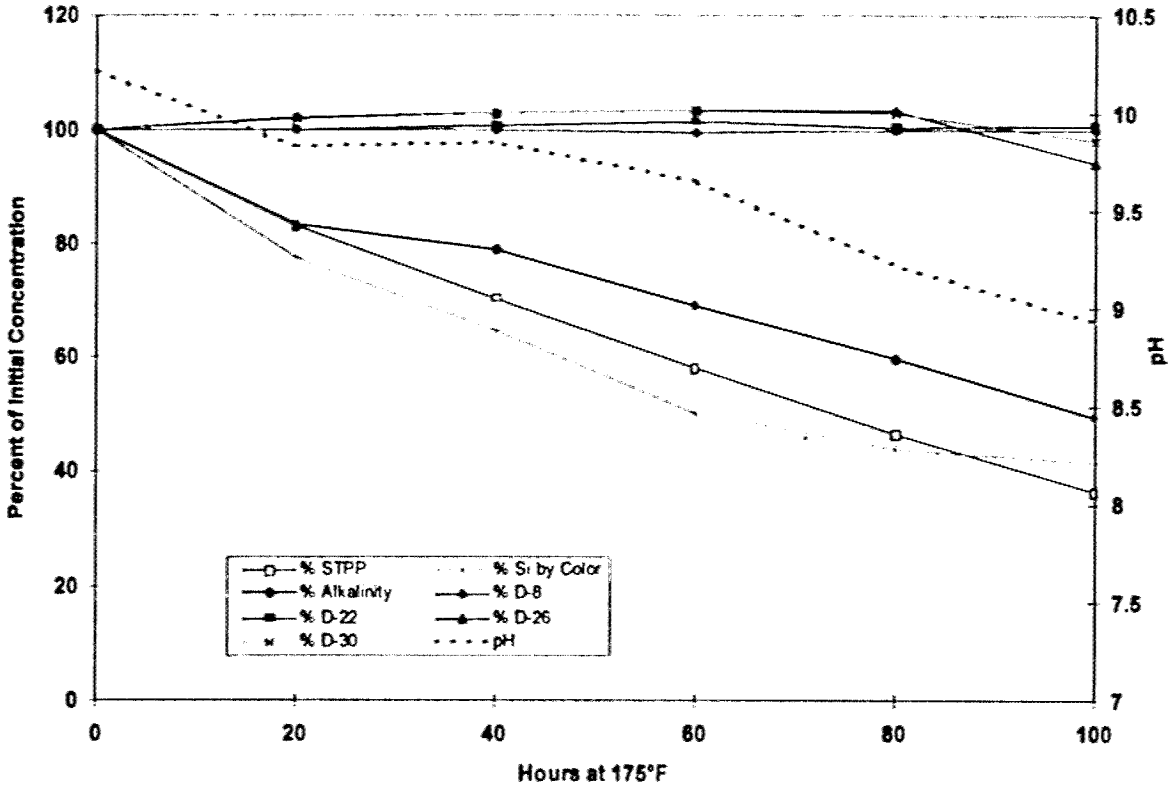


Figure 2. Percent Depletion of All Components at 175°F

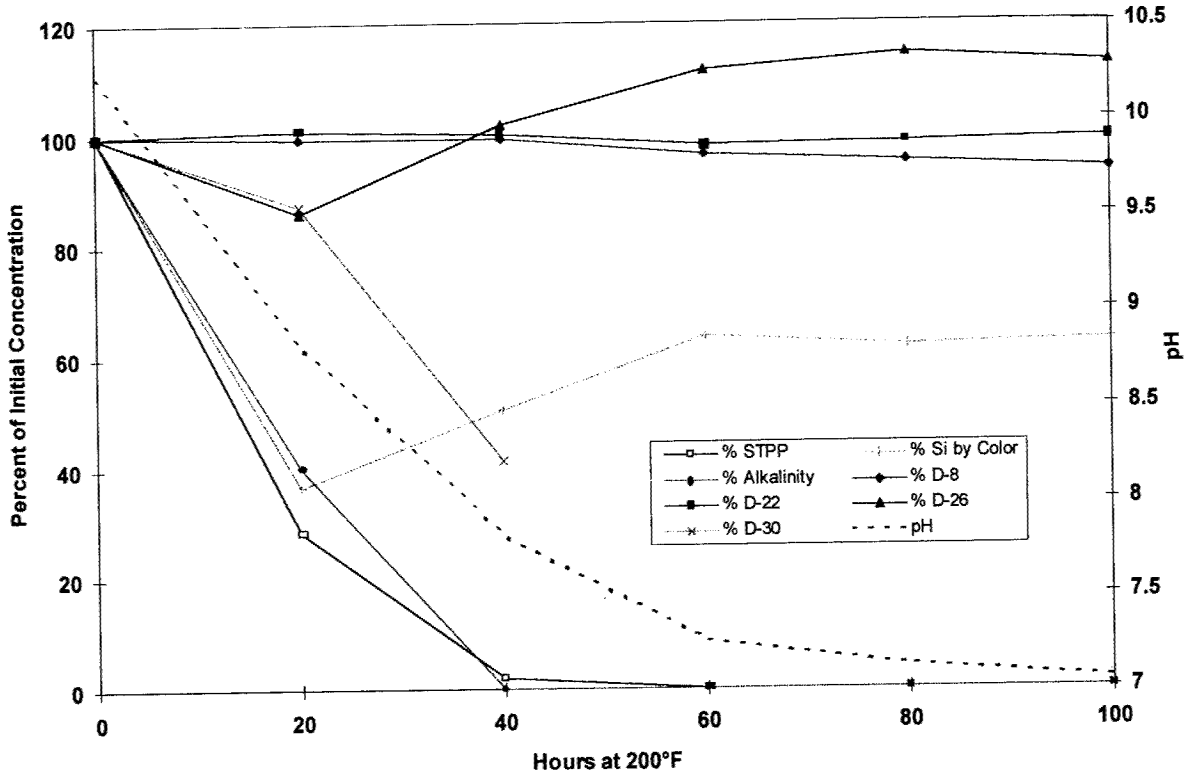


Figure 3. Percent Depletion of All Components at 200°F

Sodium Tripolyphosphate (STPP)

Sodium tripolyphosphate (STPP) functions as a builder in the alkaline cleaner. Builders are added to cleaners to sequester water-soluble polyvalent ions (alkaline earth and transition metals) and prevent them from interfering with detergents in the cleaner. In addition, STPP deflocculates dirt particles and contributes to the alkaline buffer capacity[1]. Tripolyphosphate ($P_3O_{10}^{5-}$) is the linear form of triple condensed orthophosphate. Depletion of STPP occurs when a tripolyphosphate molecule is hydrolyzed to form one molecule of orthophosphate (PO_4^{3-}) and one molecule of pyrophosphate ($P_2O_7^{4-}$). Further hydrolysis of the pyrophosphate results in two molecules of orthophosphate[2]. Figure 4 shows the concentration of STPP and its hydrolysis products over time at the three temperatures as a percentage of the molar phosphorous concentration.

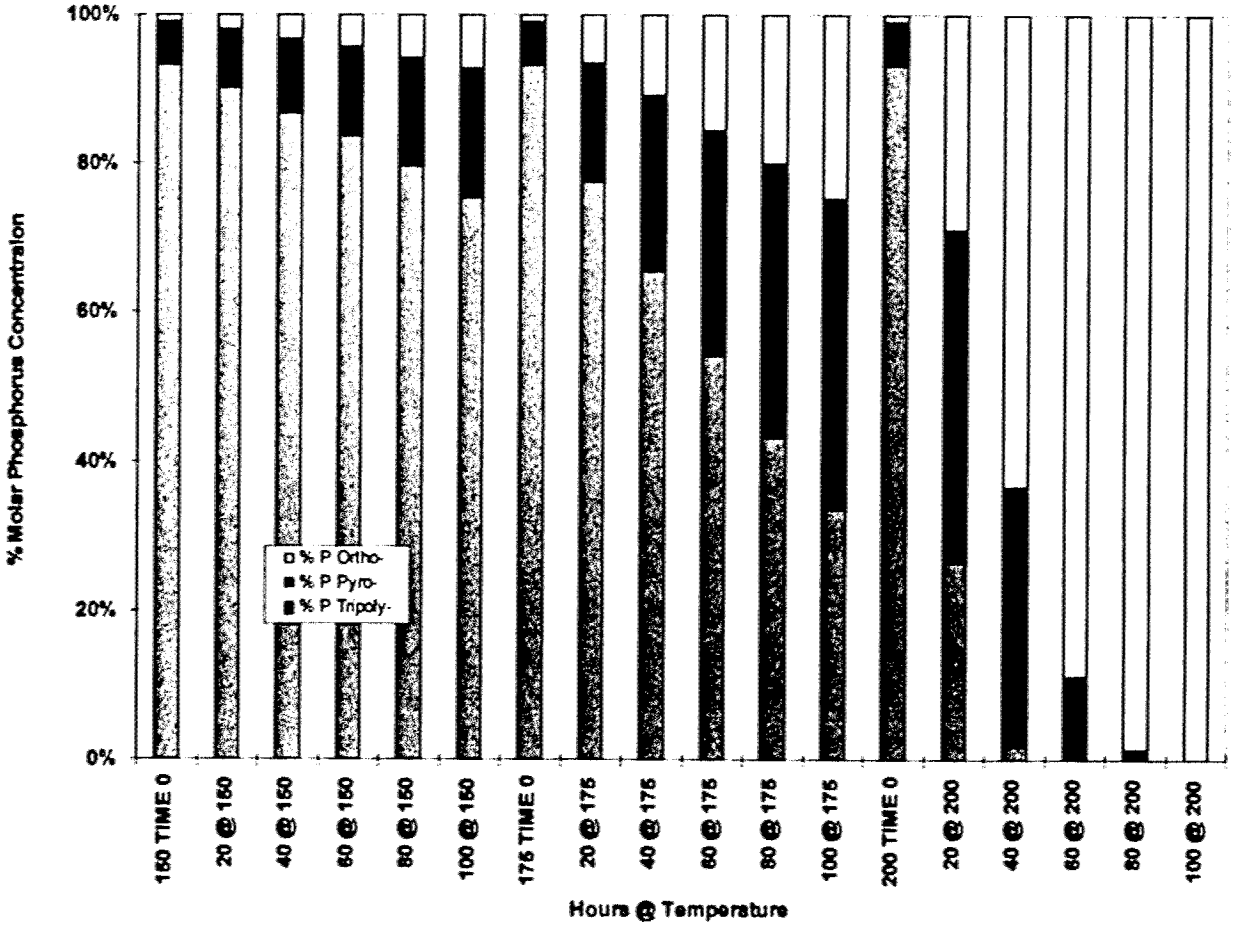


Figure 4. Speciation of Phosphates at 150, 175 and 200°F

This figure illustrates the effect temperature has on the hydrolysis rate of STPP. The magnitude of this effect, particularly at 200°F, supports the theory that localized intense heat from the heat source can significantly accelerate the loss of STPP from cleaning solutions.

Sodium Metasilicate (SM)

Sodium metasilicate functions as a corrosion inhibitor, deflocculant, and wetting agent. Figure 5 compares the silicon results from ICP-AES and UV/Vis colorimetric analysis (heteropolyblue silicomolybdic complex) of the samples collected during the temperature cycle study. A significant difference is observed between the silicon results obtained by the two procedures. This discrepancy can be attributed to sensitivity differences of the two procedures for various silicon species. (A literature search is in progress to determine the silicate forms for which the colorimetric method is sensitive.)

The results suggest that the colorimetric method is less sensitive to the polymeric silicates than the ICP-AES method. The latter method detects any form of soluble silicon that is aspirated into the plasma.

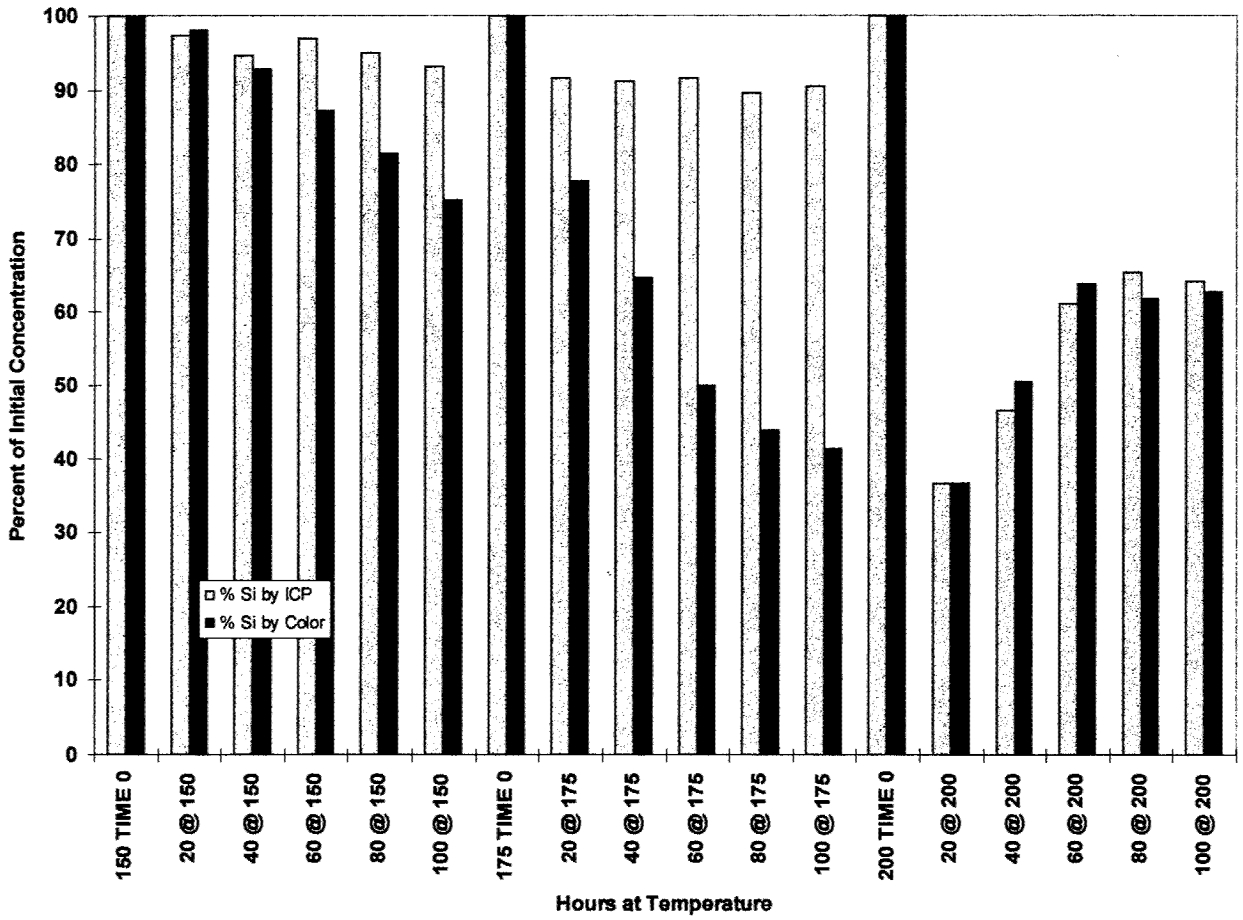


Figure 5. Metasilicate at 150, 175 and 200°F

It has been determined experimentally that the metasilicate monomer is the dominant species the at a pH greater than 10.9. However, longer silicate polymers, colloids, and possibly crystalloids are formed when the pH is lower[3]. Figures 2 and 3 show a steady decline in pH. Figure 5 shows a significant difference in metasilicate concentration measured by the two analytical techniques at 175°F. Apparently, at this temperature the pH is decreasing at a rate slow enough to observe the formation of longer, soluble silicate polymers. The rate in the decline of pH is much faster at 200°F than 175°F. At 200°F, an insoluble silicate residue was collected from each of the samples and the results of ICP-AES and colorimetric analysis are essentially the same.

Alkalinity and pH

Alkalinity is a measurement of the buffer capacity of the solution to accept free acid. The performance of most aqueous cleaners is optimal under alkaline conditions and over a limited range in pH. In addition, ferrous surfaces are less susceptible to corrosion in an alkaline environment. It should be noted that the method for determining alkalinity in this study is a direct titration method to an end point near a pH of 7. Typically, measurement of free alkalinity provides meaningful data concerning the buffer capacity of a solution to accept H^+. Tripolyphosphate is the component of this alkaline cleaner that serves as a buffer over the useful pH range. It is difficult to establish appropriate acceptance values for free alkalinity because the buffering capacity of the wash solution is continuously shifting as the STPP is hydrolyzed. Thus, free alkalinity monitoring is less meaningful to this aqueous cleaning solution.

Anionic and Nonionic Detergents

The alkaline cleaner contains four surfactants. D-8 and D-22 are the numerical references assigned to the anionic surfactants and D-26 and D-30 refer to the nonionic surfactants. The actual names and composition of the surfactants are proprietary. The production database indicates that the surfactant concentrations remain relatively constant throughout hardware cleaning. The temperature cycle study verifies that the surfactants are thermally stable. This is particularly true of the anionic surfactants which showed no decomposition at any of the temperatures. Figures 1, 2 and 3 illustrate the concentration behaviors of the surfactants over time at the tested range of temperatures. These charts also show that D-26 and D-30 were stable at 150°F and 175°F. However, at 200°F the concentration of D-30 decreased below detectable levels and D-26 increases in concentration. Size exclusion chromatography was the method used to monitor the concentration of D-26 and D-30 and it is possible that a converted form of D-30 is being detected as D-26 by this technique.

Conclusions of Temperature Study

The temperature study presented herein is an attempt to understand the reason for depletion of primary components of Brulin 1990 GD during the acceptance limit testing. A great deal of information has been gained by monitoring the individual components after exposure to elevated temperature. The temperature study strongly supports our suspicion that increasing the temperature of the aqueous cleaning solution does accelerate the depletion of the STPP and metasilicate. In addition, the pH of the solution decreases as a function of temperature and may have a role in depletion of the key components as well. The information gained during the temperature study will be used to direct a literature search to determine possible mechanisms for depletion.

INTRODUCTION OF DEPLETION MECHANISM

The results of the temperature study were reviewed in conjunction with full-scale production data. This review revealed four factors that limit useful bath life of the production system wash solution.

The first factor relates to the instability of all components at the extreme temperature of 200°F. The wash solution is exposed to this temperature because of localized heating in the area near the steam heated coils in the holding tank. To circumvent this problem, a circulating pump was installed in the holding tank to reduce pockets of intense heat and eliminate the heating gradient.

The remaining three factors were the decrease in the nominal concentration of metasilicate, pH and tripolyphosphate. The decrease in the concentration of the three components was observed at varying degrees at all three temperatures. The depletion of the SM is the most significant because the concentration fell below established production acceptance limits in approximately eight days.

The information from the temperature study was combined with additional information obtained from literature sources to develop a correlation between STPP hydrolysis and the depletion of other components. In 1984, a kinetic study on the hydrolysis of tripolyphosphate was performed at the University of Zurich. The study described the effect that pH and temperature have upon the reaction and showed that the highest reaction rates occur at low pH and high temperature.[2] The hydrolysis reaction of tripolyphosphate and pyrophosphate occurs as follows:

Hydrolysis of tripolyphosphate,

$$P_3O_{10}^{5-} + H_2O \text{ ——— } P_2O_7^{4-} + PO_4^{3-} + 2H^+.$$

Hydrolysis of pyrophosphate,

$$P_2O_7^{4-} + H_2O \text{ ——— } 2PO_4^{3-} + 2H^+.$$

Both hydrolysis reactions liberate free acid as products. Figures 1, 2 and 3 show that both alkalinity and pH decrease as a function of temperature. The decrease of both parameters correlates closely with the liberation of acid that occurs when tripolyphosphate decomposes to orthophosphate. Identification of the hydrolysis of tripolyphosphate as a source of acid was an important breakthrough. Previously, it was hypothesized that the decrease in solution pH was caused by absorption of atmospheric carbon dioxide. However, the wash solution is enclosed in a holding tank which limits atmospheric exposure. Thus, the hydrolysis of tripolyphosphate is the probable mechanism responsible for decreasing wash solution pH.

Further research indicated that metasilicate depletion is indirectly caused by the elevated temperature. This mechanism is more a function of wash solution pH. According to technical references, soluble silicates polymerize in solution until the polymer exceeds solubility causing the formation of colloids and crystalloids. The extent of polymerization is greatly influenced by the pH of the solution[3].

In summary, the depletion mechanism as derived from both the literature and data collected in the temperature study supports the theory that the rate of STPP decomposition is a function of temperature. The decomposition of STPP is a hydrolysis reaction that liberates free acid and subsequently lowers the pH of the solution. The polymerization of sodium metasilicate increases as the pH of the cleaning solution drops. Eventually, the propagation of the silicate polymer exceeds the solubility limit and a residue is observed.

Identification of the depletion mechanism permitted the conception of an approach to extend the useful bath life of the wash solution. A key element to this approach is to maintain the pH of the wash solution above the critical level at which metasilicate precipitates. This objective can be accomplished simply by adding KOH, a primary constituent of the cleaner, to the wash solution. This approach does not prevent STPP depletion. This is acceptable because the sequestering action is mitigated by use of deionized water in the wash solution. (The possibility of reduction of the wash solution process temperature was considered. However, this approach is impractical because of foaming, cleaning efficiency and system requalification issues.)

RESULTS AND DISCUSSION OF KOH ADD BACK STUDY

A second study was designed to investigate the effect of periodic additions of potassium hydroxide (KOH) to adjust the pH of the solution back to its nominal value. Two distillation apparatuses were configured similar to that of the temperature study. The alkaline cleaner solutions were maintained at 170°F for 21 hours cycles. At the end of each 21-hour cycle the KOH was used to adjust the pH of one of the solutions back to its nominal value of 10.3. The other solution was used as a control and left unchanged. The study was extended to 15 cycles for a total of 315 hours so that the precipitation of the metasilicate could be observed in the control sample. Samples collected at the end of each 21-hour cycle were analyzed by using the methods listed in Table 1. The following figures show the results of this study.

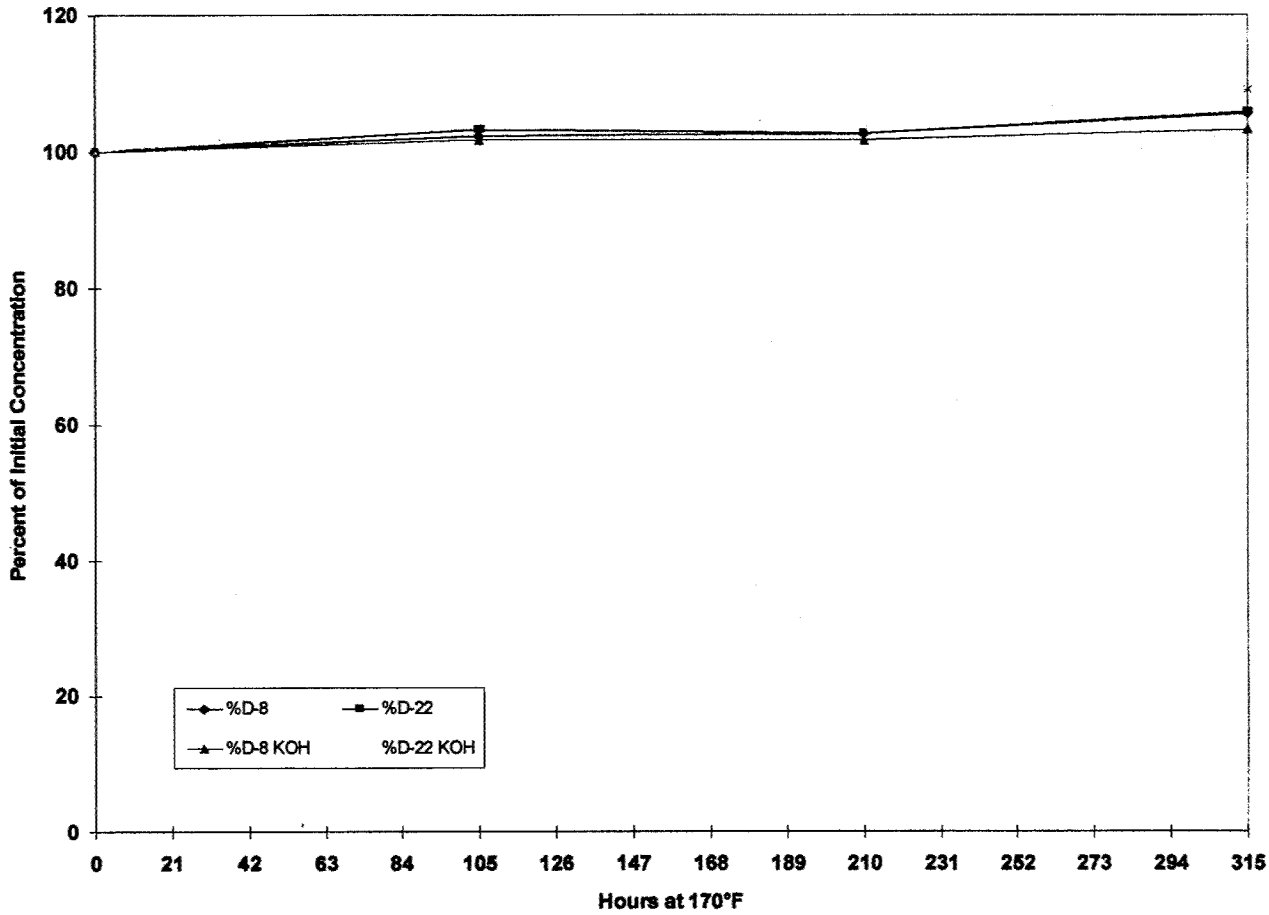


Figure 6. Anionic Surfactants at 170°F

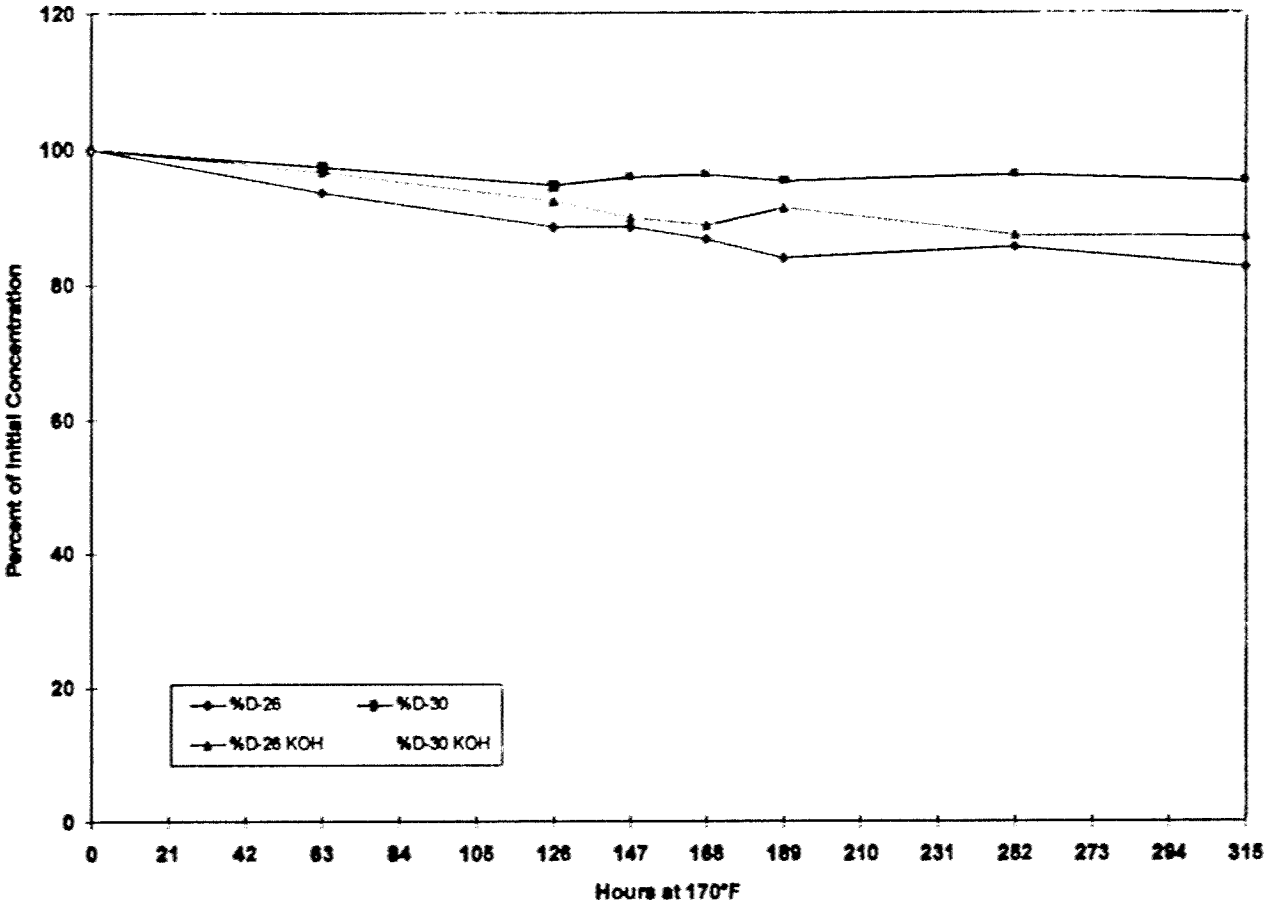


Figure 7. Nonionic Surfactants at 170°F

Figures 6 and 7 show that both the concentration of the anionic and nonionic surfactants are relatively stable and independent of additions of KOH. The surfactant package tolerates variation in temperature and pH by exhibiting exceptional soil loading and cleaning efficiency characteristics throughout sub- and full-scale testing.

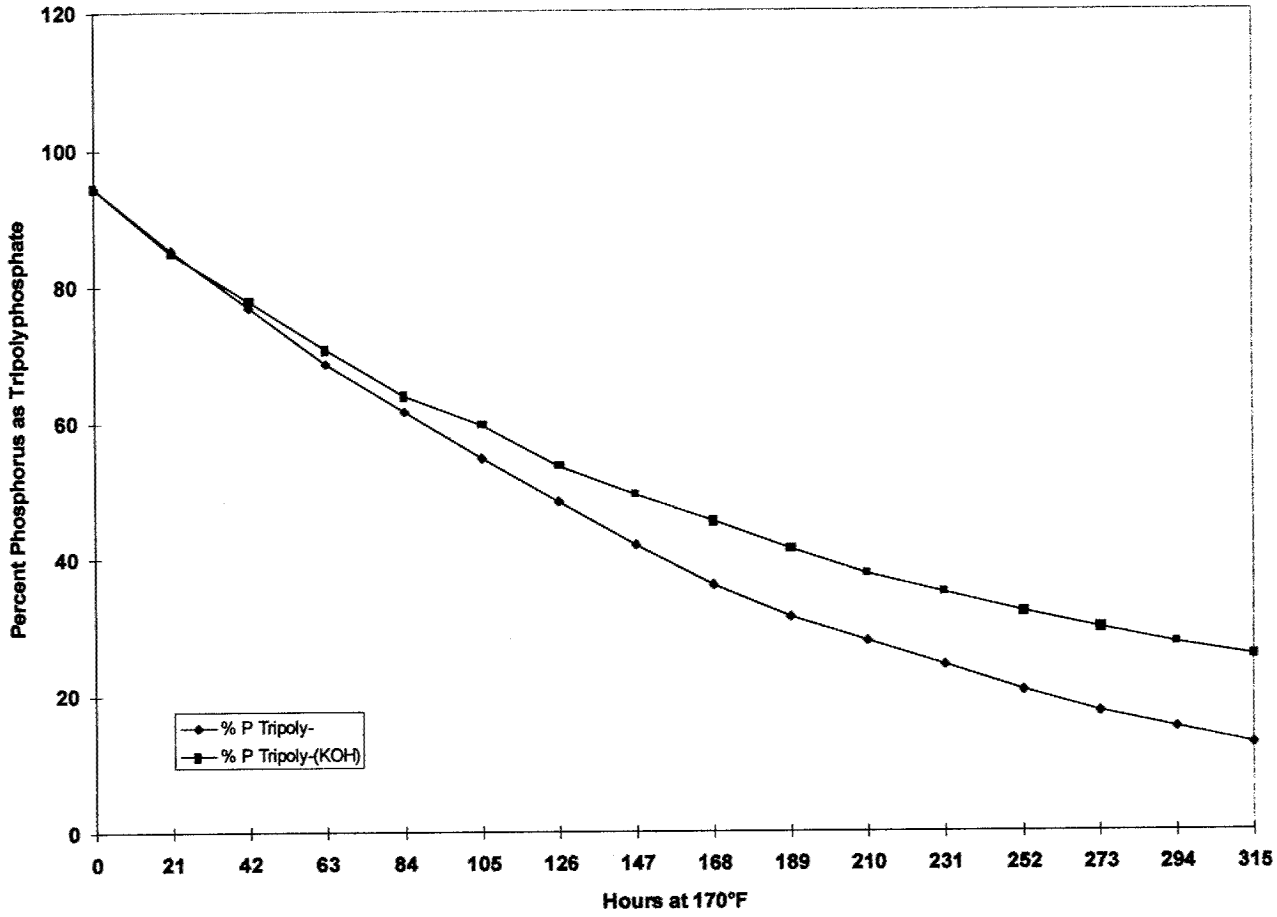


Figure 8. Sodium Tripolyphosphate at 170°F

The literature which discusses the hydrolysis of STPP states that lower solution pH accelerates the depletion of STPP. Therefore, it was anticipated that a cleaner solution with controlled pH would sustain a higher concentration of STPP than the uncontrolled solution. This outcome is exhibited in Figure 8. At zero time, both solutions measured an identical pH of 10.30. However, as the hydrolysis reaction liberated free acid, the pH of the solutions dropped. The pH of the solution with KOH additions was maintained at 10 ±0.3. Conversely, the control solution pH decreased from 10.3 to 8.6 over the duration of the study. After 315 hours at 170°F, the solution with KOH additions was approximately twice the concentration of STPP as the control sample.

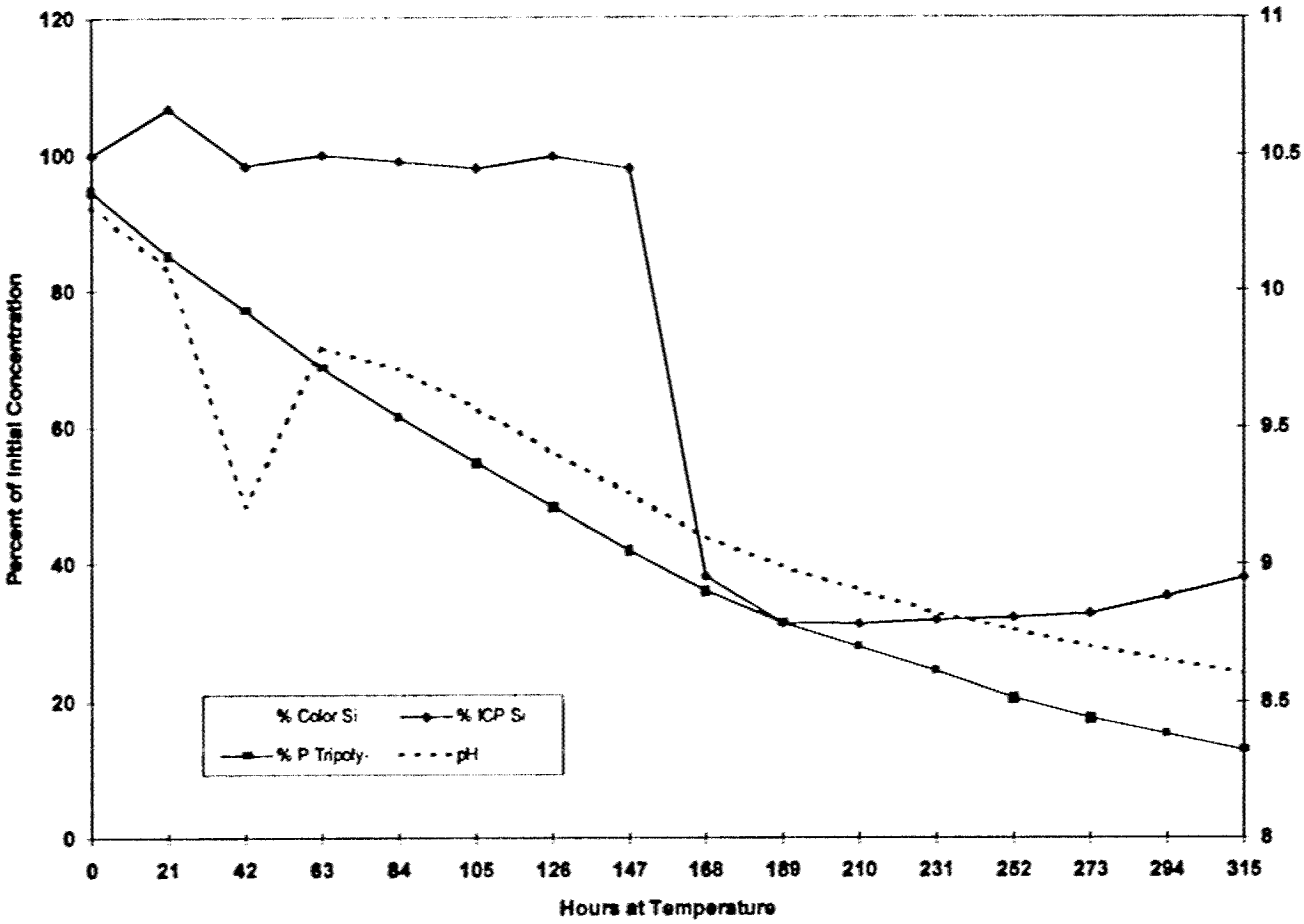


Figure 9. Aqueous Cleaner Chemistry without pH Maintained

The format of Figures 9 and 10 differs from the previous three charts. The SM concentration results of the KOH add back solution are presented separately from that of the control sample. This change allows for plotting and discussion of the effect of the STPP hydrolysis reaction on all other components. Figure 9 graphs the depletion of SM, pH and STPP as function of time at 170°F. The depletion of pH and SM is initiated by the hydrolysis of STPP which depletes to less than twenty percent of its initial concentration and liberates acid as a product of the reaction. The liberated acid causes the pH of the solution to decrease from 10.3 to 8.6 over the course of the study.

The extent of polymerization of the metasilicate as determined by the colorimetric method coincides with the decrease in pH. It is interesting to note that the deviation in pH and colorimetric results at 42 hours occurred because the sample container became unsealed which allowed interaction with atmospheric carbon dioxide. The carbon dioxide absorbed into the solution, reduced the pH, and caused the metasilicate to polymerize.

This event occurred while the sample was stored at 4°C. Two sets of metasilicate results are included in Figure 9 so that the polymerization of metasilicate can be observed. The colorimetric method is most sensitive for the monomer of metasilicate. The ICP method determines all forms of silicate except for the insoluble portion. The two methods are useful to distinguish the form in which the metasilicate is present in the solution. Initially the pH of the solution is high and favors conditions for the metasilicate monomer. As the pH is lowered by the hydrolysis of tripolyphosphate the metasilicate monomers form to soluble oligomers and polymers which is shown in Figure 9 by the decline in the data as determined using the colorimetric method. However, the soluble silicon element concentration remain unchanged until the pH of the solution decreases to 9.2 as indicated by the data obtained from the ICP method. Below this pH the concentration of the soluble silicates declines to 40-percent of the initial concentration and a precipitate of insoluble silicates is observed.

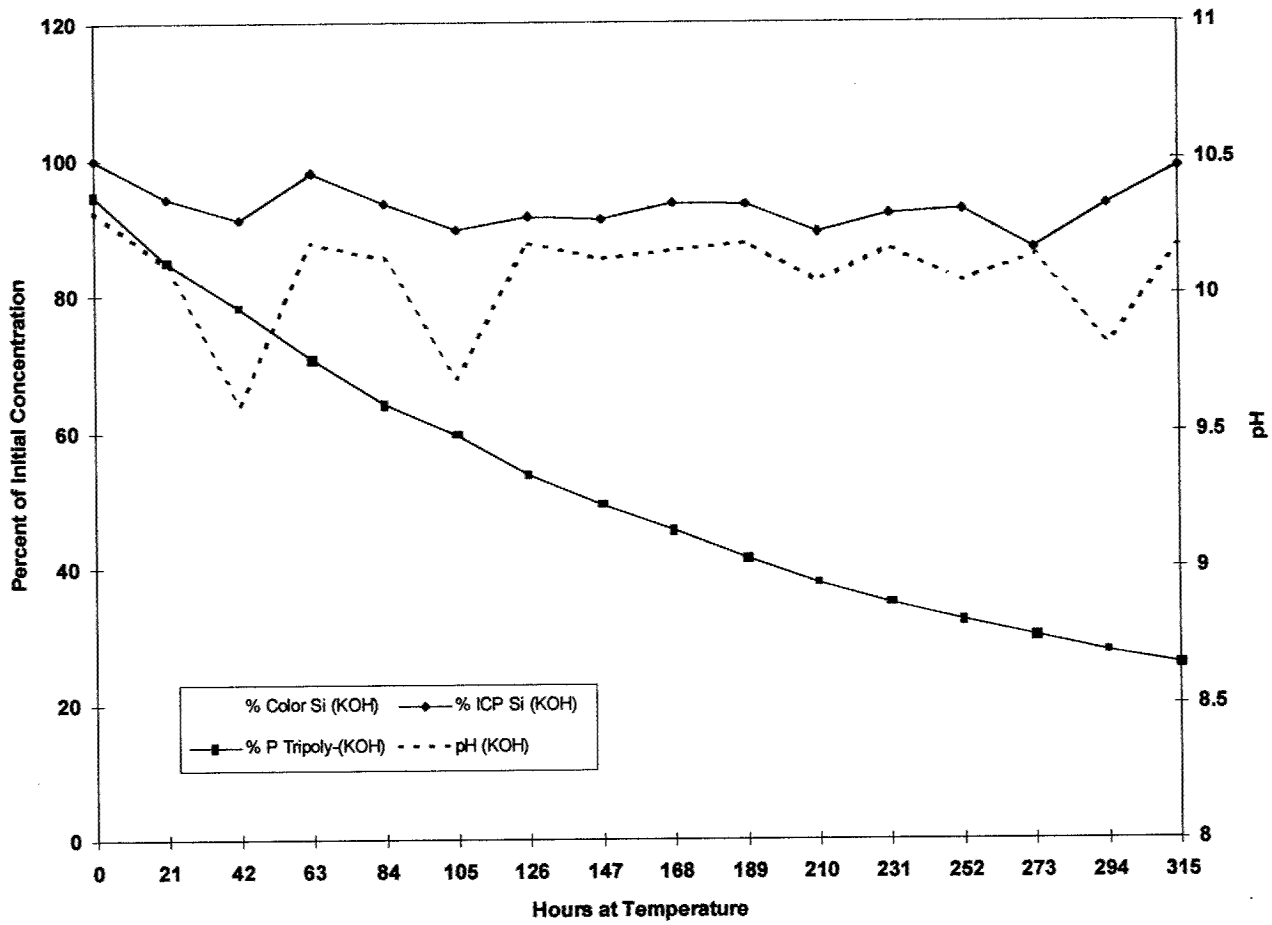


Figure 10. Aqueous Cleaner Chemistry with pH Maintained

Conclusions of the KOH Add Back Study

The results of this study confirm the theory that the rate of STPP decomposition increases significantly as a function of temperature. The decomposition of STPP is a hydrolysis reaction that liberates free acid and consequently lowers the pH of the solution. The polymerization of SM increases as the pH of the cleaning solution drops. Eventually, the propagation of the silicate polymer exceeds the solubility limit and a residue is observed. The pH and SM concentrations of the cleaning solution can be controlled by addition of KOH.

PRODUCTION IMPLEMENTATION OF THE KOH ADD BACK METHOD

The KOH add back method was recommended to the production process to control wash solution pH and SM concentrations. The effectiveness of the method was assessed in the full-scale system through a bath life study which transpired over about 125 days. (Testing was terminated to accommodate production implementation of this aqueous cleaning system.) To strengthen the KOH add back database, numerous full-scale production components were washed and rinsed throughout the study. KOH was added to this 2,200 gallon system eight times for a total of 14,230 gram (31.4 pounds) . The add back events are correlated to pH in Figure 11.

To verify the cleaning efficiency of KOH adjusted wash solution, bond testing was conducted on a weekly basis. Bond specimen test cycles consisted of fracture energy (tapered double cantilever beam) samples which simulate production bondlines (aluminum/EA 913NA adhesive and steel/EA 913NA adhesive). These samples are extremely sensitive to surface blemishes such as contamination caused by inefficient cleaning or rinsing.

pH Chemistry

Figure 11 plots the pH and STPP concentrations of the wash solution over the life of the bath during this study. Figure 11 also relates KOH addition events to pH. The KOH add back method effectively controlled the wash solution pH above the critical level (9.3) required to prevent SM precipitation. As expected, the frequency of KOH addition corresponded to pH fluctuation. Six of the seven additions occurred before 55 days of bath life during the period of greatest fluctuation in pH. Approximately 50 days elapsed between the sixth and seventh/final additions. The period of greatest pH fluctuation also corresponded to the interval of exponential rate of STPP depletion. Eventually, the pH stabilized as the STPP concentration approached zero. Any pH fluctuation subsequent to complete depletion of STPP was attributed the decomposition of pyrophosphate which also liberates free acid but at a slower rate than the tripolyphosphate.

Figure 11 also identifies the time to depletion of the STPP concentration below the production process parameter control limit. In effect, this rate limits the wash solution bath life to about 30 days under the present process control protocol. The bath life could be increased to about 120 days if the process control protocol excluded the STPP concentration limit.

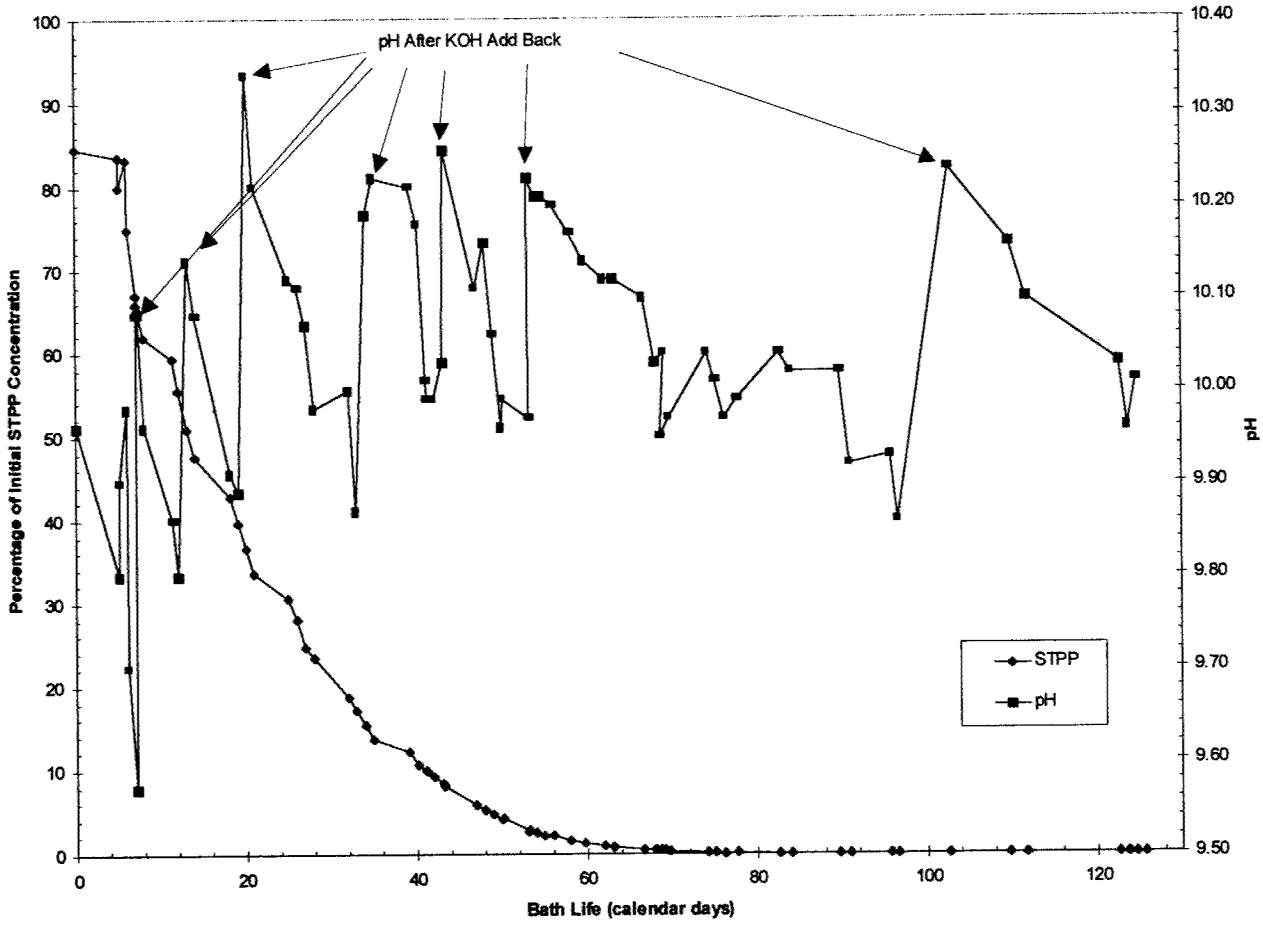


Figure 11. STPP Concentration and pH versus Full-Scale System Bath Life

Phosphate Chemistry

Figure 12 correlates the phosphate concentration data to the wash solution bath life. The hydrolysis reaction is exhibited in the behavior of the phosphate constituents in the wash solution. The STPP concentration depleted to an undetectable level (<3.3 ppm) after about 76 days.

Simultaneously, the sodium orthophosphate and pyrophosphate concentrations increased until about 55 days. Thereafter, the hydrolysis of pyrophosphate becomes the primary source of additional orthophosphate. The hydrolysis of pyrophosphate had not gone to completion when testing was terminated.

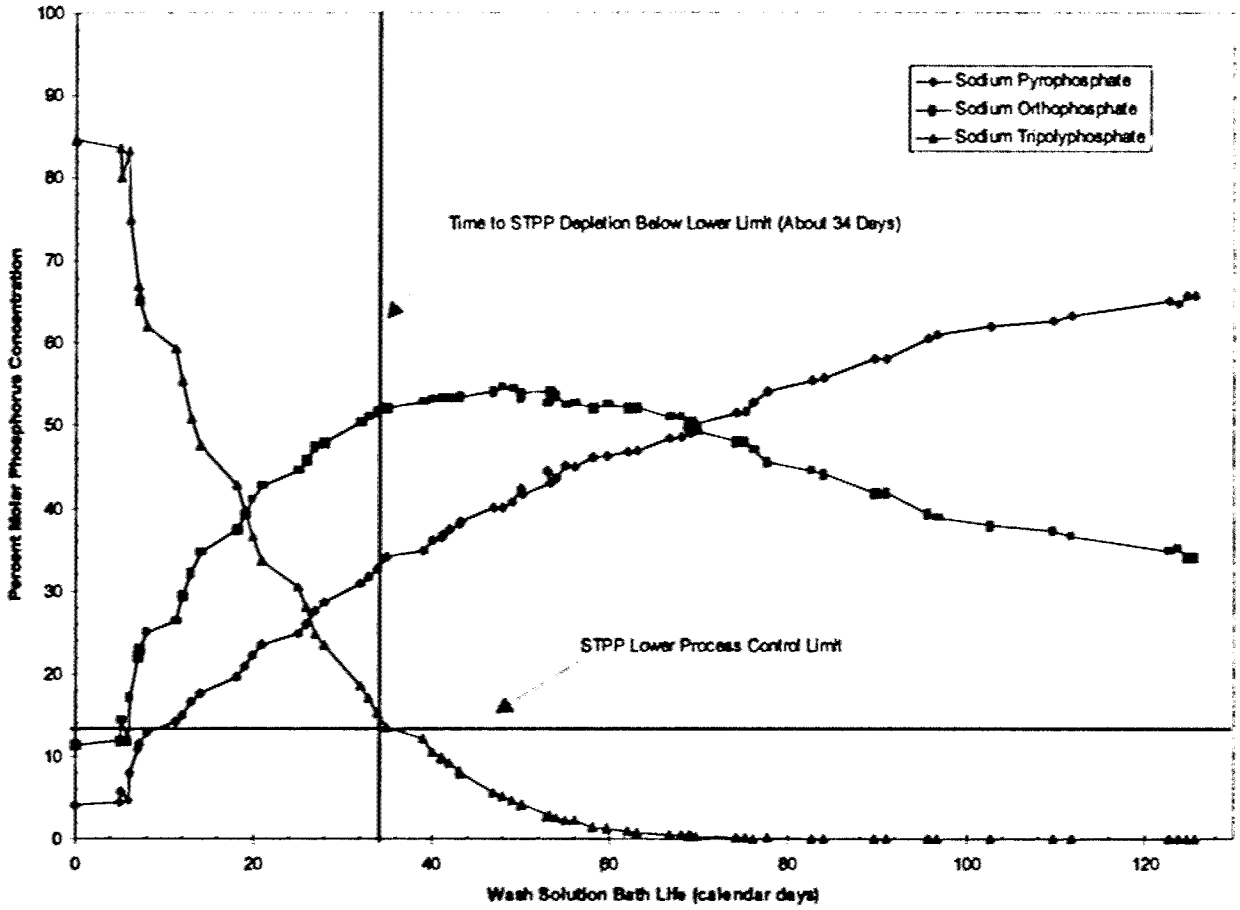


Figure 12. Phosphate Concentrations versus Full-Scale System Bath Life

Elemental Concentrations

The elemental concentration analyses are plotted in Figure 13. These concentrations are indicators of components of the alkaline cleaner of which they are elemental constituents.

Specifically:

- Silicon (Si) is a constituent of SM
- Sodium (Na) is a constituent of SM, STPP, and the anionic surfactants
- Phosphorous (P) is a constituent of the phosphates
- Potassium (K) is a constituent of KOH

The Na and P elemental concentrations remained constant in the wash solution over the life of the bath. Predictably, the K concentration increased over time because of KOH additions. The Si concentration also increased overall. This outcome is not well understood. A plausible explanation is the reintroduction into solution of sodium metasilicate contained in preexisting tank residues through pH manipulation.

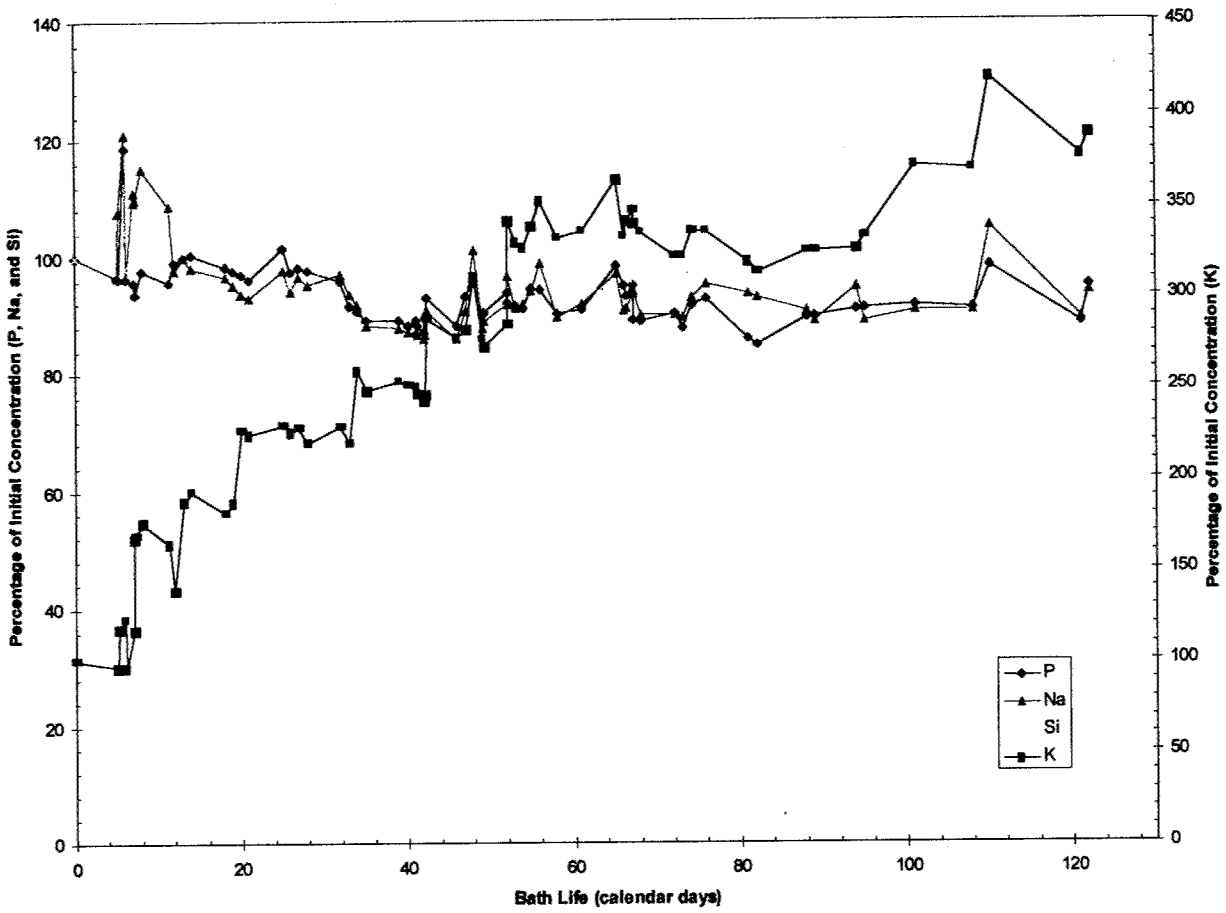


Figure 13. Elemental Concentrations versus Full-Scale System Bath Life

Figure 14 plots another relevant relationship, pH and Si element concentration vs. time. Early in the life of the bath when the pH fluctuation was greatest the Si concentration also fluctuated substantially. In fact, prior to the first KOH add back, the pH dipped to 9.39 and the Si concentration dropped close to the process control limit. This behavior is consistent with the lab study prediction of the dependency of the SM concentration on pH. Eventually, the Si concentration stabilized concurrent with pH.

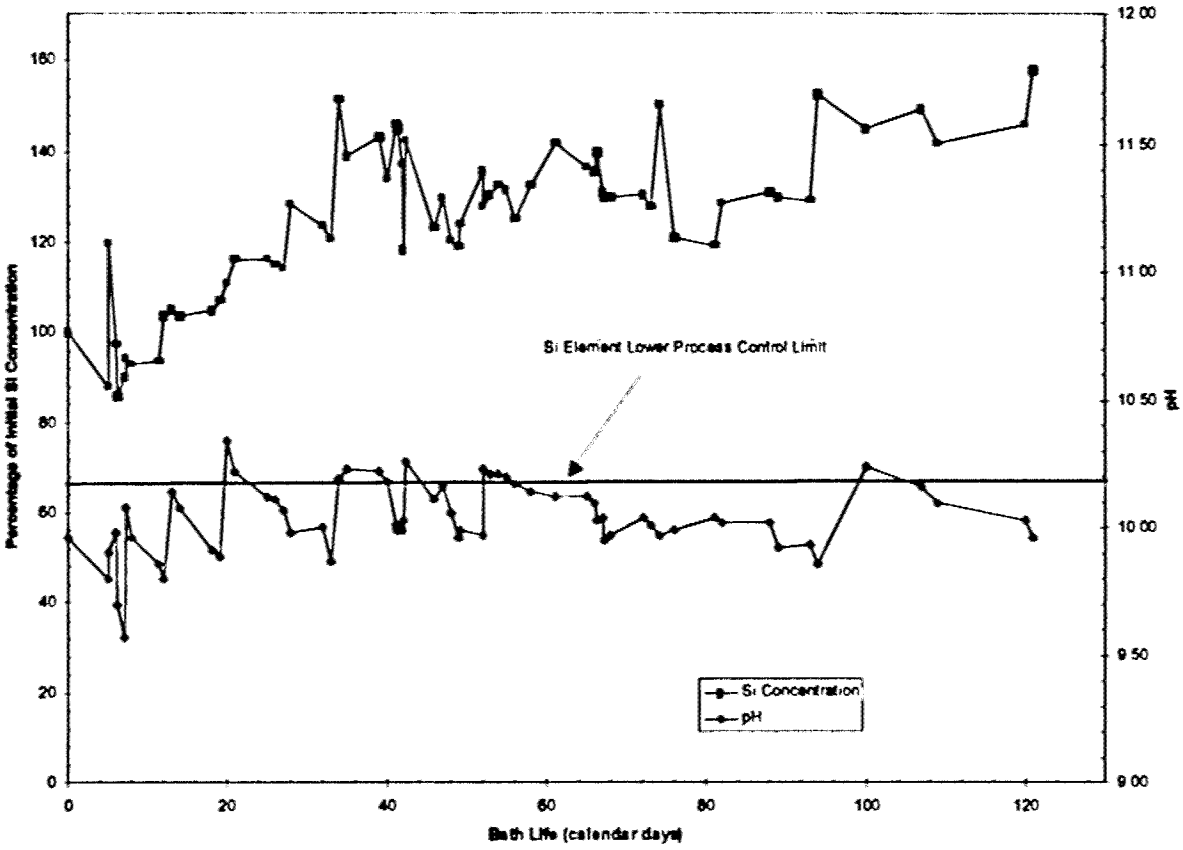


Figure 14. Si Concentration and pH versus Full-Scale System Bath Life

Surfactant Concentrations

The plot of the wash solution surfactant concentrations vs. bath life shows stable behavior of the anionic surfactant (D-8 and D-22) concentrations (Figure 15). Apparently, these constituents are thermally stable and unaffected by pH fluctuation. The nonionic surfactant (D-26 and D-30) concentrations fluctuated to a greater degree over the life of the bath. This outcome may be due to poor sampling methods. These nonionic surfactants enable the low foaming behavior by a reverse solubility mechanism. This mechanism causes the nonionic surfactants to go out of solution at higher temperatures (> 110°F). Therefore, it is crucial to operate the equipment for an extended period of time to ensure sampling of homogeneous wash solution.

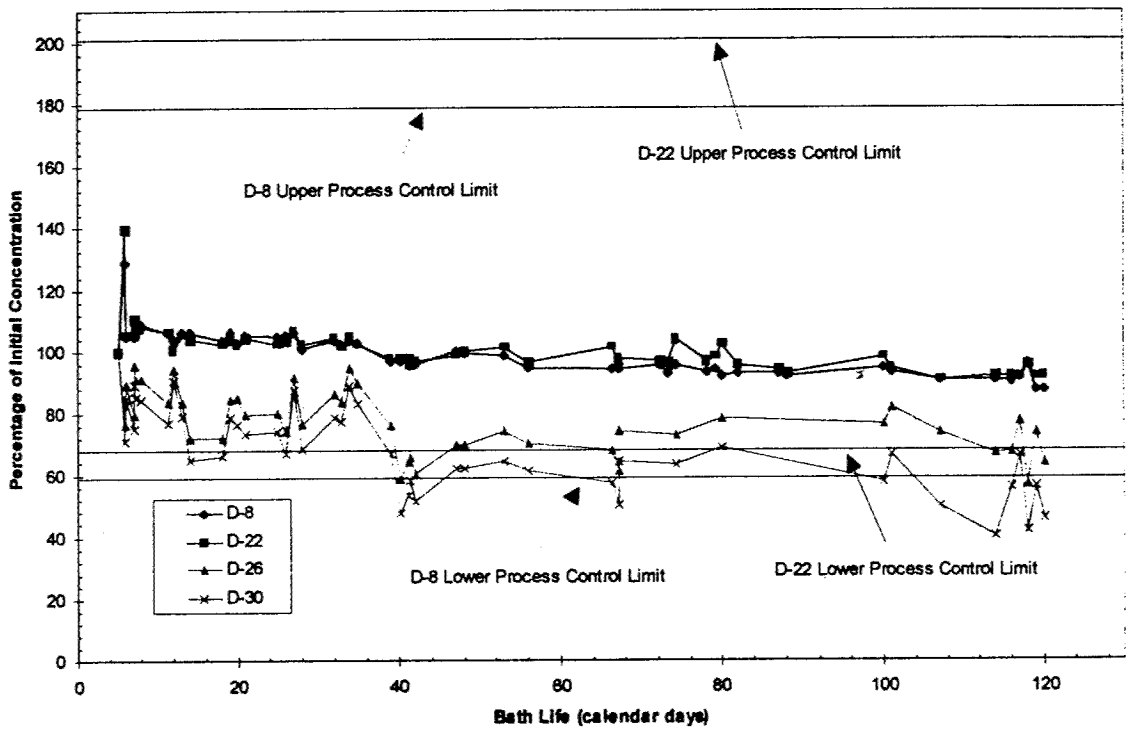


Figure 15. Surfactant Concentrations versus Full-Scale System Bath Life

Fracture Energy

The fracture energy data (aluminum/EA 913NA adhesive) are plotted in Figure 16. Fracture energy testing is sensitive to surface phenomena which affect bond strength and failure mode. Therefore, this method is effective in differentiating potential effects of wash and rinse residues on cleaning efficiency. After 57 days of bath life, the shelf-life of the lot of EA 913NA adhesive expired. Consequently, another accepted lot was introduced into the testing. In an attempt to deconfound the effect of adhesive lot switch over, double batches of specimens were cleaned, bonded, and tested as identified in the figure.

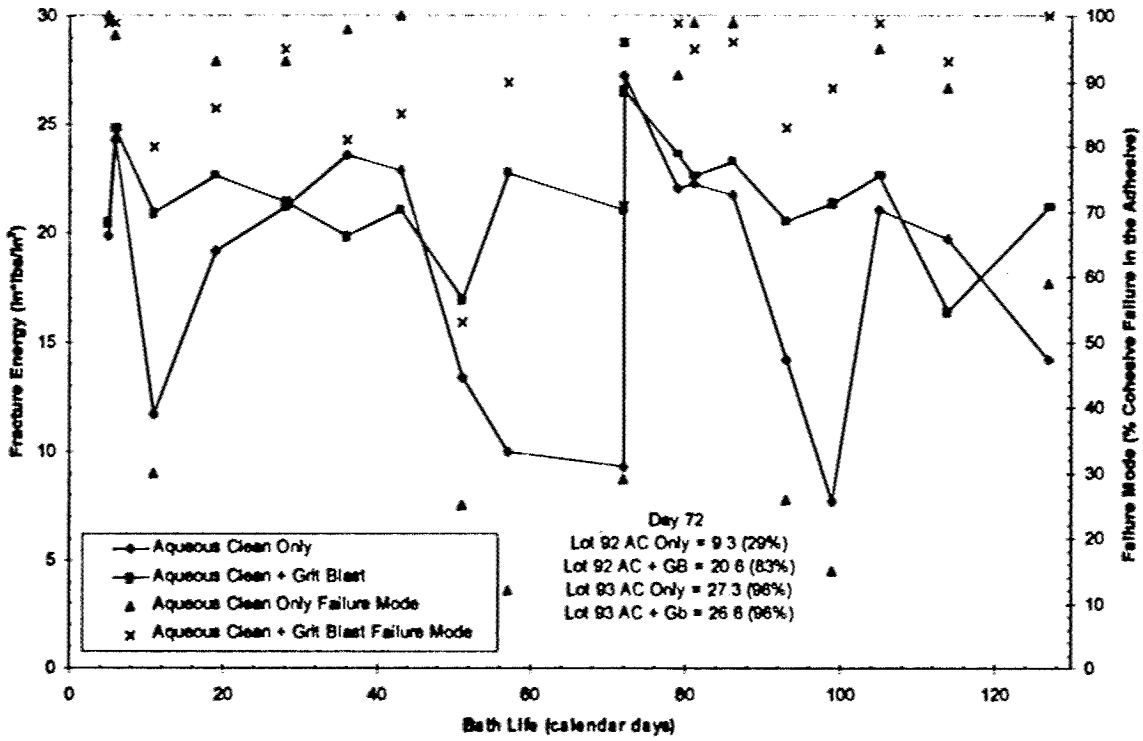


Figure 16. Fracture Energy (Aluminum/EA 913 NA Adhesive) versus Full-Scale System Bath Life

The aluminum fracture energy data (aqueous clean only) show considerable fluctuation throughout bath life. After about ten days the fracture energy dropped then recovered in subsequent sample sets. Apparently, this data point was an outlier and the cause is unknown. After about 40 days of bath life, the fracture energy began gradually declining to its lowest level at about 72 days into the bath life.

This trend corresponded to two events: (1) adhesive lot switch over and (2) increasing rinse water conductivity, which corresponds to decreasing purity. The duplicate tests showed a significant discrepancy in fracture energy due to the adhesive lot change. However, these sample sets were also rinsed with low purity rinse water. After about 100 days of bath life, the fracture energy of specimens prepared with the new adhesive lot decreased to a low level. This outcome also coincides with low purity rinse water. Apparently, there was a synergistic effect on the fracture energy caused by elapsing adhesive shelf life and lower rinse water purity. Regardless, these low values were not associated with the effects on the wash solution from KOH add back chemistry. (The steel fracture energy data did not vary as much as the aluminum data which was predictable because steel is less sensitive to surface phenomena. However, the steel fracture energy vs. bath life correlation mirrored the aluminum data.)

It is crucial to note that the gritblast step offset possible effects from ineffective rinsing because the fracture energy stabilized considerably after gritblast. These values are representative of the production surface preparation process which was designed with inherent redundancy to achieve exceptional bondline surface preparation. In this case, gritblasting compensated for a deficiency in the aqueous cleaning process (poor rinsing).

Conclusions of the KOH Add Back Study in the Full-Scale System

The chemistry properties of the wash solution in the full-scale system responded as predicted by the laboratory studies. Also, the KOH add back method effectively controlled the SM concentrations and pH in the full-scale system without negatively affecting the cleaning effectiveness of the wash solution. In addition, control of the wash solution pH through KOH add back extended the bath life to at least 120 days.

ACKNOWLEDGMENTS

The authors of this paper wish to thanks NASA and Thiokol RSRM Program Management and Engineering for their funding and sponsorship of this study.

REFERENCES

1. Kirk-Othmer, Encyclopedia of Technology, Vol. 17, Pages 452 - 453, Wiley, New York, 1991.

2. Zinder, B; Hertz, J; Oswald, H. R., Water Res., 1984, Vol. 18, No. 5, Pages 509 - 5112.

3 Wilhelm, E., The Physical Chemistry of the Silicates, University of Chicago Press, Chicago, 1954.

Advances in Environmentally Friendly Aerospace Electronic Cleaning Technologies

John Rider Kennedy, Leonard J. Beeson, Harold Klapper and W. E. Kinne
Edgewood Research, Development and Engineering Center
Aberdeen Proving Ground, MD 21010

Lawrence G. Vettraino
Science & Engineering Laboratory
McClellan Air Force Base, Sacramento, CA 95652

Richard W. Fuchs
Independent Special Processes
Frewsburg, NY 14738

Background

Chlorofluorocarbons (CFCs) are wonderful cleaning agents for electronics. They dissolve virtually anything. They easily clean the toughest grime that can contaminate a piece of electronic hardware and leave it all but spotless. Yet they will not harm even the most delicate circuitry . They are non-flammable and virtually non-toxic. The are stable and can be used over and over again. What is more they are cheap to manufacture.

Unfortunately, they also have a "minor" flaw, they deplete the ozone layer. If it were not for this one flaw, they would perhaps be the perfect answer for electronics cleaning. However, many of the CFCs which are the best solvents for electronics cleaning such as 1,1,2-trichloro 1,2,2-trifluoroethane (CFC-113), trichlorofluoromethane CFC-11, and dichlorodifluoromethane (CFC-12), as well as 1,1,1-trichloromethane (TCA) and carbon tetrachloride are classified as ozone depleting compounds (ODCs). These substances as well as several other ODCs have been banned as the result of the *Montreal Protocol*, the Clean Air Act and other treaties and legislation. The bans go beyond merely forbidding their use for cleaning purposes, in many cases, the ODCs will no longer be produced in the U.S. It is therefore imperative that users work to eliminate reliance on ODC solvents because after production ceases available supplies will become more expensive and eventually not be available at all [Verdonik].

The task of finding replacements for these outstanding cleaning agents is challenging. The alternative non-ODC solvent must not only be an effective cleaning agent, but it should otherwise environmentally acceptable. It should have a low global warming potential and not be classified as a volatile organic compound (VOC). The solvent should not be toxic nor flammable. Finally, it must be compatible with all the different types of electronic hardware. Unfortunately, many substances that would otherwise be excellent solvents for electronic cleaning must be rejected because they do not satisfy of these criteria.

Approach

The approach used in this project was to exploit to the fullest extent possible the research and development work that had already been done and to avoid the temptation to "re-invent the wheel." Further, the project sought to combine the best of the best from the available chemistries and equipment innovations to make the optimal electronic cleaning system.

Review of Cleaning Technologies

There is a wide variety of cleaning systems that could potentially replace those employing ODCs. Each system has advantages and disadvantages and what is the ideal chemistry for one cleaning application, may not be appropriate for another. Several of these cleaning chemistries were evaluated during the course of this work. The results of this investigation are briefly discussed below. The goal of this work was to find the best chemical system for cleaning electronic hardware[1].

Petroleum Based Organic Solvents

These solvents removed oils fairly well. However, they failed to remove particulate matter effectively. Another disadvantage is that these petroleum based solvents are combustible. For these reasons cleaning techniques requiring petroleum based organic solvents were rejected.

Terpene Based Organic Solvents

Terpenes are a class of organic compounds whose carbon skeletons are composed of isopentyl (isoprene) units. They are moderately toxic, flammable and are found in essential oils and plant oleoresins. Terpene based solvents often have a strong citrus and/or pine odors which have been reported by personnel working with them to be highly objectionable. However, the main objection with terpene based solvents is that they are highly combustible.

Isoproply Alcohol (IPA)

IPA effectively cleans equipment soiled with light oils, fingerprints, micron size particles and highly activated solder fluxes. However, IPA is extremely flammable. Its flash point is 12.0° C (53.6° F). Use of IPA would require specially built equipment and handling procedures. The flammability problem was the principal reason for rejection of IPA as a cleaning solvent.

Axarels

Axarels were developed by the DuPont Corporation. Pertoferm Inc. of Fernandina Beach, Florida has since purchased all rights to this line of cleaners. Axarels may be used neat or with water in what has been called a "semi-aqueous" process. The Axarels effectively remove solder fluxes and light oils. Axarels require a final water rinse. Some operators who use Axarels require explosion proof ovens and the maintenance of inert atmospheres for the drying process because of their flammability. Axarels were rejected because of the explosion proofing requirements and concerns with using water on completed electronic and electrical components.

Plasma Cleaning (RF excited gas)

This process uses fast moving argon, nitrogen and/or helium gas atoms and ions which have been excited by radio frequency electromagnetic radiation to clean surfaces. The process is carried out in a chamber which is initially evacuated to 0.1 torr. During the cleaning operation itself the pressures are 0.2 to 1.2 torr. The contamination is removed as a gas by the vacuum pumps. This process is quite slow, such that, in a time period of 20 to 30 minutes only about 0.025 mm (0.001 inch) of contamination can be removed. Efforts are underway to increase the cleaning rate as well as to investigate the effects that this process may have on solid state and wire components. There is concern that electronic components may be damaged by the high temperatures they are subjected to during the tests. Currently plasma cleaning is used for molecular level ultra cleaning. Although this process may hold promise for electronic cleaning sometime in the future, it is not yet fully developed.

Aqueous and Semi-Aqueous Systems

---

[1] The use of trade or manufactures' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

When ODCs were first banned, many workers successfully turned to aqueous or semi-aqueous cleaning systems for cleaning all metal parts from engines to printed wiring assemblies (PWAs) [Pirrotta]. Oil and particulate removal is very good if proper chemistries, equipment, and procedures are used. One problem with aqueous and semi-aqueous techniques is corrosion of steel parts, however, if special additives are used, steel corrosion problems can be controlled.

The drying method is critical. It must be well developed and carefully controlled to preclude problems with electrical components. Even if a sophisticated drying technique is used, some electrical components such as those with high voltage power supplies may not be compatible with aqueous or semi-aqueous cleaning techniques. Since the ability to clean as wide variety of electronic hardware as possible is a major goal of this effort, aqueous cleaning techniques were rejected. Although it was not a major consideration, it should be pointed out that another drawback with aqueous and semi-aqueous techniques is that drying can be time consuming. Despite these drawbacks, for many specific electronic cleaning applications, this type of technique can be very satisfactory.

Supercritical Carbon Dioxide Techniques

At standard temperatures and pressures, carbon dioxide (CO_2) is a gas. However, at high pressures above 72.9 atm., it can be compressed to a supercritical fluid. Supercritical CO_2 has been exploited as an extractive solvent in the food processing and pharmaceutical industries for several years. One of the uses of supercritical CO_2 has been the decaffeination of coffee and tea [Phelps]. Research has been underway since the early 1980s to investigate the use of supercritical CO_2 as a solvent for the polymerization of hydrocarbon monomers. Since the phase-out of the ODC solvents, there has been efforts to investigate the potential of supercritical CO_2 as a solvent for precision cleaning [Darwin].

Unfortunately, the use of supercritical CO_2 has not proven to be totally satisfactory for precision cleaning [Darwin]. Carbon dioxide, whether it is in the supercritical or liquid state, is a relatively weak solvent for most contaminants. Higher molecular-weight molecules such as heavy oils, greases, waxes, and polymers are generally insoluble in CO_2 [Beckman]. Therefore CO_2 would be incapable of removing many of the contaminants that would typically be expected to be found on electronic equipment returned from the field. Even when compressed to the extremely high pressures (typically 1200 psi or higher) to form the supercritical state, CO_2 has a weaker solvency power than hydrocarbon solvents [Rotman]. One of the reasons for the weak solvating power of supercritical CO_2 is that in the supercritical state, its viscosity, surface tension, and diffusion properties are more characteristic of a gas than a liquid. Thus, unlike a liquid, it is unable to transfer mechanical energy within the system to enhance its cleaning efficiency. This property generally rules out the use of mechanical enhancement devices in supercritical systems to improve cleaning capability [Darwin].

Another potential disadvantage of supercritical CO_2 processes is that since they operate at pressures in the range of 1,200 psi (81.6 atm), the supporting equipment will tend to have greater weights and footprints than equipment that operates at more conventional pressures.

The fact that CO_2 is environmentally safe and will always be readily obtainable is a major advantage. There are active research and development programs underway find ways to overcome the various drawbacks associated with CO_2 based cleaning. In time, practical CO_2 based cleaning systems for electronics may eventually be developed; however, because of the time constraints of this project, CO_2 based technology was rejected.

Advanced Vapor Degreasing (AVD)

Before the banning of ODCs, conventional vapor degreasing using solvents such as CFC-113 were widely used for the cleaning of electronic items and other sensitive equipment. This technique was effective, efficient and economical. However, when the ODCs were banned, the best solvents for vapor degreasing were no longer available. This severely limited the applicability of vapor degreasing as a cleaning technique.

As soon as the ODC solvents were banned, several commercial firms began intense research and development projects to find suitable replacements. One of the first solvents developed to replace the banned ODCs was the perfluorocarbons (PFCs). 3M 5060™ is an example of a perfluorocarbon. By themselves PFCs have minimal cleaning ability. The next generation of ODC replacement solvents are even more effective. The DuPont HFC™ (hydrofluorocarbons) and 3M HFE™ (hydrofluoroethers) families of products are examples of the improved AVD solvents. By themselves neither HFCs nor HFEs clean as well as CFC-113; however, their cleaning ability is greatly enhanced by adding a surfactant such as Pertoferm Solvating Agent 18™, 19™, 24™ or 70™ or by creating azeotropic solvent systems by adding such compounds as methanol or trans-1,2-dichloroethylene (trans DCE). One drawback of HFCs and HFEs is that they are relatively expensive. Although HFCs and HFEs are not ozone-depleting, vapor degreaser apparatuses that use these solvents should be modified to contain or reduce the loss of these expensive compounds. HFCs, HFEs, and their mixtures with the solvating agents and their azeotropes, are non-flammable.

The many desirable properties of HFC and HFE solvents and their mixtures with solvating agents have lead to their selection as the most desirable chemistry for this project. Investigation is still under way to determine which solvent and solvating agent is the best. It is probable that the specific solvent and solvating agent and the specific ratios used will depend upon the particular application.

Conceptually, the vapor degreaser is a relatively simple apparatus. A vapor degreaser may typically consist of a "boil" or wash sump, a rinse sump and a rapid dry area. Located above the boil and rinse sumps is a vapor zone and above the vapor zone a freeboard area. The freeboard area is kept cooled by chilling coils. The cooled freeboard area prevents the solvents in the vapor zone from escaping into the atmosphere. Advanced vapor degreasers (AVDs) have larger freeboard areas than conventional vapor degreasers. The larger freeboard area further enhances retention of solvents and makes the apparatus more environmentally friendly.

If the cleaning process is using a solvent and surfactant, the boil sump would contain a mixture of solvent and surfactant while the rinse sump would contain pure solvent. For example, if a process were using Vertrel XF ($CF_3CHFCHFCF_2CF_3$) solvent and Petroferm SA70 surfactant, the boil sump may typically contain a mixture of 75% Vertrel and 25% SA 70 while the rinse sump would contain pure Vertrel. The solvents used in the vapor degreasing process are fairly low boiling. The Vertrel XF and Petroferm SA 70 mixture boils at about 65° C (140° F) while the pure Vertrel boils at 55° C (131° F). These temperatures are sufficiently low so as not to cause damage to electronic hardware.

An item undergoing cleaning by the AVD process enters the apparatus and is lowed into the vapor zone. Being bathed in the solvent vapors not only helps clean the item, but brings it gently up to near the temperature of the liquid in the boil sump. The item is then further lowed into the boil sump. While in the boil sump, cleaning may be enhanced by ultrasonics and/or by under surface liquid sprayers. After being in the boil sump, the item is raised back into the vapor zone moved over and lowered into the rinse sump. Once the item is rinsed, it is raised out of the rinse sump and into the quick dry zone. When the item is dried it is removed from the AVD and the cleaning process is completed.

The AVD process is extremely flexible. The amount of time spent in each station can be varied by the operator. Whether or not the sprayers are used and whether or not the ultrasonics is used is up to the operator. The power level of the ultrasonics is controlled by the operator. In short, the details of the AVD process can be optimized for the maximum cleaning and the minimum time.

After investigating a wide variety of vapor degreaser technology, it was found that no "off the shelf" machine exactly suited all of our requirements. In order to produce a prototype machine that would be capable of carrying out anticipated cleaning procedures and methods, an initial design was selected and a machine special ordered from Crest Ultrasonics Incorporated, Trenton, NJ. In addition to a "standard" vapor degreaser system, the prototype has the following features: 40 gallon per minute impinging spray under immersion nozzle system, a hand held sprayer, and a microstill separator. The capability to use

ultrasonics is in both the rinse and boil sumps The frequency of the ultrasonics is 40 kHz in the boil sump and 68 kHz in the rinse sump. The maximum power level of the ultrasonics is 1000 W in both sumps. The prototype AVD also has a superheat drying area and semi-automatic parts handling. In addition, the prototype system has an air lock vestibule to move equipment in and out of the degreaser and provisions to vent the system at slightly negative air pressure relative to room pressure. These two features ensure maximum vapor containment and minimize exposure of the operators to the chemical used in the solvent/surfactant system. A diagram of the prototype vapor degreaser which was fabricated by Crest Ultrasonics is shown in Figure 1.

Performance Testing

For the series of tests described here, Vertrel XF and SA 70 were used. The boil sump contained about 75% Vertrel XF and 25% SA 70 while the rinse sump was filled pure Vertrel XF. Preliminary testing had shown that the Vertrel XF had very good potential for general electronics cleaning. The HFE 7100 and SA 70 system was also judged to have a good potential for electronics cleaning and it is expected that this chemistry will also be evaluated in the future. Other cleaning agents of interest include various azeotrope systems such as Vertrel XM (Vertrel XF/methanol), Vertrel XE (Vertrel XF/trans DCE), Vertrel SMT (Vertrel XF/trans DCE/methanol) and Vertrel XSi (Vertrel XF/hexamethyldisiloxane). The 3M Corporation also markets azeotropic systems that show promise. These include 3M HFE-71 DE (3M HFE-7100/trans-DCE) and 3M HFE-71 DA (3M HFE-7100/trans-DCE/ethanol). Some of these other solvent systems will also be evaluated in the future.

The performance of AVD cleaning was tested on a variety of different items including conformally coated bare circuit boards, PWAs with an inverted amplifier circuit, the power supply and PWAs from a Hewlett-Packard 1000 A600 computer and an automotive alternator.

Conformally Coated Coupon Circuit Boards

In addition to determining cleaning efficacy, it is important to have an understanding of the computability of the cleaning solvents with the conformal coatings commonly used on military and industrial PWAs. To test this, 5" X 1" bare circuit boards were obtained with commercial conformal coatings. Five different types of conformal coatings tested; type AR (acrylic), type ER (epoxy), type SR (silicone), type UR (urethane), and type XY (parylene). Types AR, ER, SR, and UR were coated by spraying while type XY was coated by vapor deposition. All of the conformal coatings met the specifications of MIL-I-46058C.

In first series of tests, a non-conformal coated board, a type AR coated board, a type ER coated board, a type SR coated board, a type UR coated board, and a type XY coated board were heavily "contaminated" using one of three specially prepared mixtures. The mixtures were SAE 30 non-detergent (ND) motor oil and graphite, SAE 30 ND motor oil and brass flake, or SAE 30 ND motor oil and Arizona road dust. SAE 30 ND motor oil was used because it represents a very severe grime that may be encountered in the field. Incidentally, SAE 30 motor oil is fairly close in composition to SGF 2 fog oil which is one of the most common military smoke agents used in battlefield obscuration. A non-detergent motor oil was to avoid extraneous detergents that could confuse the test results. Graphite was used because it seems to be ubiquitous around military equipment and would certainly be present if the equipment happened to be in the proximity of a fire. Also, since graphite is conductive, if the equipment were by chance to be contaminated with graphite, performance of the contaminated circuit could be adversely affected. Brass flake was used to simulate metal shavings which could find its way onto military electronic hardware. The graphite flake and brass flake was 4-7 μ in diameter and about 0.1 μ thick. Arizona road dust is a commercially available material and is frequently used to test automotive filters. It is extremely fine and can find its way into almost any cabinet and onto electronic hardware. Arizona road dust was used to simulate the soil types found in some of the world's desert regions.

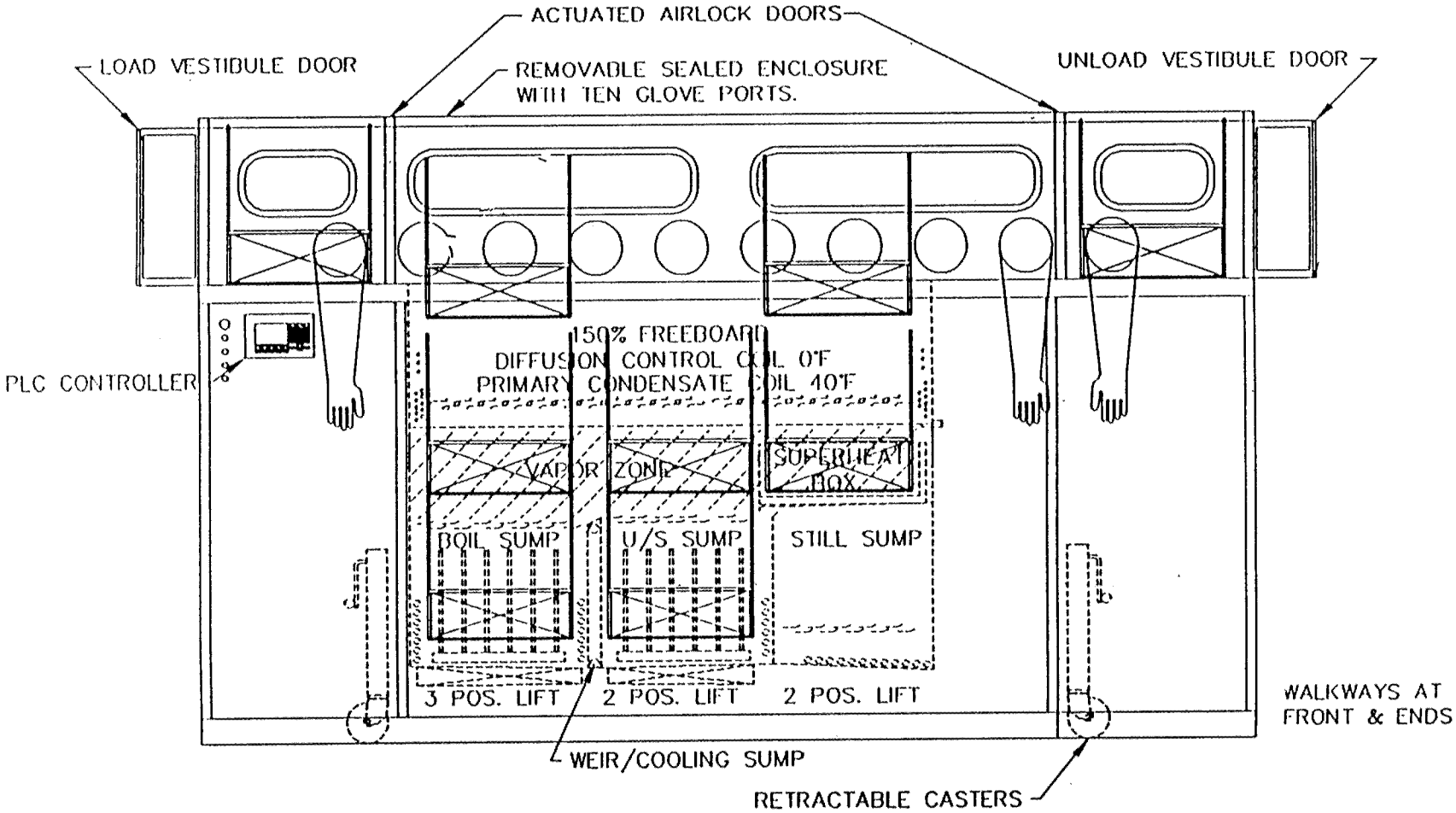


Figure 1. Prototype Vapor Degreaser.

When cleaning something, one of the questions that must be answered is: How clean is clean? On one extreme, is cleaning something just well enough for it to function satisfactory? On the other hand, does it need to be clean beyond our ability to detect the contaminant in question? The answers to these questions depend to a large extent on what is being cleaned. It makes a difference whether one is cleaning a piece of automobile hardware such as an alternator or a piece of medical equipment that will go into a human body. For many things, however, the matter is open to debate.

For the coupon circuit board cleaning, cleanliness was determined visually. A coupon was considered to be clean if after going through the cleaning process, no foreign matter could be detected visually. The materials used for contamination, especially the graphite, are visually detectable in very small amounts probably less than 0.001 g. Therefore, a slight gray color on the yellow coupon board would imply the coupon was less than totally clean, although such a level of cleaning actually be satisfactory for many practical purposes. Visually judging how clean a coupon is necessarily subjective.

As mentioned previously, the prototype AVD machine is very versatile. The time spent in the vapor zone, boil sump, rinse sump, and quick dry zone is controlled by the operator. Whether or not the ultrasonics is used and the power level of the ultrasonics is determined by the operator. The operator controls the spray under immersion nozzle system. The operator also has control of the temperature of the liquid in the boil sump, the rinse sump and the quick dry zone. Although the upper temperature limit of the sumps is dependent upon the particular solvents and solvent/surfactant ratios being used. In this series of tests, with 73% Vertrel XF and 27% SA-70 in the boil sump and 100% Vertrel XF in the rinse sump, the maximum temperatures were 62° C (143° F) in the boil sump and 55° C (130° F). By varying the various parameters the operator can design a cleaning procedure that will yield the best results. One of the objectives of these tests is to determine what the best cleaning algorithm is for a given cleaning problem.

During the conformally coated coupon cleaning tests an attempt was made to clean coupons without using ultrasonics in either the boil or rinse sumps but with boiling in the boil sump and under surface sprayers turned on in both sumps. The amount of time the coupons were in the boil and rinse sumps was about 5 or 6 minutes. It was found that although the oil was completely removed as well as the vast majority of the graphite or brass flake, graphite (gray colored areas) or brass flake (brass colored areas) was still evident on the ER, SR, and UR coated boards after the cleaning attempts. The uncoated and XY boards were found to be somewhat cleaner, but some graphite or brass could be detected. The AR coated board was found to be clean. Apparently, all of the boards with Arizona road dust were clean although in very small amounts Arizona road dust would have been difficult to detect visually.

It was noted that the AR conformal coating was removed by the cleaning process. This was to be expected as acrylic conformal coatings are readily soluable in many organic solvents. In fact, AR coatings are often selected because they are easily removed by organic solvents. It was also observed that the SR conformal coatings blistered, had been softened and had swollen as a result of the cleaning process. It was also noticed that the SR board had been quite discolored by the graphite or brass flake which was used to contaminate the board. Based on the compatibility tables published by the manufactures of Vertrel XF (DuPont) and SA-70 (Petroferm), it was concluded that the silicon conformal coating was probably affected by the SA-70 solvating agent. The uncoated boards and the ER, UR and XY coated boards, were not affected by this or any of the other cleaning procedures used in this work. Therefore, it appears that the Vertrel XF/SA-70 chemistry is completely compatible with ER, UR, and XY conformal coatings as well as uncoated circuit boards.

The same boards that had been through were then put through the same procedure again, however, this time ultrasonics was used in both sumps. The uncoated and XY coated boards come out very clean with no graphite or brass visible. The ER and UR coated boards seemed to be cleaner; however, minute amounts graphite or brass were observed still clinging to the boards.

It was clear that the most difficult boards to clean (other than the SR coated boards) would be the ER and UR coated boards. Therefore, several series of tests were run concentrating on ER and UR coated

boards. It was suspected that the boiling action and under surface sprayers may have been diminishing the ultrasonic cleaning power, so procedures were tested in which the boiling action and sprayers were turned off while the ultrasonics were turned on. Also it was suspected that too much dwell time in the initial vapor phase may not have been helpful, so there were procedures in which the part being cleaned was only in the vapor zone long enough for the condensation to stop forming or for about two minutes.

After trying a few different cleaning algorithms, it was found that the following procedure was able to produce very satisfactory results:

In vapor zone:

Until condensation stops; approximately 35 seconds.

In boil sump:

Turn off heat to stop boiling, turn off sprayers, turn on ultrasonics for one minute.
Turn on heat and resume boiling and turn on sprayers, no ultrasonics for two minutes.
Turn off heat to stop boiling and turn off sprayers turn on ultrasonics for one minute.
Turn on heat and resume boiling and turn on sprayers and ultrasonics for two minutes.

In the rinse sump:

Heat on, sprayers on, ultrasonics on for 5 minutes.

Dry zone 5 minutes.

Obviously, any number of other algorithms could have also produced good results. In all probability, the actions of the boiling, under surface sprayers, and ultrasonics all contributed to the overall cleansing of the coupons. It is apparent that it helps to have a period of time in which the ultrasonics are allowed to work without the boiling and without the sprayers.

Inverted Amplifier PWA

Very heavy contamination can affect the functioning of a PWA, especially if the contamination is with a conductive material such as graphite. In order to test if a PWA whose functioning has been affected by heavy contamination can be restored to normal functioning by AVD cleaning, PWAs containing an inverted amplifier circuit were heavily contaminated using either graphite or brass flake. The PWA used were specially fabricated by Entropic Systems Incorporated of Woburn, MA. The diagram of the circuit is shown in Figure 2. The PWAs were not conformally coated. The boards were contaminated using a cotton tipped applicator and applying heavy coat of either graphite or brass flake. Five boards were contaminated with each material. The boards contaminated with the brass flake performed normally despite contamination; however, three of the PWAs contaminated with graphite showed malfunctions. It should be noted that the PWAs used in this test are quite robust and not as sensitive to contamination as other PWAs might be. All of the PWAs were cleaned by the AVD using ultrasonics, boiling, and under surface sprayers. After cleaning all of the boards performed normally. Therefore, AVD cleaning procedures can restore heavily contaminated boards, whose performance has been affected, to normal operation.

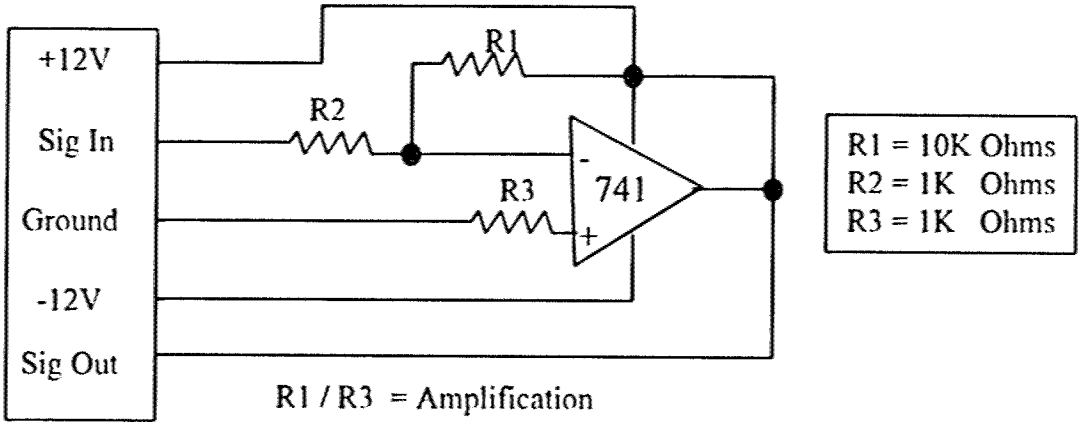


Figure 2. Circuit diagram of inverting amplifier circuit.

Test Cleaning of "Field" Contaminated Equipment

The best test subjects to test cleaning ability, of course, would be actual equipment that got dirty from normal day in and day out usage. A Hewlett-Packard 1000 A600 computer that had been used heavily for several years and had been in storage for several years more was located and used as a test subject. Figure 3 shows the power supply module as it appeared after being removed from the computer and before it was cleaned. Figure 4 shows the power supply module after cleaning. The procedure used was

In vapor zone:

Until condensation stopped, 1.5 minutes.

In boil sump:

Turn off heat to stop boiling and turn off sprayers. Ultrasonics for 2 minutes.
Turn on heat and resume boiling and turn on sprayers. Ultrasonics for 1 minute.
Turn off heat to stop boiling and turn off sprayers. Ultrasonics for 1 minute.
Turn on heat and resume boiling and turn on sprayers. Ultrasonics for 2 minutes.

In the rinse sump:

Heat on, sprayers on. Ultrasonics for 1 minute.
Sprayers off, heat on. Ultrasonics for 2 minutes.
Sprayers on, heat on. Ultrasonics for 2minutes.

In the dry zone:

5 minutes.

The circuit boards from the Hewlett-Packard 1000 A600 computer were also cleaned using the same procedure. After the power supply module and circuit boards were cleaned, they were reinstalled into the computer. The computer operated normally with no apparent faults.

The AVD was also used to clean a 12 volt alternator from a Toyota light truck. The truck was a privately owned vehicle and the alternator had been in use for several years during which time it had become very heavily soiled. The cleaning procedure used was similar to the one used for the Hewlett-Packard equipment. Figures 5 and 6 are before cleaning and after cleaning, respectively.

Discussion

Although several chemistries for AVD cleaning have been developed over the last couple of years, the Vertrel XF/SA-70 system was used exclusively in this work. Vertrel XF is the solvent and SA-70 acts as a surfactant. For the cleaning described in this work, SA-70 is essential to effect good cleaning.

Vertrel XF alone will not do the job. The Vertrel XF/SA-70 is compatible with uncoated boards and types UR, ER, and XY conformal coatings. This solvent system completely removes type AR coating and causes blistering and softening of type SR conformal coating.

The cleaning procedures tested in this work used relatively brief dwell times (five minutes or less) in the boil and rinse sumps. For dwell times this brief, the use of ultrasonics was necessary for particulate removal. It was also found that the ultrasonics is more effective if the under surface sprayers are turned off and if there is no boiling action in the sump during sonification. Petroleum oils and probably other non-particulate contaminants can be removed without use of ultrasonics.

The AVD tested in this work uses 40 kHz in the boil sump and 68 kHz in the rinse sump. The higher frequency generates smaller bubbles and is presumably more effective for removing smaller particles. Having different frequencies in the boil and rinse sumps seems to be a desirable feature.

One concern about any cleaning system must be the operating cost. The AVD used in these tests was a specially ordered prototype with a wide range of special features. Its cost was around $100 K. The primary solvent used was Vertrel XF. Its cost is currently around $247 per gallon. The cost of SA-70 is around $52 per gallon. The AVD used in these tests requires about 70 gallons of Vertrel XF and 14 gallons of SA-70. Therefore the cost of the initial charging the AVD with solvent and surfactant is a little over $18,000. Although this seems to be expensive it must be kept in mind that the solvent and surfactant can be used time and again and that due to the design of the AVD the loss rate from evaporation and carryout is quite small. A cost analysis of using this AVD technology versus conventional electronics techniques (primarily by hand) at a large military electronics repair depot has been conducted. The results of this analysis indicates that despite the large capital cost of buying the AVD and high chemical costs, replacing conventional cleaning with AVD cleaning is not only economically viable, by will result in cost savings.

Plans for future work include evaluating other solvent systems such as 3M HFE-7100/SA-70 and the azeotropic Vertrel systems such as Vertrel XMS. This work will be initially carried out on the laboratory scale. Other planned work includes further testing on actual hardware. The ultimate goal will be to optimize the chemistries and procedures to maximize cleaning efficacy.

Conclusions

Advanced vapor degreasing coupled with newly developed non-ozone depleting solvents and surfactants has been suggested as an answer to the need for environmentally friendly electronics cleaning. In this work, AVD technology and a non-ozone depleting solvent, Vertrel XF, and a non-ozone depleting surfactant, Petroferm SA-70, has been evaluated for electronics cleaning. Based on the results of this evaluation, it is concluded that AVD technology using non-ozone depleting chemicals definitely has the potential provide to users with an efficient method of cleaning a wide variety of electronic hardware.

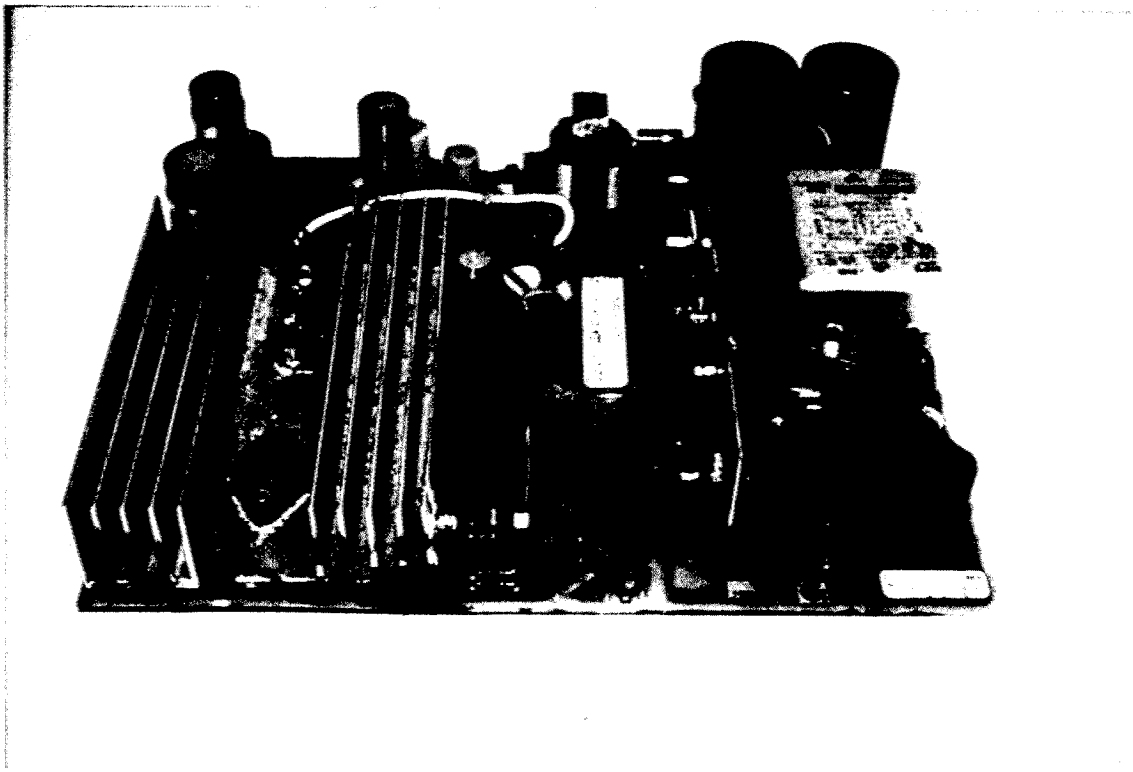


Figure 3. Power supply from a Hewlett-Packard 1000 A 600 computer before cleaning.

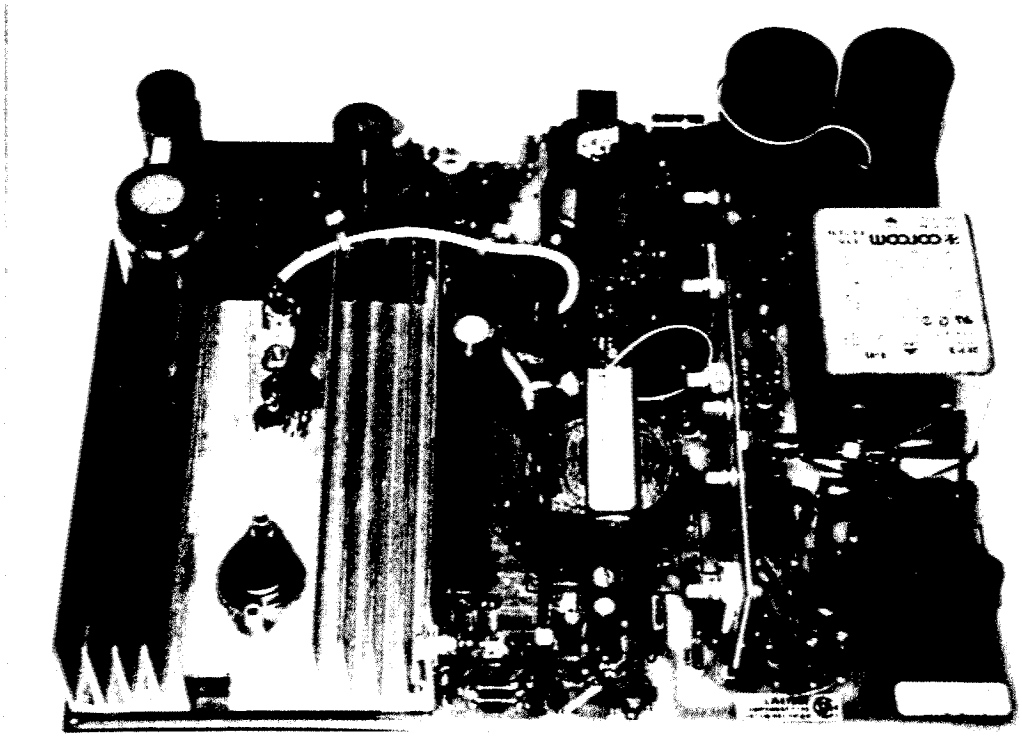


Figure 4. Power supply from a Hewlett-Packard 1000 A600 computer after cleaning by advanced vapor degreaser.

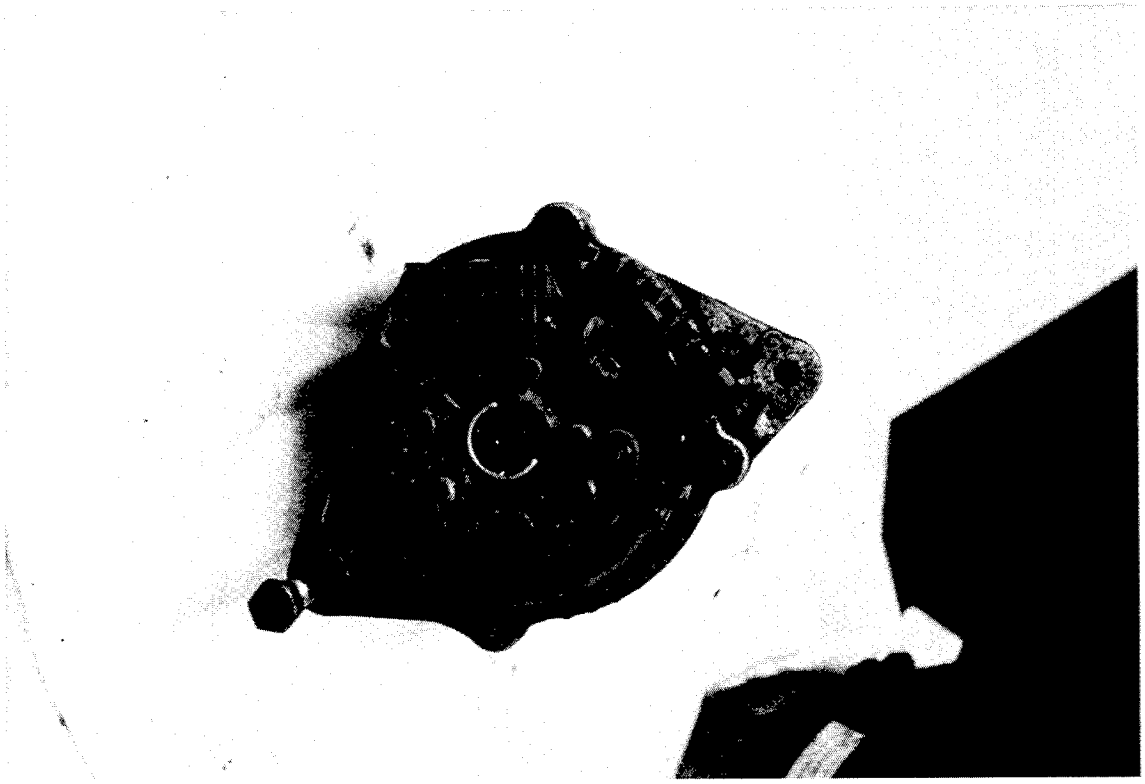


Figure 5. Twelve volt automotive alternator before cleaning.

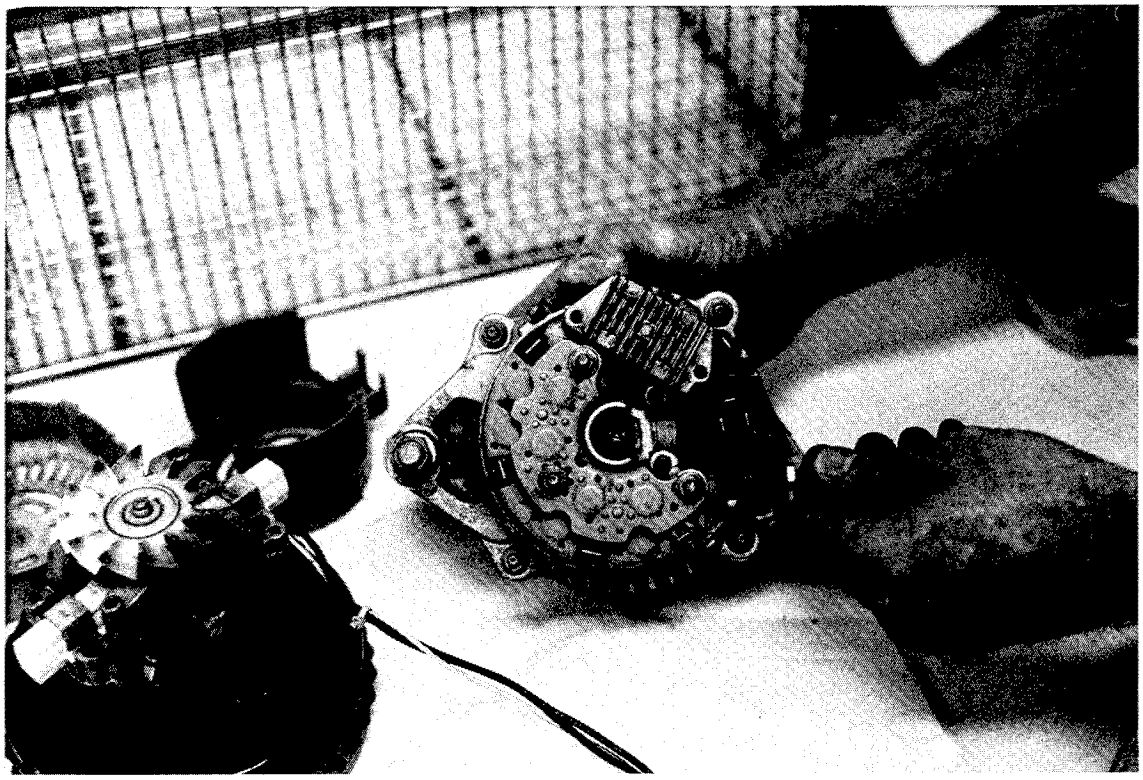


Figure 6. Twelve volt automotive alternator after cleaning by advanced vapor degreaser.

References

Beckman, E. J., *Science* **271**, (1998), pp.613-614.

Darwin, Charles H. and Lienhart, B.; *International Conference on Ozone Protection Technologies Conference Proceedings*, "High Performance Metal Cleaning Using Liquid CO_2 and Surfactants," 12-13 November 1997, Baltimore, MD, The U.S. Environmental Protection Agency, Washington, DC.

Darwin, Charles H. and Liehart, R. Bradley; "Surfactant Solutions Advance Liquid CO_2 Cleaning Potential," *Precision Cleaning*, Vol. VI, No. 2, February 1998, pp.28-29.

Kennedy, J. R.; Kinne, W. E.; Vettraino, L. G.; and Fuchs, R. W.; *Advanced Environmentally Friendly Cleaning*, 23rd Environmental Symposium and Exhibition Proceedings, 7-10 April 1997, New Orleans, LA, American Society for Defense Preparedness, Arlington, VA.

Phelps, C. L.; Smart, N. G.; and Wai, C. M.; *J. Chem. Educ.*, **73**, 1996, pp. 1163-1168.

Pirrotta, Richard D., *23rd Environmental Symposium and Exhibition Proceedings*, "Case Studies of Successful Implementations of Aqueous Cleaning Systems", 7-10 April 1997, New Orleans, LA, American Defense Preparedness Association/National Security Industrial Association, Washington, DC.

Rotman, D., "CO_2 Challenges Organic Solvents," *Chemical Week*, January 1-8, 1997, p. 41.

Verdonik, Danniel P. and Bush, Thomas A., *Strategic Guidance and Planning for Eliminating Ozone-Depleting Chemicals from U.S. Army Applications*, U.S. Army Acquisition Pollution Prevention Support Office, 1995, p. i-1-i-2, III-2.

Evaluation of Solvent Alternatives for Cleaning of Oxygen Systems

Harold Beeson
NASA Johnson Space Center
White Sands Test Facility
Las Cruces, New Mexico

Paul Biesinger and Rafael Delgado
AlliedSignal Technical Services Corp. Team
White Sands Test Facility
Las Cruces, New Mexico

Neil Antin
Naval Sea Systems Command, CO3L
Arlington, Virginia

The NASA White Sands Test Facility (WSTF) in a joint program with the Naval Sea Systems Command has evaluated a number of solvents as alternatives to the use of chlorofluorocarbons currently utilized for cleaning of oxygen systems. Particular attention has been given to the cleaning of gauges and instrumentation used in oxygen service, since there have been no identified aqueous alternatives. The requirements identified as selection criteria, include toxicity, physical properties consistent with application, flammability, oxygen compatibility, and cleaning ability. This paper provides a summary of results and recommendations for solvents evaluated to date.

ALTERNATIVE SOLVENTS

While many evaluations of alternative aqueous processes 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 NAVSEA, 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

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, hydrochlorofluorocarbons, hydrofluorocarbons, and hydrofluoroethers. 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 combined concerns related to toxicity and flammability. In addition not all solvents tested for oxygen compatibility were evaluated for cleaning efffectiveness, particularly if the solvent showed gross incompatibility with oxygen.

Table 1. Solvents Studied and their Physical Properties

Solvent	Boiling Point (°C)	Threshold Limit Value (ppm)	Flammability
PCE	121	25[a]	No
TCE	87	50[a]	Yes
Ethanol	78	1000[a]	Yes
AK 225®	53	50[b]	No
HCFC 141b	32	500	Yes[c]
HFE 7100®	60	600[b]	No
Vertrel MCA®	39	200[b]	No[d]
Vetrel XF®	48	200[b]	No
HFE 71DE®	41	200[b]	No[d]
OS-10®	100	200[b]	Yes
ABZOL®	71	100[b]	Yes[c]
EnSolve®	69	100[b]	Yes[c]
CFC 113	48	1000[a]	No

[a] *Guide to Occupational Exposure Values*, American Conference of Governmental Industrial Hygienists, 1994.

[b] TLV data provided by manufacturer.

[c] Flammability limits have been established, but Material does not have a flash point.

[d] Flammability of the mixture has not been determined, and it has no flash point.

® AK 225 is a registered tradename of Asahai Glass America, Vertrel XF and Vertrel MCA are registered tradenames of E.I. DuPont Nemours Company, HFE 7100 and HFE 71DE are registered tradenames of 3M Company, OS-10 is a registered tradename of Dow Corning Company, ABZOL is a registered tradename of Albemarle Corporation, and EnSolve is a registered tradename of EnviroTech International, Inc..

The solvents were evaluated using a variety of gauges and instrumentation types including 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 Spinestic 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 the nonvolatile residue (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 because 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 other cleaning operations in which solvents are used to flush components where mechanical action is present and the HFE 7100 would be expected to perform well. Also of note is the increased cleaning efficiency that is obtained when the neat solvent is blended with 1,2 Transdichloroethylene (DCE), compare Vertrel XF with Vertrel MCA and HFE 7100

with HFE 71DE. The addition of DCE increases the solvent efficiency by 10 to 20 percent; however the DCE may increase the toxicity of the solvent and increases the flammability of the solvent in an oxygen system(see below).

Table 2. Average Solvent Cleaning Efficiencies

Solvent	CE Gauges	OE Gauges	Average
Tetrachloroethylene	74	97	87
Ethanol	82	86	85
Trichloroethylene	84	98	92
AK 225	100	98	99
HCFC 141b	96	98	97
HFE 71DE	99	98	98
HFE 7100	93	91	92
Vertrel MCA	98	98	98
Vertrel XF	80	88	84
AK-225S	96	96	96
CFC 113	99	95	97

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 high-pressure 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. In many instances flammability has been evaluated based on results obtained in air; however, oxygen enriched environments are known to increase the flammability of materials including rendering solvents, which would in air be considered nonflammable, flammable.

The AIT and Ambient Pressure Liquid Oxygen (LOX) Impact Sensitivity was determined for the test solvents according to the procedures described in ASTM G-72 and ASTM D 2512, respectively. The AIT for each solvent was determined at 50 and 2000 psig and the purge procedure was modified so that the solvents would not evaporate during the purge. The LOX impact testing was accomplished using a stainless steel insert and the standard grease cup which provides a solvent thickness of .050 inch under the impact striker pin and provides maximum confinement of the sample during the impact event. The results for all the solvents tested are given in Table 3, while specific test results for HCFC 141b are given in Table 4. In all tests the neat solvent was tested and not panels which had been rinsed with the solvent and allowed to dry since this procedure only test the panels reactivity in oxygen and not the solvent's.

An AIT was observed for PCE, TCE, Vertrel MCA, Vetrel XF, HFE 7200, HFE 71DE, OS-10, ABZOL, and EnSolve, 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 AIT was measured (Table 4). The AIT recorded for TCE is low compared to other compounds typically considered oxygen compatible. The AIT determined for solvents that contain DCE seems to be associated with the DCE itself since the AITs are all within the same range for the data presented. 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 3. AIT Results for Solvents Tested

Solvent	AIT @50 psi (°C)	AIT @2000 psi (°C)	LOX Impact[1]
CFC 113	NI	NI	NO
Tetrachloroethylene	136	161	NO
Trichloroethylene	108	77	NO
HFE 71DE	NI	157	YES
Vertrel MCA	NI	167	NO
HFE 7100	NI	NI	NO
Vertrel XF	NI	241	NO
HCFC 141b[2]	NI	NI	NO
HFE 7200	NI	262	NO
OS-10	125	224	Yes
ABZOL VG & EnSolve	102	185	Yes
HCFC 225	NI	NI	NO

NI = No Ignition (did not ignite at maximum test temperature of 450 °C)
[1] Reactions in Mechanical Impact at 72 ft lbs
[2] Nonvolatile residue of solvent was less than 17 ppm.

Table 4. HCFC 141b Oxygen Compatibility Test Compared to NVR

NVR (ppm)	AIT @ 50 psig & @ 2000 psig	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 ignitions: 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 psig 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, HFE 71DE, OS-10, ABZOL, and EnSolve 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. HFE 71DE also contained a high level of NVR due to the DCE and it is felt that this contributed to its impact sensitivity. Testing with an early formulation of Vertrel XF with DCE and nitromethane stabilizer 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, which does not contain nitromethane, it did not react at an energy of 72 ft-lb. The removal of nitromethane from other solvent formulations i.e. ABZOL and EnSolve; however, did not change the reactivity with oxygen.

To decrease the hazards associated with the use of solvents in oxygen systems, the reactivity of the solvent in the environment must be considered. A solvent that is reactive in the environment should not be used unless it can be shown that the solvents complete removal can be assured. This would limit some of the solvents tested application in the cleaning of assembled components or complex geometries. In particular for the cleaning of high pressure gauges, which represents a severe oxygen service since these gauges are routinely rapidly pressurized and are a dead-ended component, the use of a flammable solvent should be approached with caution and the processes engineered so that the hazard in minimized. For liquid oxygen systems a solvent that is impact sensitive should again not be used unless the solvent is carefully removed since LOX will not allow for solvent evaporation and will tend to concentrate contaminants even those present in the vapor phase at ambient temperature.

SUMMARY

To date, a series of twelve solvents has been tested to determine their effectiveness in cleaning of high-pressure gauges and instrumentation and for their compatibility with liquid and gaseous oxygen. All of the solvents tested exhibited adequate cleaning ability in this application, with toxicity and flammability as the major discriminators for the selection of fluids. Great care should be taken in the selection of solvents for cleaning of oxygen systems, and flammable solvents such as alcohols should only be used under the strictest of controls. Testing is being continued on solvents, as they become available.

REFERENCES

Antin, N. *NAVSEA Report on: Aqueous Oxygen Cleaning Products and Processes.* Naval Sea Systems Command, Arlington, VA, March 1994.

ASTM G-72 (91). *Autogenous Ignition Temperature of Liquid and Solids in a High-pressure Oxygen-enriched Environment.* American Society for Testing and Materials, Reapproved 1991, Volume 14.02, Philadelphia, PA, 1992.

ASTM D 2512. *Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold and Pass-Fail Techniques).* American Society for Testing and Materials, Volume 15.03, Philadelphia, PA, 1992.

Evaluation of HCFC AK 225 Alternatives for Precision Cleaning and Verification

Name: Donald M. Melton

Department No.: 4643

Telephone No.: (504) 257-1782

LOCKHEED MARTIN

BACKGROUND:

Maintaining qualified cleaning and verification processes are essential in an production environment. Environmental regulations have and are continuin to impact cleaning and verification processing in component and large structures, both at the Michoud Assembly Facility (MAF) and component suppliers.

The goal of this effort is to assure that the cleaning and verification proceed unimpeded and that qualified, environmentally compliant material and proc replacements are implemented and perform to specifications.

HCFC AK 225 Critical Surface Cleaning and Verification Alternatives

REGULATORY IMPACTS:

Requirements imposed by the Louisiana Department of Environmental Air Toxic Regulations and the Clean Air Act have combined to limit/restrict the use of critical cleaning an verification solvents such as Freon 113 (PCA)

Interim replacement of HCFC AK 225 has been qualified; however, toxicity and future phase-out regulations necessitate longer term solutions

APPROACH:

Selected three (3) solvents for cleaning and verification evaluation

- Vertrel 423 (HCFC)
- Vertrel MCA (HFC/1,2-Dichloroethylene)
- HFE 7100DE (HFE/1,2-Dichloroethylene)

Selected Supersonic Gas-Liquid Cleaning System for cleaning evaluation

Selected Surf-Map II an analytical instrumental post cleaning verification technique for evaluation

Solvent Cleaning and Verification Technique

Solvent Technique Cleaning Results

Average % Cleaning Efficiency of Twenty Test Panels

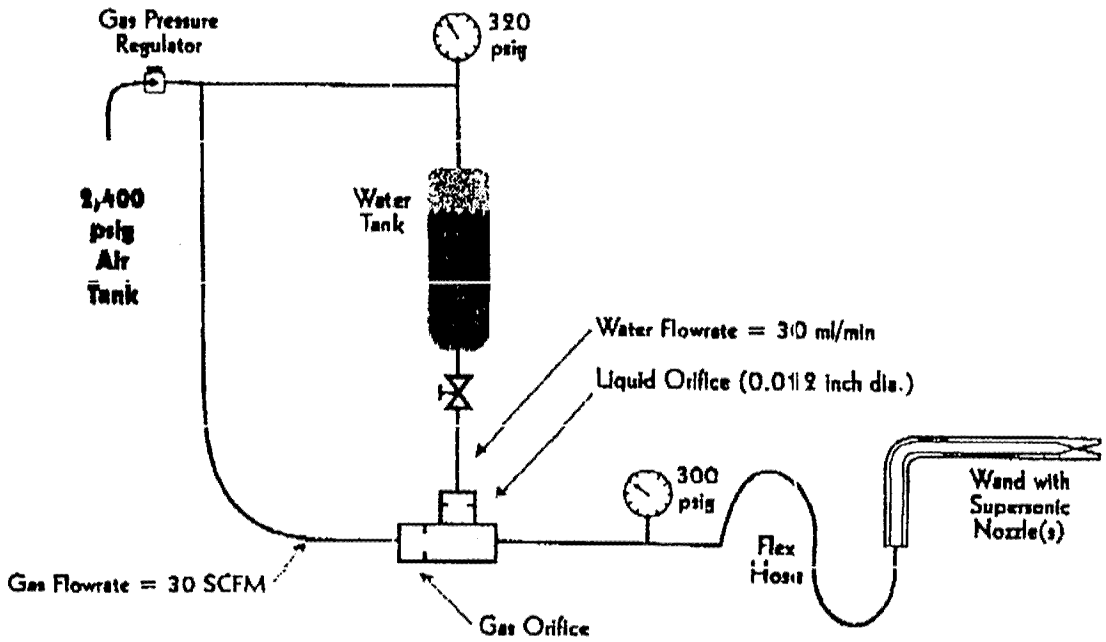
Technique	Safe-Tap	CRC 2-26	J-414
Vertrel MCA	54.6	88.6	58.8
Vertrel 423*	95.2	94.3	79.5
3M HFE71DE	45.1	78.7	55.1
HCFC AK 225	96.6	91.8	31.5
Freon 113	64.7	98.4	61.3

*Product removed from market place 1/98

LOCKHEED MARTIN

Supersonic Gas-Liquid Cleaning Technique

Supersonic Gas-Liquid Cleaning System



Line of sight application

Benefit no solvent needed no recurring disposal cost

LOCKHEED MARTIN

Supersonic Gas-Liquid Technique Cleaning Results

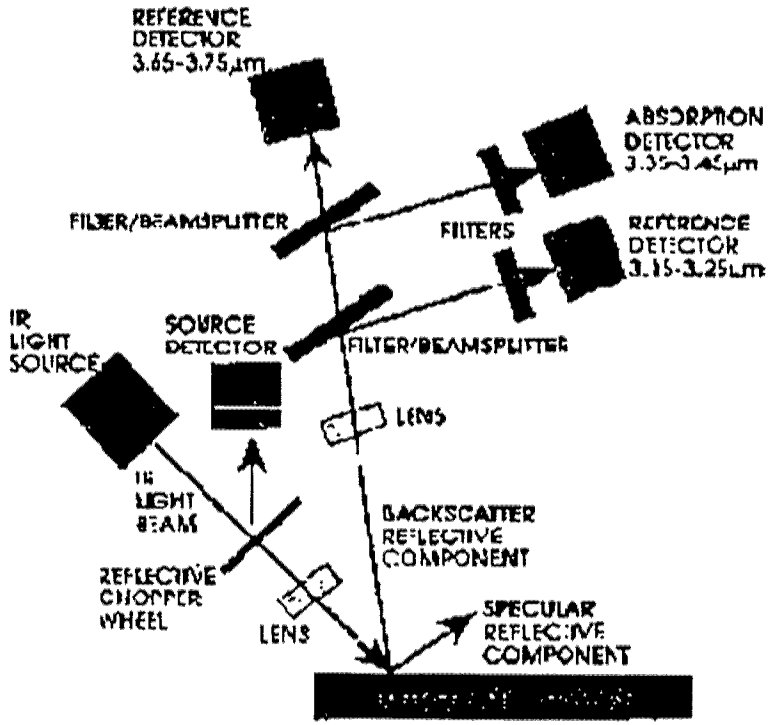
Average % Cleaning Efficiency of Twenty Test Panels

Technique	Safe-Tap	CRC 2-26	J-414
Gas-Liquid	98.1	70.0	0.0
HCFC AK 225	96.6	91.8	31.5
Freon 113	64.7	98.4	61.3

Post Cleaning Verification Technique

HCFC AK 225 Critical Surface Cleaning and Verification Alternatives

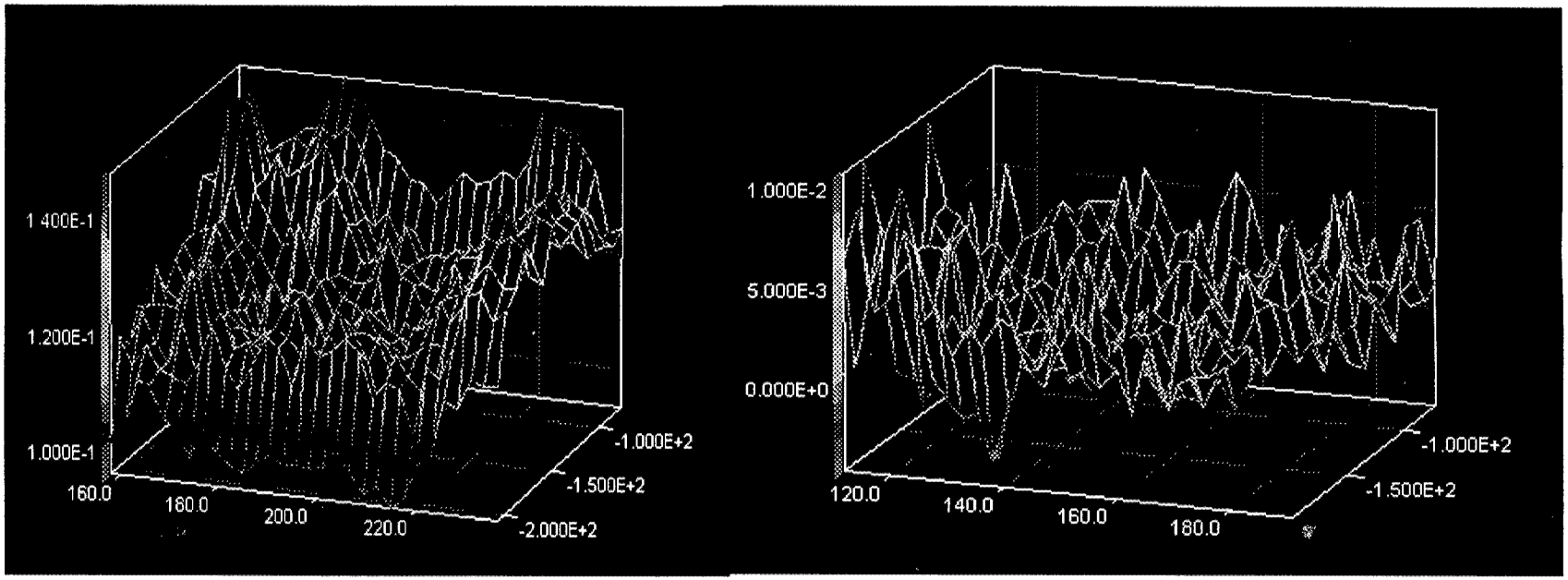
Optical Schematic of the Surf-Map II Apparatus



Some hardware limitations

Benefit no solvent needed no recurring disposal cost

Surf-Map Results of Safe-Tap Lubricant Cleaned Test Panels with Vertrel MCA



Before **After**

HCFC AK 225 Critical Surface Cleaning and Verification Alternatives

FY98 ACTIVITIES:

- Perform qualification testing of Vertrel MCA as a cleaning and verification solvent

- Perform qualification testing of Supersonic Gas-Liquid system as a cleaning technique

  Evaluate EnSolv (1-Bromopropane) as a cleaning and verification solvent

  -

- Support design modifications of Surf-Map II surface verification technique

Orbiter Program CFC-113 (Freon 113) Replacements

AET Conference
June 3, 1998

Presenter: Robert Newman
Prepared by: Carol Nguyen
M&P Engineering
Reusable Space Systems

BOEING

Objective

- Summarize Test Results of Selected Freon 113 Replacement Materials - Vertrel MCA, HCFC-225 and HFE-7100
  - Compatibility
  - Performance

BOEING

Background

- BNA - RSS Has Completed Testing for HCFC-225, Vertrel MCA and HFE-7100 As Replacement Fluids for Freon 113
  - Freon 113 Is One of the Ozone Depleting Compounds (ODC) Materials That Has Been Banned From Production Since January 1, 1996
  - Freon 113 Has Been Used Extensively to Support Orbiter Processing - Precision Cleaning/Cleanliness Verification, Wiping, Vapor Degreasing, Testing Medium, Lubrication during Assembly Process, Etc.
- These Fluids Are Being Considered for Use on Orbiter Hardware at Various Sites
  - NSLD/KSC, WSTF, JSC, Palmdale and Vendors (As Required)

HCFC-225 Has Promising Properties Comparable to Freon 113

- HCFC-225 (Dichloropentafluoropropane) Is Manufactured by Asahi Glass of Japan
- Has Similar Properties to Freon 113
  - Density, Viscosity, Surface Tension, Vapor Pressure
  - Non-Flammable and Very Effective In Removing NVR (Non-Volatile Residue) and Particulates
  - Not a VOC (Volatile Organic Compound)
- Approved by the EPA As an Environmentally Compliant Freon 113 Replacement With a Safety Exposure Limit of 50 ppm (vs 1000 ppm for Freon 113)
- Has an Ozone Depleting Potential (ODP) of 0.03 vs 0.8 For Freon 113 (CFC-11 Has Highest ODP of 1)
- Scheduled to Be Banned From Production in 2015
- Approved for Use Per SE-S-0073 Specification for Orbiter Oxygen and Oxidizer Hardware

HCFC-225 Has Major Advantages With Minor Disadvantages

Advantages

- Low Surface Tension (Ability to Clean/Penetrate Hard to Reach Areas)
- High Vapor Pressure (Ease in Drying Process)
- Similar Density to Freon 113
- Has Excellent Solvency (Ability to Remove Hydrocarbon Contaminants)
  - Hydrocarbon Material Must Be Removed Due to Concern of Reaction in Oxygen and Oxidizer Systems
- Not Flammable (Passes Oxygen Impact Test and Does Not Have An Auto-Ignition Temperature
  - Per NHB 8060.1 Requirements for Orbiter Hardware

Disadvantages

- Has Stringent Toxicity Requirement (50 ppm) vs 1000 ppm for Freon 113
  - Should Not Be Used in Assembled Breathing Hardware
  - Use Requires Either Facility Upgrade or Personnel Protection Equipment to Meet Safety Requirements
- Being Regulated by the EPA and Will Be Banned From Production in 2015
- Material Has High Cost (~$200 Per Gallon)

BOEING

HCFC-225 Compatibility and Performance Test Data Available

- Compatibility
  - Metallic Materials Included CRES 300 and 400 Series, Inconel, Titanium, Aluminum, Brass, E-Brite 26-1, PH CRES, Tungsten Carbide, Tungsten, Custom 455, Invar, Ni Span C, Monel K-500
    - All Tested Metals Are Acceptable
  - Non-Metallic Included Teflon PTFE, Vespel SP-21, Kalrez, EPR, Rulon, Kynar, Neoprene, Viton, Buna-N, Butyl Rubber, Silicone Rubber, Ceramic Macor, Fluorosilicone, Super Koropon, Mil-P-23377 Primer
    - Viton Swells 23% vs 8% for Freon 113
    - Buna-N Swells 37% vs 4% for Freon 113
    - Silicone Rubber Swells 57% vs 72% for Freon 113
  - Other Metals With Coated Surfaces Such As Nitrided 440A, Mellanized Inconel, and Tin Coated Copper Wire Are Acceptable
- Performance
  - Has Excellent Ability to Remove Various Types of Heavy Cutting Fluids, Greases, Lubricants and Particulates, Better Than Freon 113

BOEING

Vertrel MCA Also Has Similar Properties As Freon 113

- Vertrel MCA Is Manufactured by Du Pont
- Has Similar Properties to Freon 113
  - Density, Viscosity, Surface Tension, Vapor Pressure
  - Non-Flammable and Effective for removing NVR (Non-Volatile Residue) and Particulates
- Is an Azeotrope of 38% of 1,2 - Trans Dichloroethylene (DCE) and 62% Vertrel XF (Decafluoropentane)
  - Azeotrope - a Constant Composition Mixture That Has a Constant Boiling Point Which Is Lower (or Higher) Than Either of the Components
- Approved by the EPA As an Environmentally Compliant Replacement Material for Freon 113 With a Safety Exposure Limit of 200 ppm (vs 1000 ppm for Freon 113)
- Is Not Being Regulated but Partially Classified as a VOC (Volatile Organic Compound)

Vertrel MCA Also Has Advantages and Disadvantages

Advantages

- Adequate Surface Tension Compared to HCFC-225 (Cleaning Capability)
- Has Higher Vapor Pressure Than HCFC-225 (Evaporates Faster)
- Has Similar Density to CFC-113
- Has Adequate Solvency Compared to HCFC-225 (Needs Agitation to Help Suspending/Removing Contaminants)
- Not Flammable (Passes Oxygen Impact Test)
- Has Less Stringent Toxicity Requirement (200 ppm) Than HCFC-225

Disadvantages

- Vertrel MCA May Fractionate
  - DCE Has Lower Boiling Point than Vertrel XF, Thus Potentially Evaporates and Re-Condenses in a DCE-Rich Form (Greater Than 38%) in Assembled Hardware
  - DCE- Rich Material (45-50% DCE With 55-50% Vertrel XF) Fails the LOX Impact Test at WSTF
- Has an Auto-Ignition Temperature of 158°C (316°F) in 2000 psi GOX
  - Should Not Be Used in Assembled High Pressure GOX or Assembled Breathing Hardware Unless Thorough Drying Can Be Confirmed
- Material Has High Cost (~$200 Per Gallon)

BOEING

Vertrel MCA Compatibility and Performance Test Data Available

- Compatibility
  - Metallic Materials Included CRES 300 and 400 Series, Inconel, Titanium, Aluminum, Brass, E-Brite 26-1, PH CRES, Tungsten Carbide, Tungsten, Custom 455, Invar, Ni Span C, Monel K-500
    - All Tested Metals Are Acceptable
  - Non-Metallic Included Teflon PTFE, Vespel SP-21, Kalrez, EPR, Rulon, Kynar, Neoprene, Viton, Buna-N, Butyl Rubber, Silicone Rubber, Ceramic Macor, Fluorosilicone, Super Koropon, Mil-P-23377 Primer
    - Viton Swells 29% vs 8% for Freon 113
    - Buna-N Swells 16% vs 4% for Freon 113
    - Silicone Rubber Swells 25% vs 72% for Freon 113
    - Fluorosilicone Swells 26% vs 11% for Freon 113
  - Metals With Coated Surfaces Such As Nitrided 440A, Mellanized Inconel, and Tin Coated Copper Wire Are Acceptable
- Performance
  - Has Good Ability (with Agitation) to Remove Various Types of Heavy Cutting Fluids, Greases, Lubricants and Particulates - Comparable to Freon 113

BOEING

HFE-7100 Properties Are Also Similar to Freon 113

- HFE-7100 (Methoxy-nonafluorobutane) Is Manufactured by 3M
- Has Similar Properties to Freon 113
  - Density, Viscosity, Surface Tension, Vapor Pressure
  - Non-Flammable and Effective in Removing Light Hydrocarbon/Greases Only and Particulates
  - Not a VOC (Volatile Organic Compound)
- Approved by the EPA As an Environmentally Compliant Replacement Material for Freon 113 With a Safety Exposure Limit of 600 ppm (vs 1000 ppm for Freon 113)
- Is Not Being Regulated by the EPA

HFE-7100 Has Advantages and Disadvantages

Advantages

- Has Similar Surface Tension As Freon 113 (Cleaning Capability)
- Has Lower Vapor Pressure Than Freon 113 (Not As Fast Drying)
- Has Similar Density to Freon 113
- Not Flammable (Passes Oxygen Impact Test and Does Not Have An Auto-Ignition Temperature)
  - Per NHB 8060.1 Requirements for Orbiter Hardware
- Has the Least Stringent Toxicity Requirement (600 ppm) Compared to the Other Replacement Fluids

Disadvantages

- Has Weaker Solvency Compared to Freon 113
  - HFE-7100 Can Remove Particulates, Light Oils/Greases, and Hydrocarbon Materials Effectively, but Not Heavy Hydrocarbon Oils/Greases
- Material Has High Cost (~$200 Per Gallon)

HFE-7100 Compatibility and Performance Test Data Available

- Compatibility
  - Metallic Materials Included CRES 300 and 400 Series, Inconel, Titanium, Aluminum, Brass, E-Brite 26-1, PH CRES, Tungsten Carbide, Tungsten, Custom 455, Invar, Ni Span C, Monel K-500
    - All Tested Metals Are Acceptable
  - Non-Metallic Included Teflon PTFE, Vespel SP-21, Kalrez, EPR, Rulon, Kynar, Neoprene, Viton, Buna-N, Butyl Rubber, Silicone Rubber, Ceramic Macor, Fluorosilicone, Super Koropon, Mil-P-23377 Primer
    - Viton Swells 12% vs 8% for Freon 113
  - Metals With Coated Surfaces Such As Nitrided 440A, Mellanized Inconel, Tin Coated Copper Wire Are Acceptable
- Performance
  - Has Ability to Remove Light Oil, Hydrocarbons, Greases, Lubricants and Particulates, but Not Heavy Hydrocarbon, Cutting Fluids Compared to Freon 113 and The Other Replacement Fluids

There Is No Drop-in Replacement Materials for Freon 113

Solvent	LOX/ Oxid. Hard.	GOX Hard.	Non-Oxid. Hard.	Partic. Verf.	NVR Verf.	Tox/ ppm	Flam	AIT[6]	Degra-dation	ODP[2]/ GWP[3]	Avail $/gal	Fac. Upg. Reqd	Fluid Spec Upd	Implemt. Time/ Cost
CFC-113	Yes	Yes	Yes	Yes	Yes	Very Low/ 1000	No	No	No	0.8/ Hi	May be/ 200	No	Not Req'd	Curr. In Use
HCFC-225[5]	Yes	PP[4] Only	Yes	Yes	Yes	Very Hi/ 50	No	No	No	0.03/ Lo	Until 2015/ 200	Yes	Yes/ Appr.	Up to 18 Mos/ High
Vertrel MCA[5]	Yes	PP Only	Yes	Yes	Yes	Mod/ 200	No	Yes	No	0.0/ Lo	Yes/ 200	Yes	Yes/ Not Comp	Up to 18 Mos/ High
HFE-7100[5]	No	No	Yes	Yes	May Be[7]	Low/ 600	No	No	No	0.0/ Lo	Yes/ 200	May be	Yes/ Not Comp	Up to 18 Mos/ Mod

[1] Non-Volatile Residue
[2] Ozone Depleting Potential (max. = 1.0)
[3] Global Warming Potential
[4] Piece Part (Details)
[5] Compatibility Test Results Available (Back-Up Chart)
[6] Auto-Ignition Temperature
[7] Depends on Type of Contaminants; Able to Remove Light Oils/Hydrocarbons/Greases Only, Not Heavy Hydrocarbon Oils/Greases

Summary

- HCFC-225, Vertrel MCA and HFE-7100 Have Been Tested for Both Compatibility and Performance
  - HCFC-225 Has Been Added to the SE-S-0073 Specification for Oxgyen and Oxidizer Systems
    - Limited Applications Due to Stringent Toxicity Requirement
    - Will Be Banned From Production in 2015
    - Approved for Use on Some Orbiter Main Propulsion System Hardware
  - Vertrel MCA and HFE-7100 Need to Be Added to the SE-S-0073 Specification for Various Subsystems
    - Neither Are Regulated by the EPA
    - Vertrel MCA Should Not Be Used in Assembled High Pressure Oxygen Systems and Breathing Systems
    - Both Have Less Stringent Toxicity Requirements (200 and 600 ppm Respectively) Than HCFC-225
    - May Still Require Equipment to Ensure Worker Safety and/or Recapture Solvent Vapor Due to High Material Cost

Elimination of Carbon Tetrachloride for Quantitative Hydrocarbon Analysis

Vonnie M. Douglas
The Boeing Company
Rocketdyne Propulsion & Power
6633 Canoga Avenue
Canoga Park, CA 91309-7922

ABSTRACT

Carbon tetrachloride, which has been identified as an ozone depleting chemical, was banned from manufacture in 1995. An exemption for laboratory use was given by Federal agencies which allowed the use of carbon tetrachloride for analytical purposes. However, due to anticipated future regulation and the uncertainty of the availability of this chemical, more permanent options are being pursued. The majority of the procedures which utilized carbon tetrachloride at Rocketdyne were replaced by alternatives before the end of 1996. The last remaining application which required an alternative technique was the quantitative analysis of hydrocarbons by infrared spectrometry.

The final goal for carbon tetrachloride elimination was to identify a solvent or alternative technique for this analytical procedure. Several methods were investigated which do not require the use of ozone depleting chemicals. The proposed techniques included high pressure liquid chromotography (HPLC), gravimetric procedures, total organic carbon analysis (TOC), gas Chromotography (GC) and alternative infrared procedures. A review of these alternatives and the current status of the experimentation will be provided. The implementation of successful alternatives will result in complete elimination of carbon tetrachloride at Rocketdyne.

BACKGROUND

A world-wide ban was placed on carbon tetrachloride as well as other ozone depleting chemicals in 1995. Production of these ozone depleting chemicals was halted as of Dec. 31, 1995. An exemption for laboratory use was given and mandated by Federal Register Vol. 60, No. 90 Appendix G to Subpart A. This allowed the use of carbon tetrachloride for analytical purposes only. However, due to anticipated future regulations more permanent options were pursued.

Prior to 1996 carbon tetrachloride was used in the laboratory for extractions and for standard preparation, sample dilutions and as a pick up solvent for Fourier transform infrared (FTIR) techniques. It was also utilized as a flush solvent for hardware cleanliness verification procedures, including non-volatile residue (NVR), handwipe applications and particle count determinations. Cyclohexane gravimetric NVR and Total Organic Carbon (TOC) analysis replaced many of the cleanliness verification techniques which utilized carbon tetrachloride. Cyclohexane and Soxhlet extractions utilizing CO_2 were used as alternatives to many laboratory applications. All procedures which utilized carbon tetrachloride were replaced by alternative methods by 1996, with the exception of quantitative hydrocarbon analysis by FTIR methods.

After 1996, cleanliness verification of transducers and wipe/swab analysis still utilized carbon tetrachloride for hydrocarbon determination. Transducers were incompatible with the TOC technique due to the electrical connectors and did not contain a large enough surface area to be used with gravimetric methods. Wipes and swabs were extracted with cyclohexane, but still required quantitative techniques that could attain the low detection limit provided by FTIR methods. During these analyses, an aliquot of the final flush solvent was collected and evaporated to dryness. The remaining residue was taken up in a known quantity of carbon tetrachloride and was subsequently analyzed on an infrared spectrometer.

Initially, various solvents were investigated which could be utilized as drop-in replacements. Alternative solvents for the FTIR technique must ideally meet all of the following requirements; no infrared absorbance within the C-H stretch region, no ozone depleting chemicals, personal exposure limit greater than 100 ppm and effectively remove hydrocarbon residue from hardware. A drop-in replacement solvent was not found that could meet all of these requirements, which led to the investigation of alternative analytical methods. Requirements for new analytical methods include the following: a minimum detection limit of 0.01 mg, no ozone depleting chemicals, no materials which would pose a health hazard for personnel, cost effective procedures and total analysis time equivalent to or better than the carbon tetrachloride technique.

Many techniques were initially evaluated and were quickly rejected for various reasons. These include gravimetric, Nuclear Magnetic Resonsance (NMR), GC/Pyroylsis and HPLC procedures. In order to reach the required detection limit of 0.01 mg, the gravimetric method would require a precision balance and a specially designed balance room to control noise, vibration, temperature and humidity. Even with the environmentally controlled room, this technique had a high potential for error and was eliminated as a viable option. HPLC and NMR techniques were considered, but due to the immediate unavailability of equipment and the high cost of procurement, these methods were not investigated. A GC/Pyroylsis technique is in the early stages of testing and preliminary results indicate this may be a viable procedure, but to date, no conclusive data have been obtained. TOC analysis and two alternate FTIR methods were chosen for further evaluation.

TOTAL ORGANIC CARBON TECHNIQUE

Introduction

A total organic carbon (TOC) technique has been utilized since 1996 for performing cleanliness verification of rocket engine hardware. Hardware is exposed to ultrasonic agitation in a heated water bath and an aliquot of water is analyzed on a total organic carbon analyzer (TOCA). However, many small pieces of hardware such as pressure and temperature transducers can not be exposed to water or ultrasonic agitation. A TOC method was investigated which involved flushing hardware with cyclohexane, evaporating the solvent to dryness, adding water and analyzing the water by TOC techniques. Cyclohexane is an approved solvent for cleanliness verification and has been proven effective for removing contaminants typically used at Rocketdyne. This new procedure would involve combining two previously approved methods, cyclohexane flushing and TOC analysis.

Test Procedure and Results

Flat test coupons and transducers of various configurations were utilized for qualification testing. The test pieces were contaminated with a known amount of contaminant and flushed with cyclohexane. The solvent was collected in a clean 50 ml glass beaker and evaporated to dryness. A nominal amount, typically 20 ml, of distilled water was added to the beaker. The beaker was placed in a water bath heated to 55°C and exposed to ultrasonic agitation for 10 minutes using a Blackstone 25kHz ultrasonic bath. A 200 ul aliquot of the sample water was injected into a Rosemount DC-190 Total Organic Carbon Analyzer and total carbon content was determined.

A single component contaminant and a mixture of five soils typically used in manufacturing were utilized for this testing. Dye penetrant, which is commonly observed on transducers during manufacture was utilized for the single component contaminant. A hydrocarbon mixture was prepared from the contaminants listed below in Table 1. Contaminant descriptions are outlined in Table 2.

Table 1.
Hydrocarbon Contaminant Mixture

Contaminant	% by Weight
Rapid Tap Lubricant	43.7 %
Mil-H-83282 Hydraulic Fluid	3.9 %
LS-10 Lubricant	3.7 %
Bio-Pen P6F-4, Dye Penetrant	3.5 %
Turco 4215 Additive	5.2 %

Table 2.
Contaminant Description

Contaminant	Percent by Weight	Manufacturer	Description
Rapid Tap	43.7	Relton	Lubricant, containing mineral oil, paraffin and soybean oil
Mil-H-83282 Hydraulic Fluid	3.9	Bray Oil Co.	Synthetic hydrocarbon fluid containing triphenyl phospate
LS-10	3.7	ITW Fluid Products Group	Fatty alcohol based lubricant
Bio-Pen P6F-4	3.5	Ardox Inc.	Fluorescent, water-soluble dye penetrant
Turco 4215 Additive	5.2	Elf Atochem, Turco Products	Non-ionic detergent, containing diethylene glycol monobutyl ether and nonnylphenoxypoly (ethyleneoxy) ethanol

The contaminants were prepared in cyclohexane and applied to the test articles using a gas-tight syringe. The concentration of the dye penetrant solution was 1 mg/ml and the hydrocarbon mixture was 0.278 mg/ml. Aliquots from 50 to 700 ul were applied to the test pieces, which correlates to 10 - 500 ug of contaminant on the test articles. The results from the TOC analysis are outlined in Tables 3 and 4.

Table 3.
Test Coupon Results

Hydrocarbon Mixture			Dye Penetrant		
Amount Applied (ppm)	Amount Recovered (ppm)	Percent Recovery	Amount Applied (ppm)	Amount Recovered (ppm)	Percent Recovery
0.695	0.63	91	0.5	0.45	90
1.39	1.47	106	0.5	0.45	90
2.09	2.08	100	1.5	1.33	89
2.78	2.55	92	2.5	2.69	108
2.78	2.75	99	5	5.18	104
5.56	4.39	79	5	4.65	93
9.73	10.6	109	10	10.7	107
2.78	2.68	96	12.5	14.4	115
1.99	2.07	104			
Average Recovery		**97**			**99**
Standard Deviation		**9.2**			**8.6**

Table 4.
Transducer Test Results

Trandsucer	Amount Applied (ppm)	Amount Recovered (ppm)	Percent Recovery
Servo343	1.39	1.27	91
	1.39	1.55	112
S/N 5168	2.78	2.12	76
	0.69	0.65	94
	1.39	1.52	109
S534333	11.12	10.7	96
	5.56	5.47	98
M-22697	4.17	3.6	86
	4.17	4.12	99
S/N 16977	2.085	1.75	84
Average Percent Recovery			**95**
Standard Deviation			**11**

INFRARED TECHNIQUES

Introduction

Historically, quantitative analysis using FTIR techniques involved the following steps.

1) Cyclohexane was obtained from hardware flushing or wipe extractions.
2) The solvent was evaporated to residue.
3) Remaining residue was picked up in carbon tetrachloride.
4) The carbon tetrachloride solution was transferred into a quartz cell.
5) Hydrocarbon analysis by FTIR was performed on the carbon tetrachloride solution.

Two analytical procedures were investigated which involved evaporating cyclohexane directly onto a sampling device followed by subsequent analysis of the residue using a FTIR spectrometer. This would eliminate the need for carbon tetrachloride as a pick up solvent. Both procedures are similar, but utilized unique FTIR equipment and accessories.

One method utilized a zinc selenide Horizontal Attenuated Total Reflectance (HATR) trough manufactured by Pike Technologies. The trough attached directly to an FTIR spectrometer. This procedure was appealing in that it utilized existing FTIR instrumentation, a Bio Rad FTS-45 spectrometer, which was significantly less costly than procurement of an entirely new system.

The second FTIR method utilized a portable diffuse reflectometer, Model SOC-400, manufactured by Surface Optics Corporation. The unit contains an integrating spherical adapter designed specifically for this application and currently has a patent pending by Surface Optics Corporation. The sample holder is a hemispherical gold plated container, which attaches directly to a matching hemispherical part on the main unit. When the two hemispheres are attached by threaded closures a complete sphere is formed. The beam enters through a small hole from the detector side of the sphere and is reflected off of the sampling hemisphere, which contains the sample residue. The beam is reflected many times within the sphere, which amplifies the signal and increases sensitivity before reaching the detector. The reflectometer measures data collected over the entire hemispherical area for any set of incident or reflected angles.

The portability of the unit is a desirable feature, but was not deemed as important as the sampling device. The advantage of this design is that the solvent could be directly evaporated into the sample holder. The sampling device has a capacity of 5 ml, which allows easy transfer of the solvent. This could minimize sample loss and decrease analysis time. The SOC-400 also has the capability of detecting organic contaminants directly on the surface of flat metal surfaces. That application was not evaluated during this study but has been the subject of previous authors.

Test Procedures

HATR Infrared Analysis Procedure - This method involved evaporating solvent onto a Horizontal Attenuated Total Reflectance (HATR) trough accessory and analyzing the remaining residue with a Bio Rad FTS-45 Fourier transform infrared spectrometer.

Flat stainless steel test coupons were initially utilized for FTIR testing with the HATR accessory. A known amount of contaminant was applied to the test coupons and allowed to air dry. The coupons were then flushed with approximately 25 ml of cyclohexane. The cyclohexane was collected in a glass beaker and evaporated to residue. A nominal amount, 0.5 ml, of cyclohexane was utilized to transfer the residue to the HATR. The solvent was allowed to air dry on the HATR trough. The trough was placed in a Bio-Rad FTS-45 spectrometer and an infrared absorption spectrum was obtained between 3000 cm^{-1} and 2800 cm^{-1} wavenumbers. Thirty-two (32) scans at 8 cm^{-1} resolution were obtained. It was previously determined that cyclohexane would efficiently remove contaminants from hardware and preliminary testing with the entire contamination process for this technique resulted in good recoveries. Therefore the remaining samples were

evaporated directly onto the trough. This eliminated the process of contaminating the coupons, which accelerated the testing schedule.

A calibration curve was obtained from using mineral oil standards prepared in cyclohexane. The final calibration concentrations ranged from 0.01 mg to 0.50 mg. These spectra were used to compute the least squares regression calibration coefficients. Reference Figures 1 and 2. The amount of hydrocarbon (mg) in the samples was determined by using the least squares regression calibration curve.

Samples were analyzed by the HATR technique and also by the currently utilized carbon tetrachloride method. Contaminants include the hydrocarbon mixture used for the TOC testing (Ref. Tables 1 and 2) and Mil-H-83282, mineral oil, paraffin wax, Rigidax and Spinnestic 22 Oil. The results from the HATR technique were comparable to the carbon tetrachloride technique. A description of the contaminants is listed in Table 5. The test results are listed in Table 6.

Table 5.
Contaminants Utilized for HATR Evaluation

Contaminant	Description
Mineral Oil	Light paraffin oil
Mil-H-83282 Hydraulic Fluid	Synthetic hydrocarbon fluid containing triphenyl phospate
Spinnestic 22 Oil	Petroleum lubricating oil
Paraffin Wax	Low melting wax
Rigidax	High melting wax containing calcium carbonate

SOC-400 Infrared Procedure - This method involved evaporating solvent onto a gold plated integrating spherical sampling accessory and analyzing the remaining residue with an SOC-400 FTIR spectrometer.

The test procedure utilized for the SOC-400 was similar to the HATR technique. Mineral oil standards were prepared and evaporated directly onto the sampler. Standard solutions of mineral oil were prepared in cyclohexane. A calibration curve was obtained from 0.01 mg to 0.50 mg on the SOC-400 Fourier transform infrared spectrometer. Reference Figure 3. An infrared absorption spectrum was obtained between 3000 cm^{-1} and 2800 cm^{-1} wavenumbers. Sixty four (64) scans at 8 cm^{-1} resolution were obtained.

Only a minimal amount of testing has been performed using this technique and evaluation is still in progress. At the time of testing the sample holder was not in an enclosed unit and thus the system may have been subject to environmental effects, such as humidity and noise. Results obtained thus far are outlined in Table 7. The recoveries and repeatablity are very good with the exception of the low-end standard. The lowest standard on the calibration curve contained a significantly higher absorbance than predicted. More testing is required to determine if this problem can be resolved.

Table 6.
HATR vs CCL4 Method Comparison

Contaminant	HATR		Carbon Tetrachloride	
	Amount Detected (mg)	% Recovery	Amount Detected (mg)	% Recovery
Hydrocarbon Mix	0.03	100	0.03	100
	0.14	100	0.12	86
	0.03	100	-	-
	0.03	100	-	-
	0.03	100	-	-
	0.03	100	-	-
	0.02	80	-	-
Hydraulic Fluid	0.47	94	0.50	100
	0.50	100	-	-
	0.46	92	-	-
	0.42	84	-	-
	0.50	100	-	-
Spinnestic Oil	0.46	92	0.50	100
	0.26	104	-	-
	0.28	112	-	-
	0.24	96	-	-
	0.25	100	-	-
Rigidax	0.20	80	0.20	80
	0.03	100	0.03	100
	0.03	100	0.03	100
Paraffin Wax	0.28	112	0.23	90
	0.03	100	0.03	100
Mineral Oil	0.53	106	0.50	100
	0.26	102	0.25	100
	0.13	96	0.13	100
Average		98		96
Standard Deviation		7.9		7.0

Table 7.
SOC-400 Test Results

Amount Applied (mg)	Amount Detected (mg)	Percent Recovery
0.01	0.02	200
0.01	0.02	200
0.01	0.02	200
0.01	0.02	200
0.03	0.03	100
0.03	0.02	80
0.05	0.05	100
0.13	0.11	85
0.13	0.10	77
0.25	0.27	108
0.50	0.49	98
0.03	0.03	100
0.25	0.23	92
0.50	0.40	80

CONCLUSIONS

Total Organic Carbon Technique

The Total Organic Carbon technique meets the desired requirements for quantitative analysis of hydrocarbons for this application. The ability of utilizing existing equipment and the ease of the procedure are advantages for using this technique. This technique is economically favorable because it utilizes two techniques already approved and in-use. Thus, this eliminates the need for costly equipment and minimizes personnel training. This method is also easily capable of reaching the required 0.01 mg detection limit and provides good repeatability at these low concentrations. The disadvantages to this technique are that the procedure is relatively time consuming when compared to other available methods and qualitative analysis can not be performed. Extreme care must be taken when handling glassware and sample containers, as cleanliness is very important. Also it is vital that all residual cyclohexane be thoroughly evaporated prior to performing the TOC analysis. Residual solvent will interfere with the TOC reading, indicating high total carbon values and inaccurate test results.

HATR Infrared Technique

The HATR technique has demonstrated the capability of reaching the desired detection limit and sample recovery and repeatability were acceptable. This method meets the required environmental goals and does not impose a health hazard to employees. This technique however is somewhat precarious in the transfer of the sample residue. The residue must be picked up in a small volume of cyclohexane and transferred to the HATR trough, which contains a limited surface area. Loss of sample in this transfer is possible and care must be taken when performing this step. The skill of laboratory personnel is vital when performing this technique.

The cyclohexane must be thoroughly evaporated before an infrared absorption spectrum is taken or erroneously high readings will be obtained. This is a relatively time-consuming step. When using 0.5 ml of cyclohexane, ten minutes under air purge was found to be the minimum time required for complete removal of residual solvent. Reference Figure 4. Other problems encountered during evaluation of this technique include trough alignment and unleveled working surfaces. The alignment of the trough must be exact to ensure the beam is contacting the sample area. The fume hood used for evaporation must be level to ensure even distribution of the sample residue on the trough.

This technique has been approved for use at Rocketdyne in a laboratory environment. With the approval of this technique the goal of complete elimination of ozone depleting chemicals has been attained.

SOC-400 Infrared Technique

This technique is a possible alternative method of hydrocarbon determination for cleanliness verification. The advantage of using this technique over the HATR method, is the larger sampling device. The ability to hold a larger volume will allow easier transfer of the solvent with less room for errors and possibly a shorter analysis time. The high recoveries at the low end of the calibration curve are a concern, but may be resolved through procedural development. It is likely the calibration curve covers too wide of a range and may require a second curve. When the calibration points were divided into two linear curves the recovery at the low end was much closer to the predicted values. This technique is still in the preliminary stages of evaluation and more data must be collected before a final recommendation can be made. More testing is required for this procedure, but the results thus far look promising.

ACKNOWLEDGEMENTS

The author would like to recognize Larry Hill for his contributions in the development of the infrared techniques and also expresses gratitude to Mary Maseda and Andy Hsu for performing the required laboratory analysis in support of this project.

Figure 1. HATR Calibration Standards

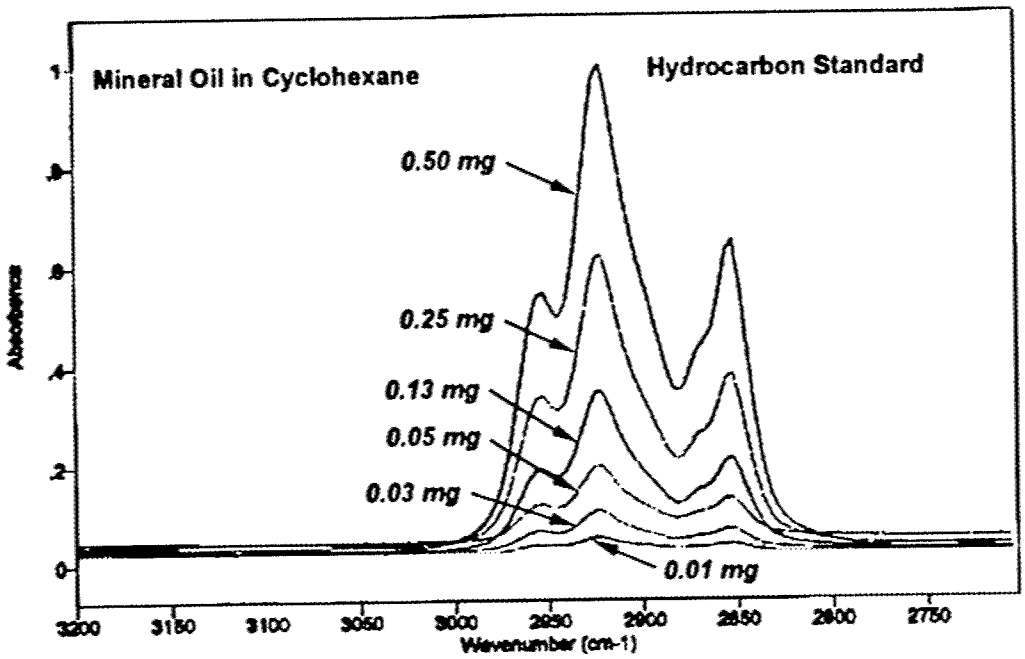


Figure 2. Carbon Tetrachloride Calibration Standards

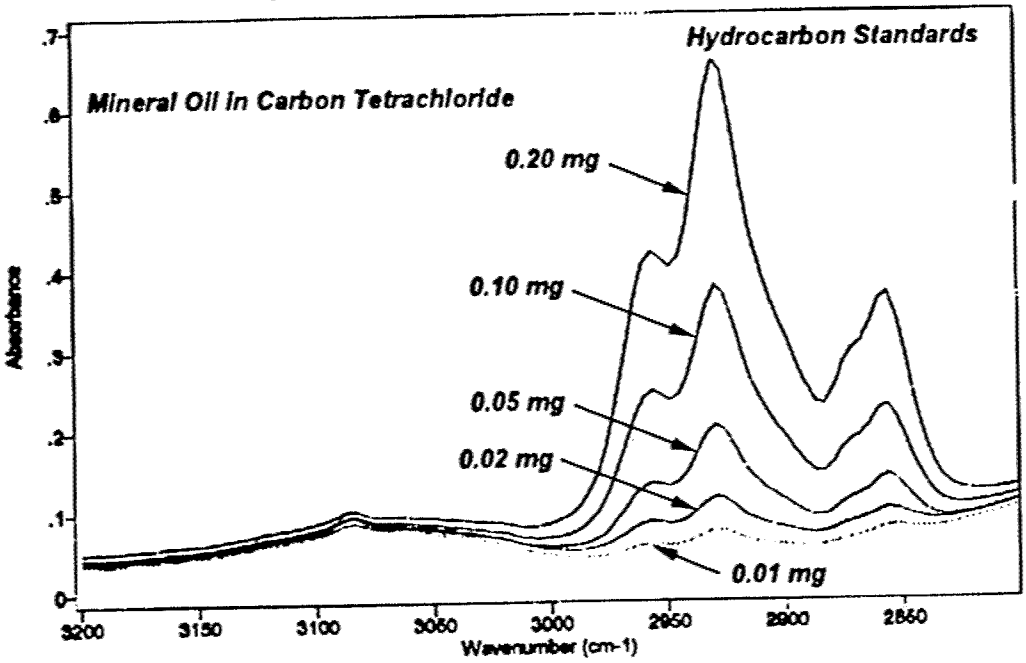


Figure Page 1

Figure 3. SOC-400 Calibration Standards

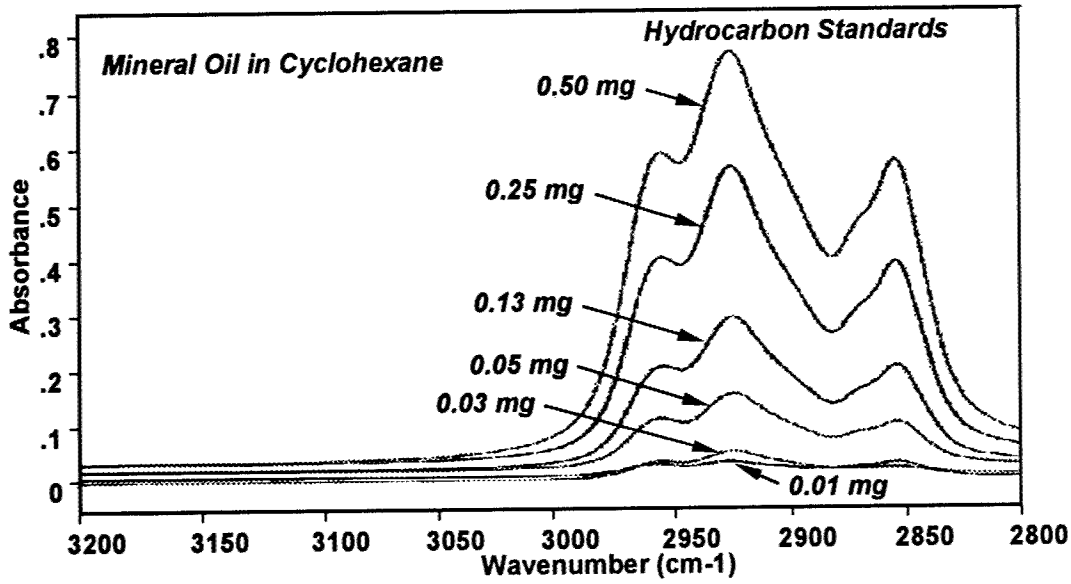


Figure 4. Residual Cyclohexane

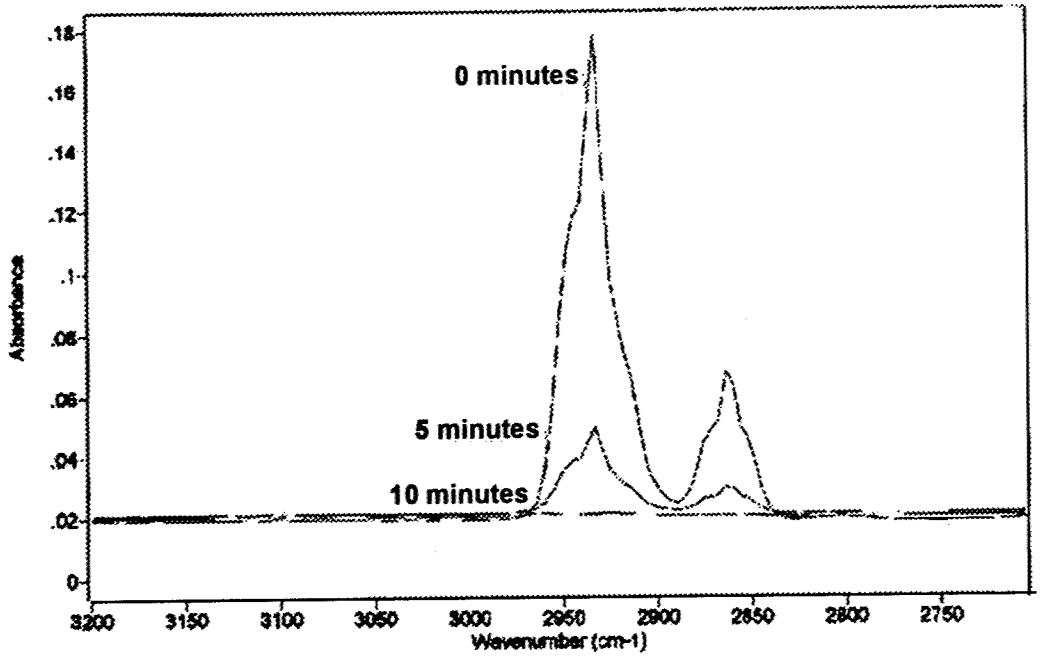


Figure Pages 2

BOEING

McDonnell Aircraft and Missile Systems - Aerospace Support

FLASHJET®
Coatings Removal Process

General Information Package

26 March 1998

Tom Nied
314-232-5761

Boeing Proprietary

BOEING

FLASHJET

FLASHJET End Effector Assembly

Boeing Proprietary

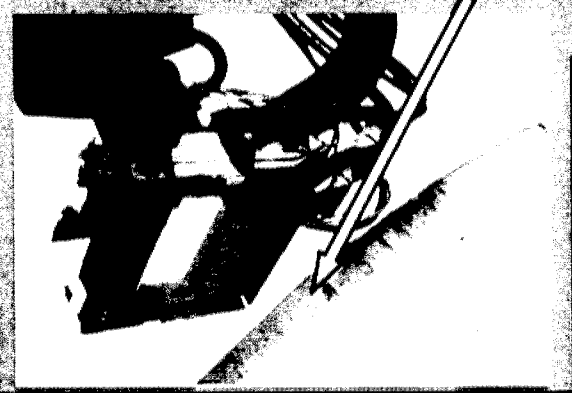
BOEING

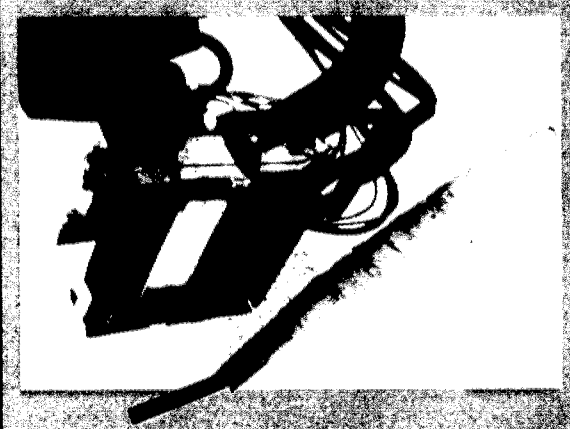
FLASHJET

FLASHJET Coatings Removal Process

Three Simultaneous Processes

1. Pulsed-Light Energy Ablates Coating





2. Dry Ice Cools and Cleans Surface

3. Effluent is Vacuumed into Capture System

Results:

- Efficient Coatings Removal
- Safe for Metallics and Composites
- Low Volume of Residual Effluents
- Minimal Safety Requirements (Eye and Ear Protection)

Boeing Proprietary

BOEING

FLASHJET

Flashjet Discriminators

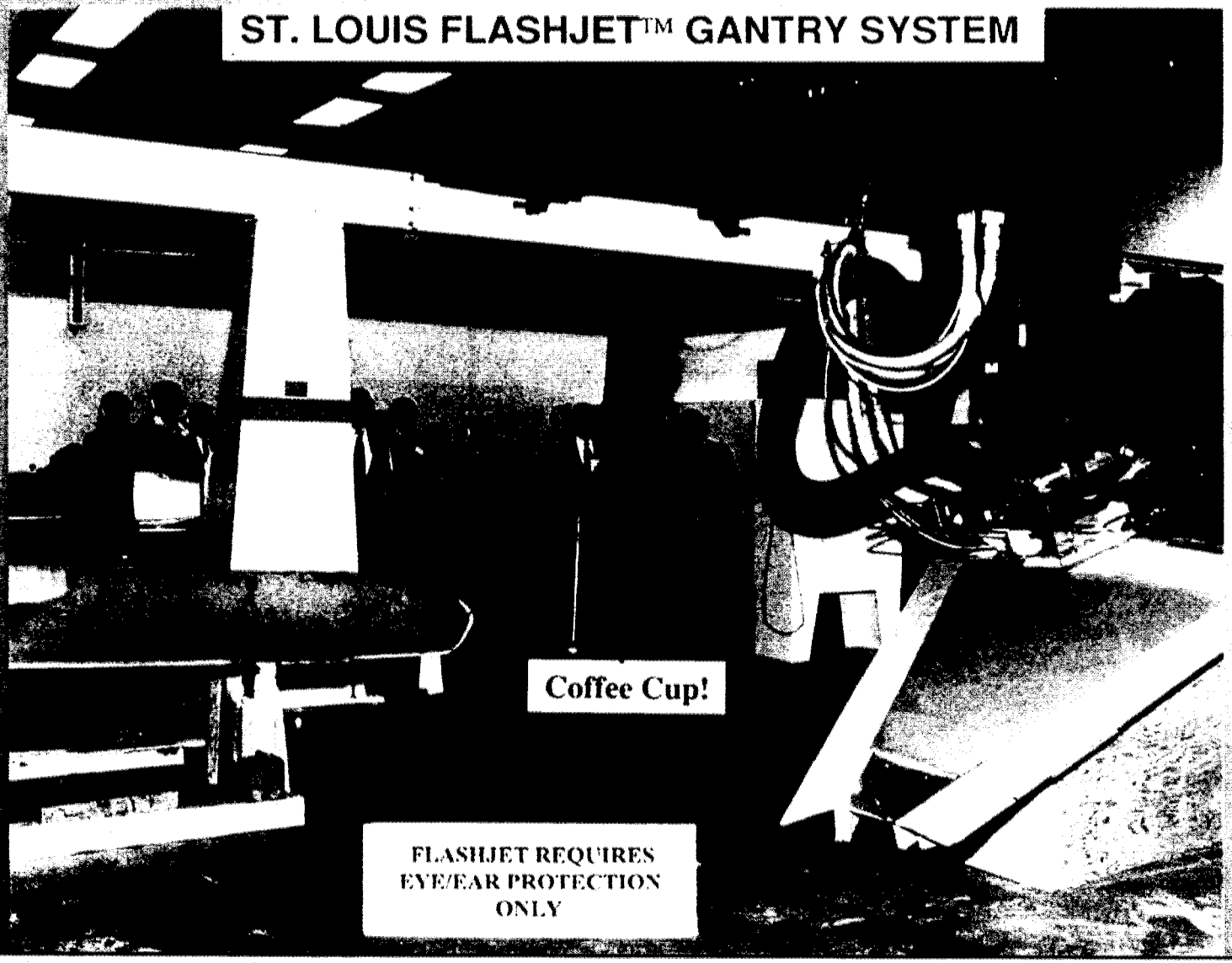
- Favorable Operating and Life Cycle Costs
- Environmental Compliance - Clean Process
- Best Solution for Composite Materials
- Boeing as Military/Commercial Aircraft OEM
- Product Development Maturity

Boeing Proprietary

BOEING

FLASHJET

ST. LOUIS FLASHJET™ GANTRY SYSTEM



BOEING

FLASHTEN

Customer Requirements

- Demonstrated Performance
- "x%" Solution how to strip remaining "x" of moldline
- System Operational Reliability (MTBF, Availability, etc)
- Minimum of Facility Modifications/New Construction
- Ease of Operator Use
- Safe Around Aircraft (NEC, damage to aircraft)
- Boeing Product Support

BOEING

FLASHJET

FLASHJET Products and Services

Products

- Integrated coatings removal systems for aircraft and components
  - Robotic Gantry Systems - component level
  - Robotic Gantry Systems - tactical/bizjet size aircraft
  - Systems - Transport Aircraft
  - Systems - Unique requirements
- Process equipment subsystems for existing/other manipulators
  - Existing customer robotics infrastructure

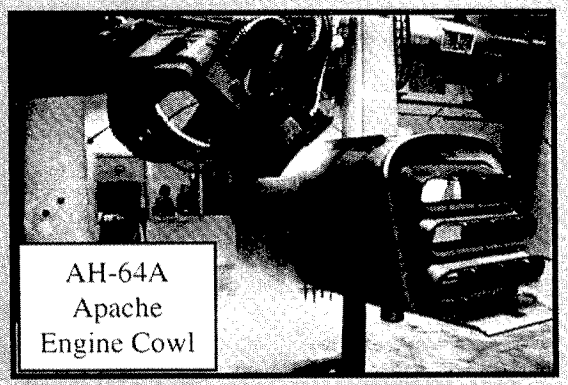
Services

- Boeing turnkey depaint/paint "fly-in" service centers
- Operate customer or Boeing owned systems at customer site

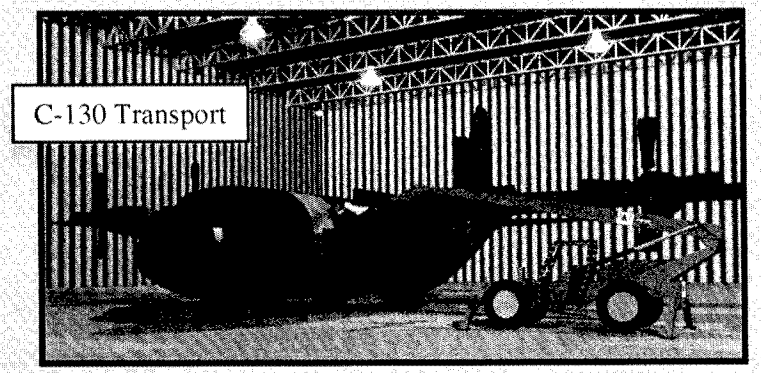
BOEING

FLASHJET Application Systems

Small Gantry System for Off-Aircraft Parts



Mobile Systems for Transports/Bombers



Large Gantry System for Mid-Size Aircraft

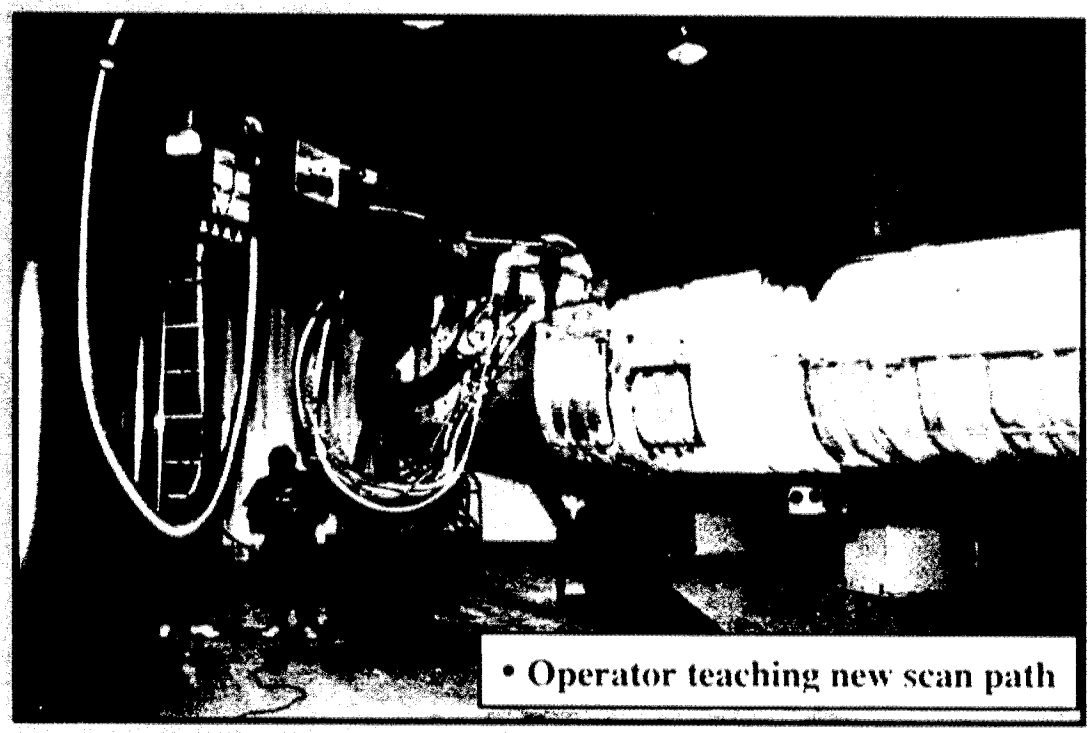
- **Each type system now in operation or construction**
- **Gantry and mobile systems sized to accommodate wide range of parts or aircraft**
- **Flexible designs for depaint production and facility requirements**

Boeing Proprietary

BOEING

Boeing AH-64A Apache System

Mesa, AZ



• Operator teaching new scan path

Performance

- Cost to strip = $2,300 (fuselage + components)
- Cycle Time = 3 shifts
- Reliability > 90%
- Operators = 1 or 2

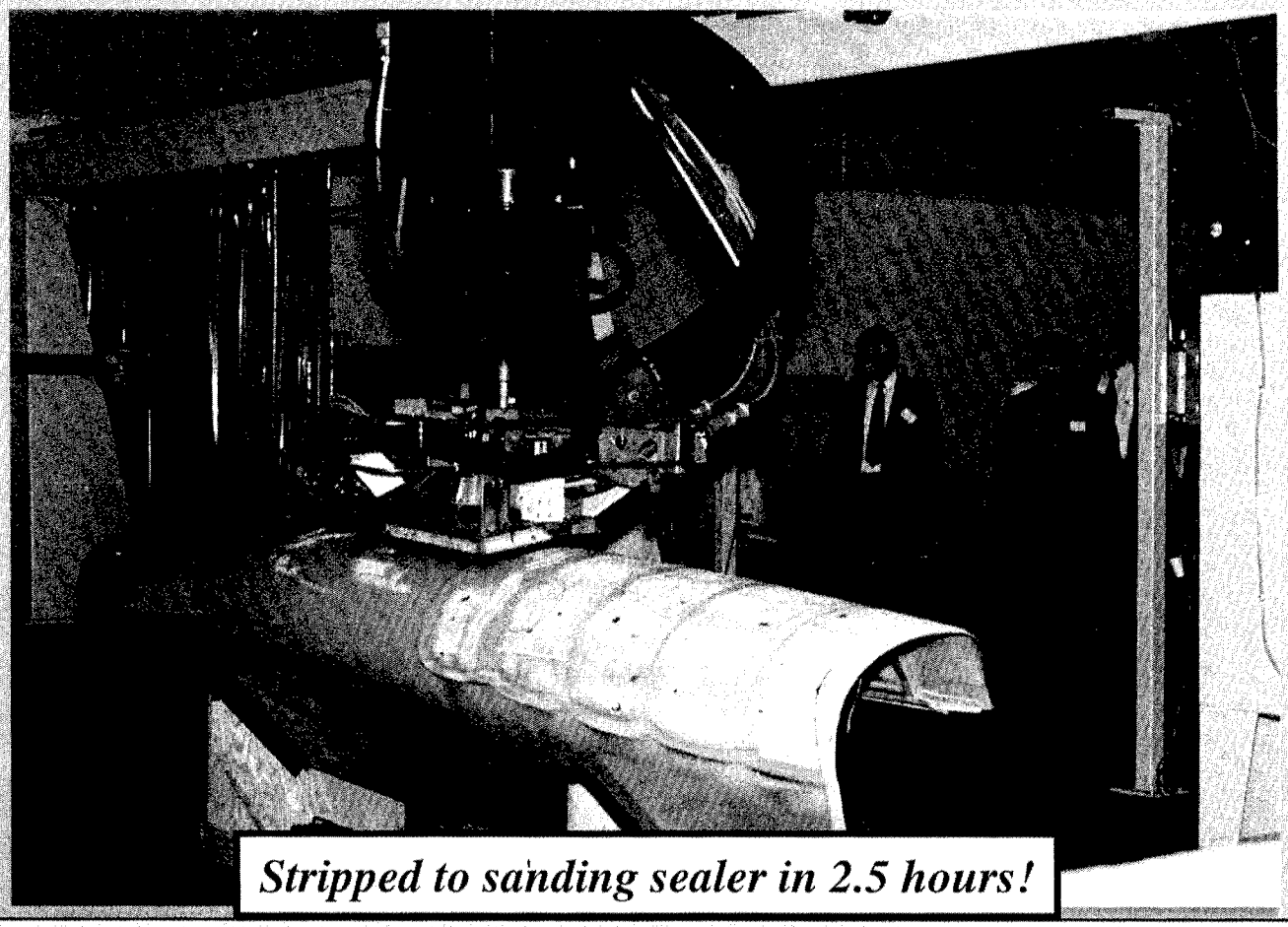
- *44 Aircraft Stripped Since May 1996; Ramp up to 6 Aircraft Per Month*
- *Validated* Recurring Cost, Cycle Time, Environmental, *and* Reliability *Objectives*
- *Paint Shop Workers Operate System and Train New Operators*

Boeing Proprietary

BOEING

FLASH

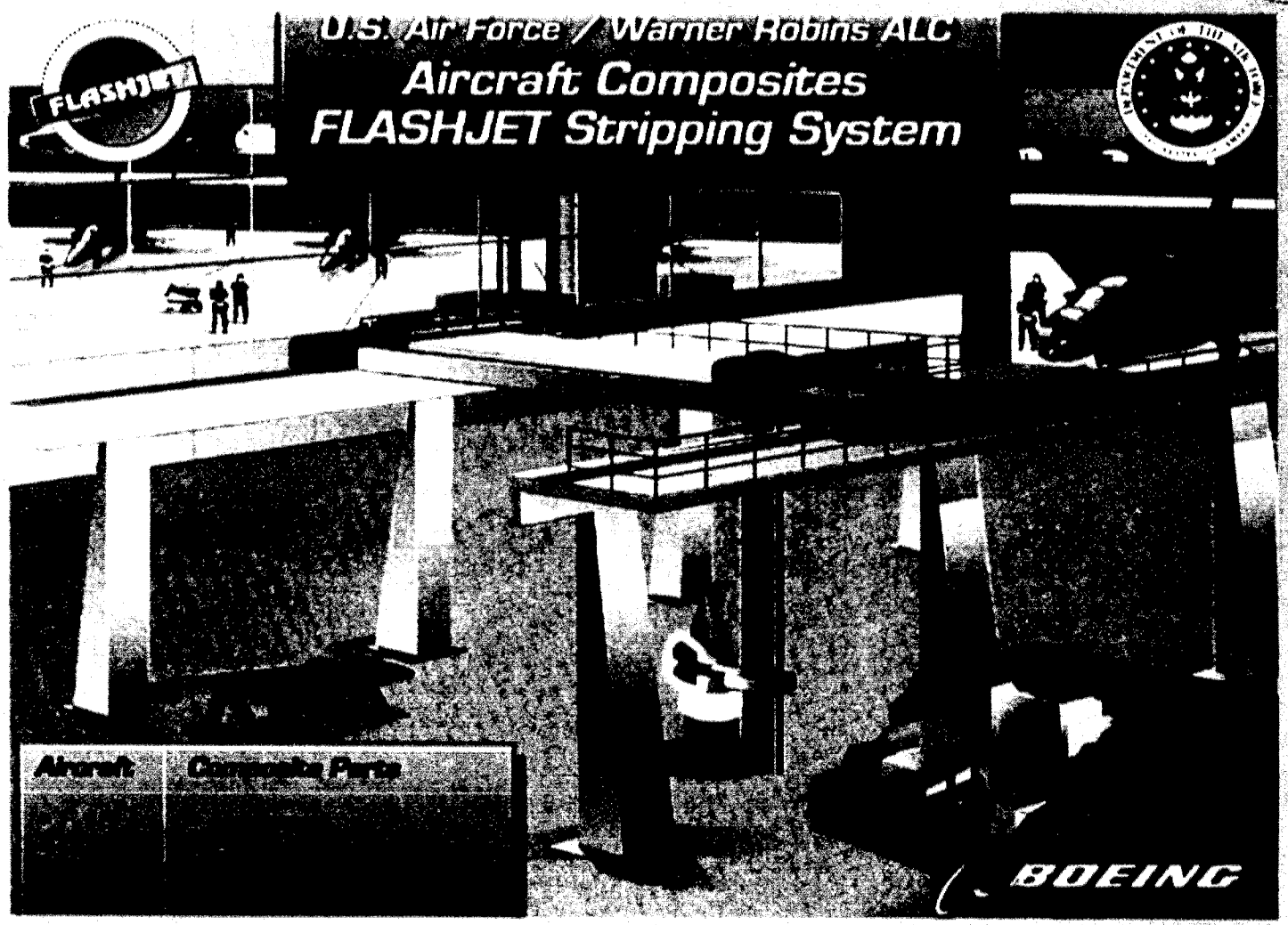
Boeing 747
Fiberglass "Canoe" Fairing



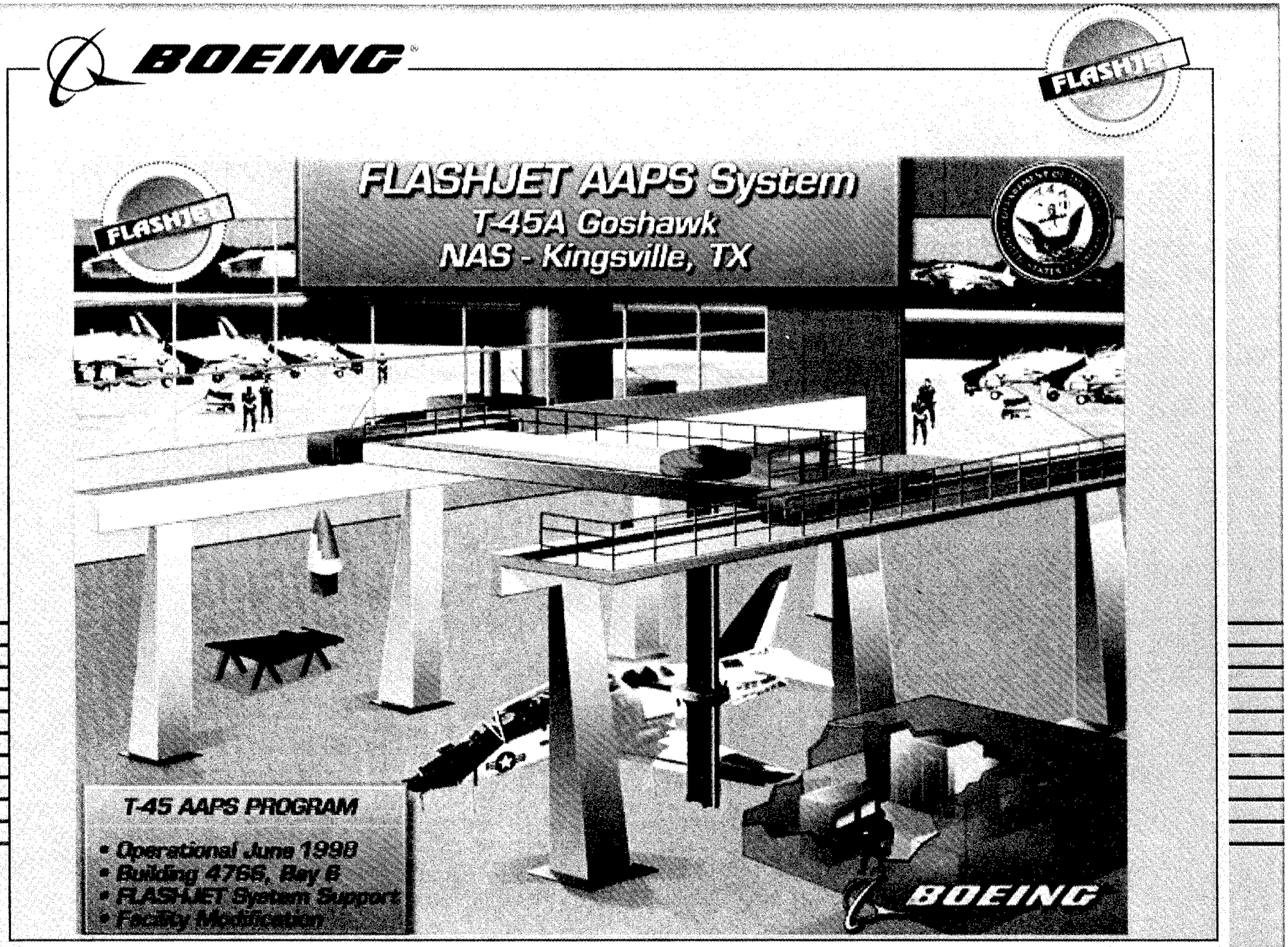
Stripped to sanding sealer in 2.5 hours!

Boeing Proprietary

BOEING

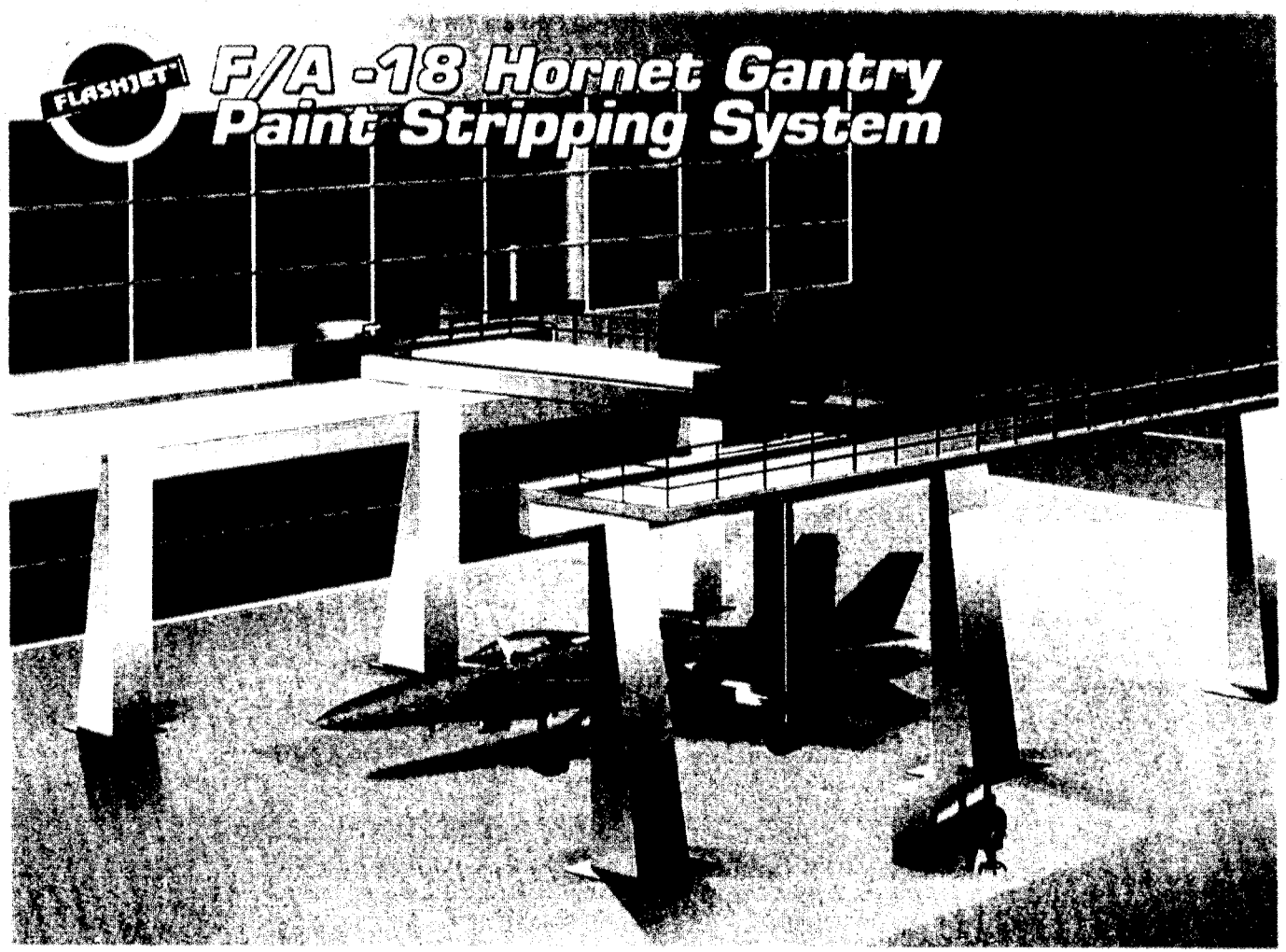


Operational 1Q 1999


BOEING
FLASHJET
FLASHJET AAPS System
T-45A Goshawk
NAS - Kingsville, TX
T-45 AAPS PROGRAM
• Operational June 1998
• Building 4766, Bay 6
• FLASHJET System Support
• Facility Modification
BOEING

BOEING

FLASHJET

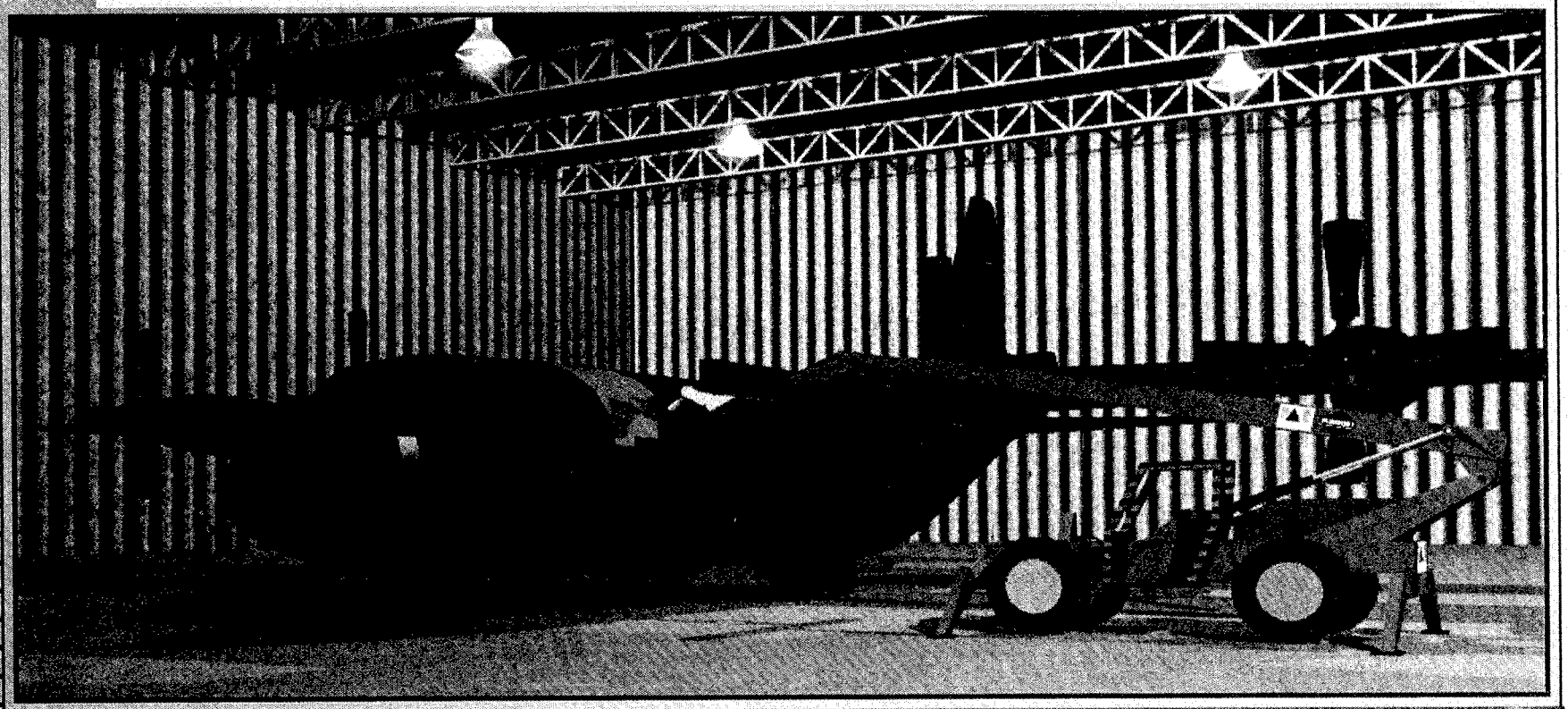


Full Aircraft or Off-Aircraft De-paint Capability

BOEING

FLASHJET

C-130 Mobile Manipulator Program



- First Integrated Transport Aircraft Flashjet System - designed for all types
- USAF C-130 System Demonstration/Validation at Boeing-Tulsa - Mid 1998
- Deliver to Singapore Technologies - Depaint SAF & USMC Aircraft - late 98

Boeing Proprietary

BOEING

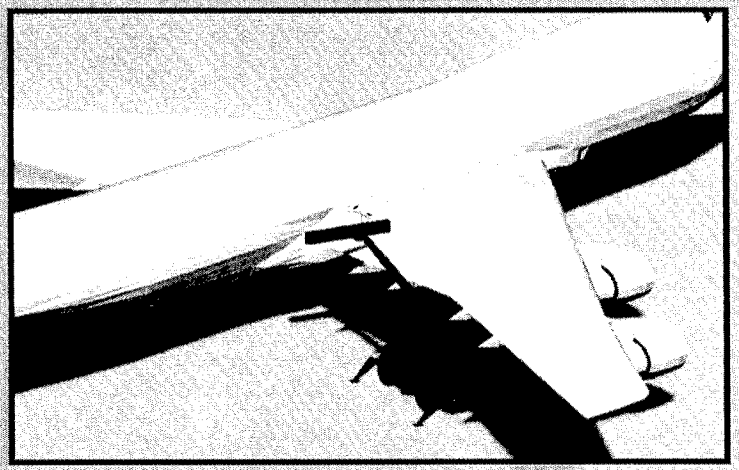
FLASHJET

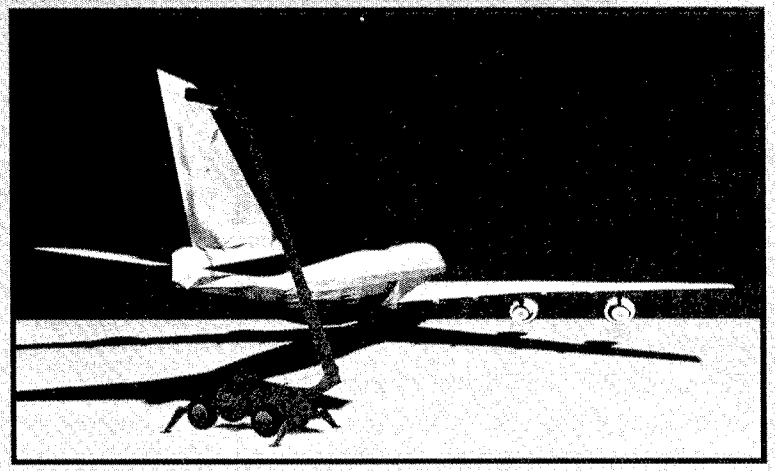
C-130 Aircraft Demonstration
Concept

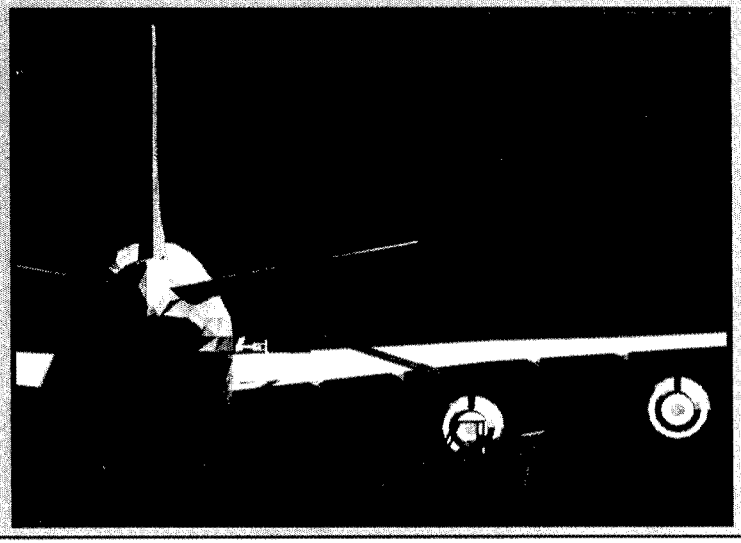
- **Boeing Developed System As Non-developmental Item**
  - Internal R & D funding for design, integration and test
- **3 Month Demonstration/Validation - May-July 1998**
  - Tulsa, OK facility
- **"Borrow" Civilian C-130 aircraft**
  - 100% depaint - (90+ % with FLASHJET, remainder with TBD process)
- **Formal Performance Objectives**
  - 15 specific criteria including recurring cost and strip cycle time metrics
- **Invite DoD/Industry Participation/Observation of Dem/Val**

BOEING

FLASHJET Mobile Manipulator



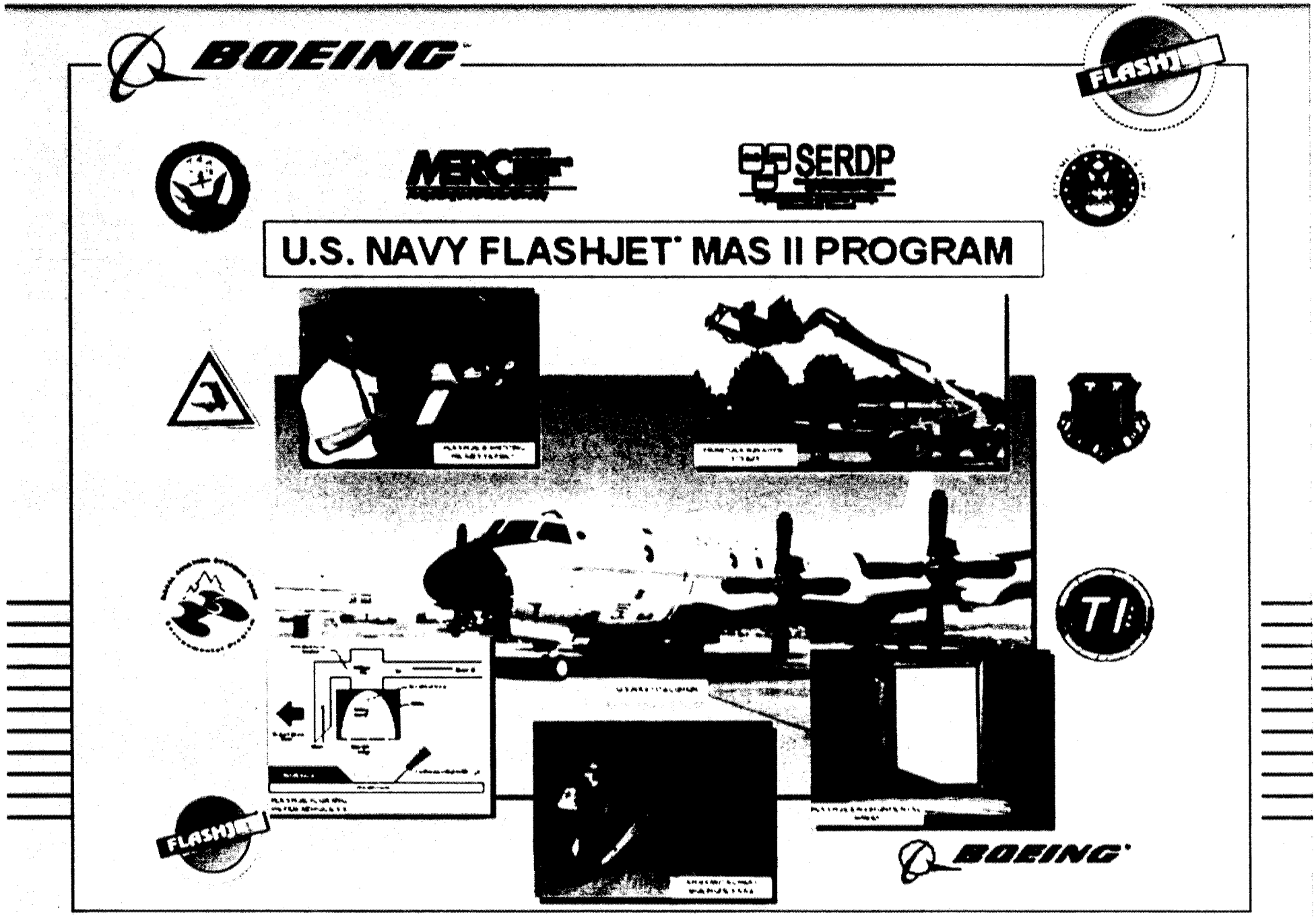




Manipulator System

- **Boom Truck Based System**
- **Concept Demonstration Mid-1998**
  (C-130 Demonstration)
- **Designed for range of transports**
  (Narrow/Wide body - up to 747/C-17)
- **Multiple Unit Operation (2-4 units)**

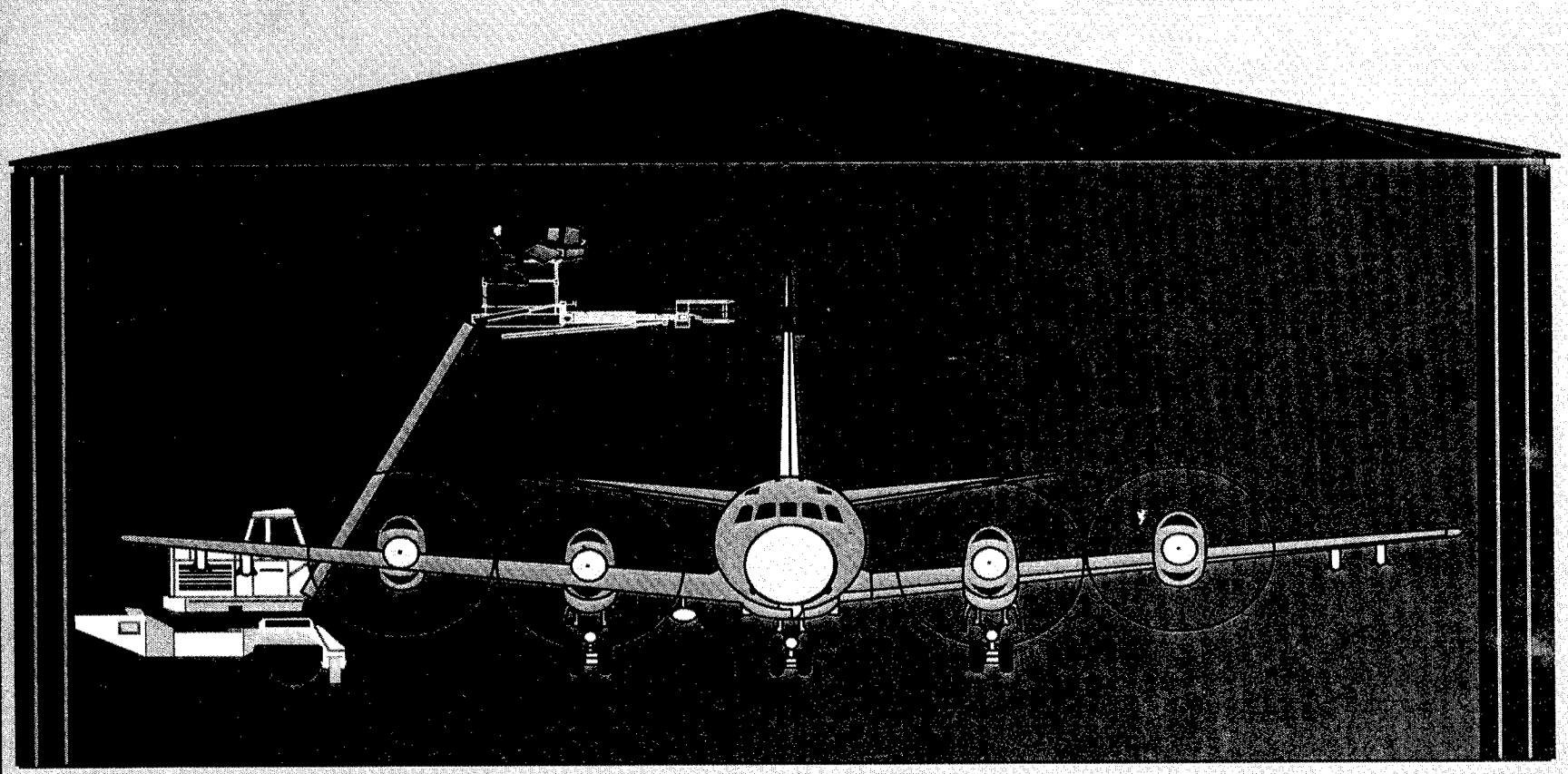
Boeing Proprietary


BOEING
FLASHJET
MERCE
SERDP
U.S. NAVY FLASHJET MAS II PROGRAM
TI
FLASHJET
BOEING

BOEING

FLASHJET

P-3 MAS Installation at NADEP-JAX



Operational April 98 for Demonstrations and Testing

Boeing Proprietary

BOEING

FLASH!

Current Process Approvals

- **Douglas Aircraft**
  - Approved for all substrates
  - No restrictions on cycles
  - Accepted by FAA
- **Boeing Process Specs**
  - St. Louis - All aircraft
  - Mesa - All helicopters
  - Long Beach - All types
- **US Navy**
  - Metallics - Fixed wing aircraft
- **US Air Force**
  - Verbal TO 1-1-8 Revision

1998 Process Approvals

- Boeing Commercial - Internal approval evaluation
- US Navy Composites - Fixed wing aircraft
- US Air Force - TO 1-1-8 Revision
- US Army - TBD....tied to CCAD System
- ESTCP Helo Program - Tri-Service/OEM approva
- Gen. Aviation OEMs - Cessna, Raytheon, Gulfstream

BOEING

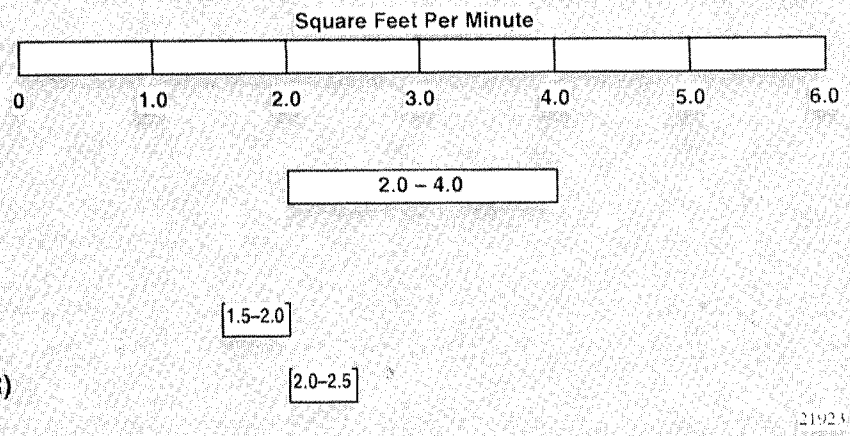
FLASHJET

Life Cycle Cost and Cycle Time

- **Life Cycle Cost**
  - **Unit cost** ~$2.9M - established catalog pricing
  - **Recurring cost** < $4 per sq. ft.
    - » Minimal preparation and post-strip labor
    - » Low operator labor cost - automated system
  - **Pay back period** 1.5 to 2.5 years depending on utilization
    - » Recurring cost is *1/3rd PMB*, *1/4th Chemical strip*
- **Cycle Time**
  - FLASHJET *depaint rate* is *2 to 4 sq. ft. per minute*
  - *Eliminate* most *pre - and post-depaint preparation time* (washing/masking)
  - *Eliminate re-alodine process* (conversion coating) of aircraft

BOEING

FLASHJET Nominal Strip Rates



- TO PRIMER (4 MILS TOPCOAT)
  METAL OR COMPOSITE
- TO BARE METAL (5 MILS TOPCOAT & PRIMER)
- TO BARE COMPOSITE (5 MILS TOPCOAT & PRIMER)

Paint Systems Stripped With Flashjet Process

- Primers: Epoxy , Polysulfide, Polyurethane
- Topcoat: Polyurethane, High Solids, Unicoat, CARC

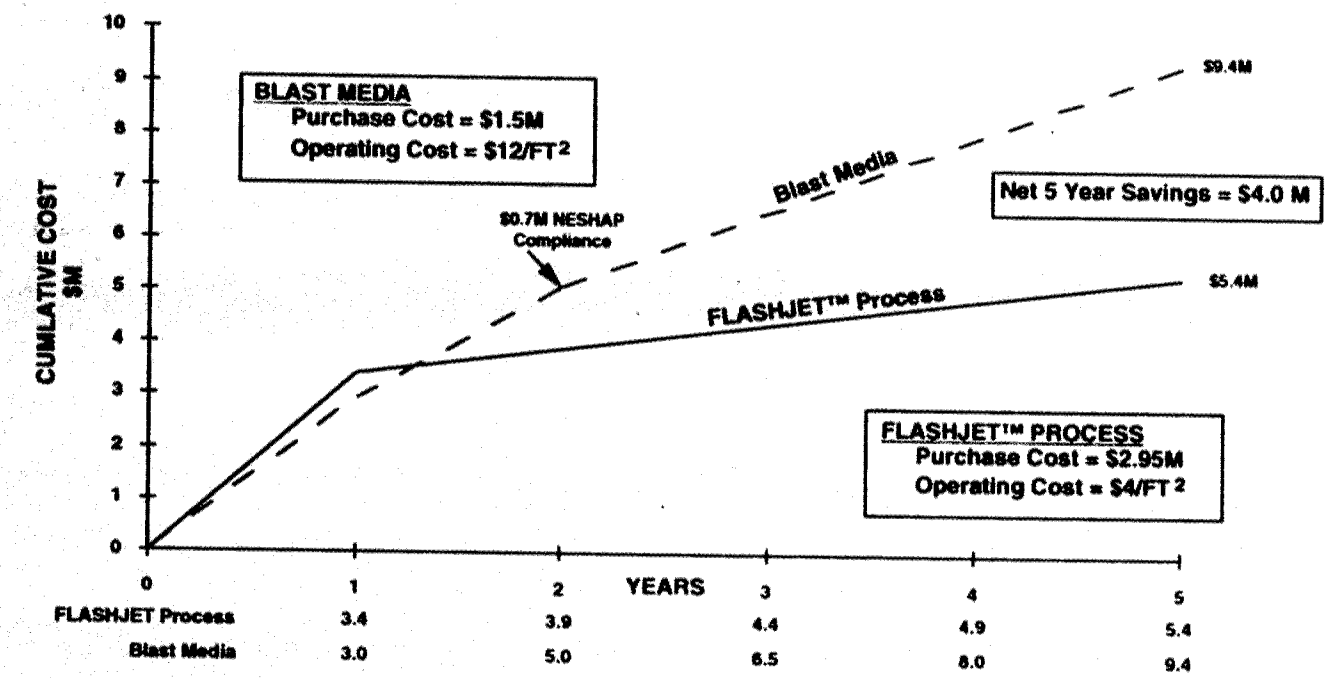
Boeing Proprietary

BOEING

FLASHJET Process Vs. Blast Media

Five Year Life Cycle Cost Comparison

CASE A1: Invest in Either New FLASHJET System or New Blast Media System



	0	1	2	3	4	5
FLASHJET Process		3.4	3.9	4.4	4.9	5.4
Blast Media		3.0	5.0	6.5	8.0	9.4

Assumptions:
1. 120,000 square feet stripped per year (50% capacity)
2. Blast media capital cost is 50% of FLASHJET Process capital cost
3. Blast media NESHAP compliance cost = $0.7M
4. Assumes one-shift operation only

BOEING

FLASHJET

C-17 Feasibility Study Results

- Comparison Based On Kelly AFB Facility
- Actual C-5 PMB Cost and Cycle Time Adjusted For C-17 Moldline
- 120 Unit C-17 Fleet - Each Aircraft Depainted Twice (240 Net) in 20 years
- 1997 Economics (Not Discounted)

Item	FLASHJET Per C-17	PMB Per C-17	FLASHJET Total LCC	PMB Total LCC
Total Cost	$78,288	$307,100	$24.64M	$73.70M
Depaint Cost per Sq. Ft.	$3.52	$13.81	n/a	n/a
Labor Cost	516 hrs	3,374 hrs	123,840 hrs	809,760 hrs
Materials Cost	$14,213	$22,032	$3.41M	$5.29M
HAZMAT Disposal - Cost	$673	$6,835	$0.16M	$1.64M
HAZMAT Disposal -Volume	112 lbs.	1,092 lbs.	26,880 lbs	262,080 lbs.
Total Depaint Flow Time	125 hrs (2 units)	159 hrs	30,000 hrs	38,160 hrs

Boeing Proprietary

BOEING

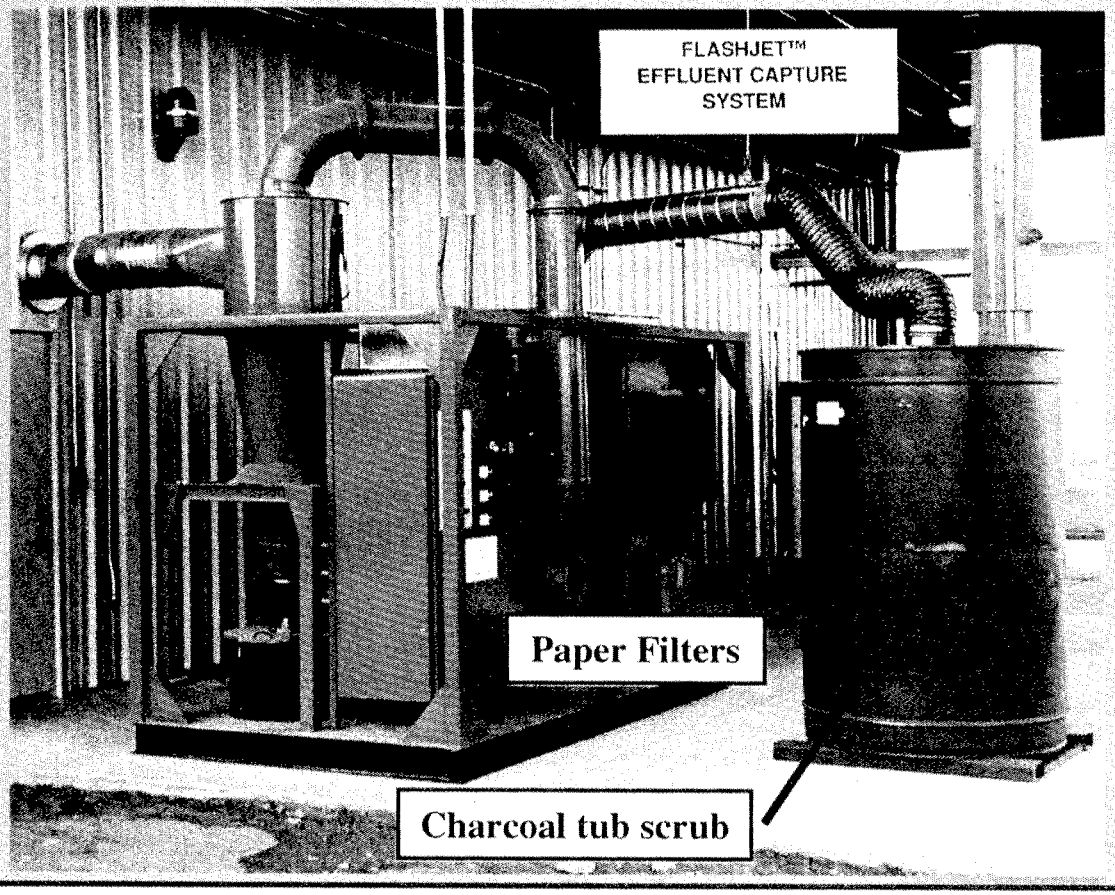
FLASH!

Environmental Issues

- **Process Does Not Use Or Produce Media**
  - No hazardous chemical or dry media disposal
  - Particulate and fume effluent is captured in disposable filters
- **Process Does Not Produce Hap Emissions**
  - Compliant with HESHAP and OSHA regulations
- **System Captures Airborne Contaminants**
  - Residual paint effluent and chromium emissions captured at source
- **Minimal Worker Safety Requirements**
  - Eye protection for ultraviolet light emissions
  - Hearing protection for compressed air noise emissions (~92db @ 3 feet)
  - Air exchange to vent CO_2 vapor
- **Eliminate Re-alodine of Aircraft**

BOEING

FLASHJET Effluent Capture System



Waste is captured in paper filters (dust/ash) or charcoal scrubber (fumes)

Boeing Proprietary

BOEING

FLASH!

Worker Health/Safety

- Hearing and Eye Protection Are Only Requirements
- No Hazardous Chemicals/solvents of VOCs
- Airborne Contaminants - Trace Levels (Below Minimums)
- No Exposure to Chromate/heavy Metals
- No Explosion or High-pressure Media Hazard
- No Fire Hazard From Surface Combustibles
- No Caustic Detergents Required for Pre-cleaning

FLASHJET System Installation Requirements

- **Minimize Facility Modifications**
  - Use existing hanger facilities
- **Electrical Power**
  - 480 volts/3 phase/700 amp service per system
- **External Concrete Pad**
  - Liquid CO_2 storage tank
  - Air compressor and air cooler unit
  - Effluent Capture System
- **Ventilation**
  - Standard exhaust to outside

BOEING

FLASH!

1998 Special Events

• USN P-3 Demonstration at NADEP-JAX	April-July
• F-15 Wing/Fuselage Demo at Mesa	2Q
• WR-ALC Gantry System Ground Breaking	2Q
• C-130 Mobile System Dem/Val at Tulsa	June-July
• T-45/NAS-Kingsville System Ribbon Cutting	July
• ESTCP Helicopter Demonstration at Mesa	3Q-4Q
• Singapore Mobile System Operational	4Q

Boeing Proprietary

BOEING

FLASHJET

The Best Paint Stripping Solution

Customer Requirements	FLASHJET
• **Safe** For ALL aerospace substrates	✔
• **Cost Effective** Both operating and facilities costs	✔
• **Fast** Satisfy operator throughput requirements	✔
• **Environmentally Compliant** Federal, State and Local regulations	✔
• **Improved Worker Conditions** Improved productivity and morale	✔

Boeing Proprietary

General LASERTRONICS Corporation

Engineering Excellence

LASER COATINGS REMOVAL

PRESENTED AT

3rd AEROSPACE ENVIRONMENTAL TECHNOLOGY CONFERENCE

June 1-3, 1998

BY

Terry L. Fuchser, Product Manager

PRESENTATION OVERVIEW

- Coatings Removal Requirements
- Removal Technologies
- Why Lasers?
- Product Status
- Environmental/Social Impact
- System Features/Options
- Current Programs
- Bottom Line

COATINGS REMOVAL REQUIREMENTS

- The Coatings Removal System Should:
  - Be environmentally Friendly
  - Be non-toxic
  - Be user friendly
  - Have low life cycle costs
  - Be safe for personnel
  - Be cost effective
  - Have no affect on paint adhesion
  - Produce no damage to the substrate
  - Have minimal clean-up cost
  - Be controllable
  - Be non-corrosive
  - Be as fast as chemical stripping

REMOVAL TECHNOLOGIES

Wheat Starch

Steel Shot

Flash Lamp

CO_2 Pellets

LASER

Flash Lamp/CO_2 Pellets

Waterjet

Sodium Bicarbonate

Plastic Media

WHY LASERS

- Non-Media Based - No Impact Damage To Substrate
- Reduced Waste Disposal
- Controllable - Depth & Color
- Environmentally Friendly
- Non-Toxic
- User Friendly
- Personnel Safe
- No Clean-Up Cost
- Removes Light Corrosion

WHY LASERS (CONT'D)

- Scaleable Removal Rates
- No Intrusion Problem As With Chemicals Or Media
- No Masking Or Special Apparel Necessary
- Low Life Cycle Cost - High Reliability, Low Maintenance
- Cost Effective
- Highly Versatile

CURRENT PRODUCT STATUS

- ***LAZE-ABLATOR*™ Product Line**
  - Mobile, Autonomous, Handheld Capability
  - Selective Coating Removal: Color & Depth
  - Performed Testing On Aircraft Composite Materials As Well As Metals
  - In Process of Validating Technology Through Lockheed Martin Skunk Works Program
  - Certified For Class 1 Use (Eye Safe / Skin Safe) Through FDA

PHOTO OF DEMONSTRATOR

PHOTO OF HANDHELD UNIT

ENVIRONMENTAL / SOCIAL IMPACT

- **Laser Most Environmentally Sound:**
  - Coatings Are Made Up Of Two Chemical Compounds
    - Organic Compounds (Fillers, Binders)
    - Inorganic Compounds (Pigment, Fillers)
  - Lasers Vaporize All Organic Compounds, Leaving Only The Inorganic Compounds To Be Collected For Waste Disposal
  - Most Coatings Are Approximately 70% Organic

IMPACT (CONT'D)

- **Our Systems Have A Complete Waste Management Module Tailored To A Specific Application**
  - Our Systems Process all Gases, Fumes and Residue, Before Venting
  - The Remaining Inorganics Are Captured In A Canister Or Filter Bag

SYSTEM FEATURES/OPTIONS

- Portable
- Handheld, Tele-Robotic Or Robotic Integration
- Color Feedback System For Selective Stripping
- Waste Management System
- Programmable For Geometric Shapes
- Workhead Interchangeability
- Safety Features
- Scaleable

PROGRAMS

- Air Force contract for developing a semi-automated system for paint stripping and NDI (Non Destructive Inspection) on underbodies of transport aircraft
  - The technologies include:
    - > Laser
    - > Water Jet Blasting
    - > Plastic Media Blasting
    - > Flashjet
  - The candidate aircraft include:
    - > C130
    - > C141
    - > C17
    - > C5

LTS VIDEO

PROGRAMS (CONT'D)

- Air Force program (Phase l SBIR) to design and build a portable, non-damaging depaint system for removing coatings from small areas of various aircraft
  - Laser technology will be employed, featuring a handheld workhead
- Collaboration with Lockheed Martin Skunk Works for coating removal characterization, aircraft safety studies and other applications validation

PROGRAMS (CONT'D)

- Joint EPA/NASA/USAF Interagency Depainting Study
  - Laser and other depainting technologies are being tested for use on military and commercial aircraft
  - *LASERTRONICS* has been chosen to provide the laser technology and perform the stripping operations on prepared samples for this study
- Technical Advisory Committee Includes:
  - Aircraft Owners & Pilots Assoc.
  - The Boeing Co.
  - Delta Airlines
  - Lockheed Martin Space Operations
  - Northrop Grumman
  - Ratheon Aerospace
  - United Airlines
  - Sikorsky Aircraft Corp.

BOTTOM LINE

LASER COATINGS REMOVAL SYSTEM:

- Provides Flexibility & Versatility of Application
- Reduces Costs Associated With Setup, Process Equipment, Cleanup and disposal
- Environmentally & User Friendly
- May Be Tailored To A Full Range Of Applications
  - Customized to meet customer's specific operational requirements

Interagency Depainting Study Status

Marceia Clark-Ingram
Beth Cook
NASA/MSFC

Regulatory Background

- The National Emission Standards for Hazardous Air Pollutants for Aerospace Manufacturing and Rework Facilities **(Aerospace NESHAP**) regulates Depainting Operations
  - limits methylene chloride usage for coating removal
  - **commercial :** 26 gallons/craft/year
  - **military:** 50 gallons/craft/year

Regulatory… (Continued)

- Initial Aerospace NESHAP promulgated in **September 1995** - subsequent versions exist.
- First substantive compliance date for existing sources is **September 1998.**
- The Occupational Safety & Health Administration (OSHA) established stringent Permissible Exposure Limits (PEL) effective April 1997.

Partners are:

- EPA

  Emission Standards Division (ESD)

- NASA

  Headquarters, Code JE

  Marshall Space Flight Center (MSFC)

- USAF

  Robins Air Force Base (RAFB)

  Wright Patterson Air Force Base (WPAFB)

Committees are:

- Executive Steering Task Force (ESTF)

  comprised of EPA/HQ, EPA/ESD, NASA/HQ, and NASA/MSFC

- Technical Implementation Committee (TIC)

  comprised of NASA/MSFC

- Technical Advisory Committee (TAC)

  comprised of EPA/ESD, NASA/HQ, NASA/MSFC, USAF/WPAFB, USAF/WRAFB, USCG, General Aviation and Airline Industry

Processes Being Evaluated

- Chemical Stripping
- COLDJET™ (CO_2 Blasting)
- TOMCO$_2$ (CO_2 Blasting)
- FLASHJET™ Coating Removal
- Laser Stripping
- Plastic Media Blasting
- Sodium Bicarbonate Wet Stripping
- Water Stripping
- Wheat Starch Blasting

* COLDJET ™ and TOMCO $_2$ processes deleted from evaluation after 1st stripping.

Initial Parameters of the Study

- Substrates

  2024-T3 clad Al, in 64, 32, and 16 mil thicknesses

  2024-T3 non-clad Al, in 64, 51, and 16 mil thicknesses

- Paint System

  primer: MIL-P-23377F, Type 1, Class 2

  topcoat: MIL-C-83286B, urethane

- Five sequences of panel preparation and stripping.

Current Parameters of the Study

- Substrates - no change
- Paint System (implemented in 2nd sequence)

  primer: no change

  topcoat: MIL-C-85285B (high solids, low voc)

  – previous topcoat no longer available from vendor
- Three to five sequences of panel preparation and stripping.

Stages in Each Sequence

- Coating Application
- Measurements - coating thickness
- Aging
- Stripping
- Measurements - substrate thickness, surface roughness
- Specimen Cleaning - WBF surface
- Chromate Conversion
- Measurements - substrate thickness and weight, surface roughness
- Repeat for next sequence

Preparation of the Test Specimen

- Cleaning Steps:

  MEK hand clean.

  Vapor degrease with perchlorethylene, 10 min.

  Immerse in Turco 4215, 25 min.

  Hot DI water rinse, 5 min.

  Immerse in Turco Smut-Go #1, 11 min.

  Cold DI water rinse, 5 min.

  WBF test, DI water.

Test Specimens ..... (Continued)

- Aging Steps per ***ISO/SAE MA4872***:

  Precondition : 12 hours @ 120F, 95%RH

  Hold at -65 for 1 hour

  Thermally cycle for -65F to 160F 400x.

  Return to chamber to ambient temperature.

  Repeat steps 1-3.

Material Evaluation Testing

- Fatigue and Tensile - *baseline & final stripping*
- Sandwich & Immersion Corrosion -*completed*
- Hydrogen Embrittlement - *completed except for Gage*
- Crack Detectability - *PMB, Wheatstarch, Sodablast, on-going*
- Clad Penetration-***baseline & final stripping***
- Surface Roughness - *on-going*
- Material Loss, Change in Thickness - *on-going*

Status to Date

- Current process status:

Chemical Stripping	completed 4 of 5 strippings
COLDJET™	dropped from study
$TOMCO_2$	dropped from study
FLashjet™	completed 3 of 3 strippings
Laser Stripping	completed 2 of 3 strippings
Plastic Media Blasting	completed 3 of 4 strippings
Sodium Bicarb. Wet Stripping	completed 3 of 3 strippings
Water Stripping	completed 3 of 3 strippings
Wheat Starch Stripping	completed 3 of 3 strippings

Next Steps

- Conclude stripping sequences.
- Initiate final material testing to compare to baselines.
- Evaluate process performance.
- Provide conclusions to EPA.
- Targeted conclusion of study is December 1998.

Process Comparisons

- Unable to recommend one process over another due to following:
  - manual vs. automatic
  - ease of use, operability
  - capital investment costs
  - no final fatigue data at present

Chemical Stripping

- Data taken from three sequences.
- Approximately 40 candidates - downselected to 10 chemical strippers (5 alkalines & 5 acids)

Chemical Type	Dwell Time
Baselines	12 minutes
Alkalines/Neutrals	5.3 hours
Acids	5 hours

CO_2 Blasting

- Two systems: COLDJET™ Model 65-250 and TOMCO$_2$ DI-250.
- COLDJET™ system caused significant deformation on 16 mil specimens and even 64 mil specimens showed surface damage.
- TOMCO$_2$ system was capable of some coating removal but allowable pressure was too low for efficient stripping.

Flashjet™ Coating Removal

- Generous time and effort donated by McDonnell Douglas in St. Louis, MO.
- Data taken from two sequences.

Substrate Thickness	Strip Rate
16 mils	109 in^2/min
51 mils	136 in^2/min
64 mils	128 in^2/min

Plastic Media Blasting

- Data taken from two sequences.
- Media: type V Plastic Media, 20/30 & 16/20 mesh
- Nozzle diameters: 0.25" @ throat ,0.50" @ exit

Substrate Thickness	Blast Pressure	Strip Rate
16 mils	30 psi	17 in^2/min
51 mils	35 psi	20 in^2/min
64 mils	40 psi	18 in^2/min

Sodium Bicarbonate Wet Stripping

- Data taken from two sequences.
- First sequence was manual with great variance in strip rate.

Substrate Thickness	Strip Rate
16 mils	-----
51 mils	145 in^2/min
64 mils	167 in^2/min

Water Stripping

- Data taken from two sequences.
- Stripped using a customized system of robotics and spray equipment.

Substrate Thickness	Strip Rate
16 mils	139 in^2/min
51 mils	408 in^2/min
64 mils	390 in^2/min

Chemical Stripping

- Maintain environment at an rH of 34% and a temperature between 80 & 86 F.
- Apply fine mist of stripper over panel.
- Apply heavier mist 30 minutes later.
- Check at 2 hour intervals.

  if any paint is released, brush panel and reapply stripper as before.

Wheat Starch Stripping

- Generous time and effort donated by CAE Electronics, Montreal Canada.
- Data taken from two sequences.

Process	Substrate Thickness	Strip Rate
semi-automated	16 mils	249 in^2/min
semi-automated	51 mils	459 in^2/min
semi-automated	64 mils	459 in^2/min
manual	16 mils	76 in^2/min
manual	51 mils	96 in^2/min
manual	64 mils	76 in^2/min

The Successful Transfer of Space Derived Convergent Spray Technology (TM): An Application for Industrial Roof Coatings and Interstate Bridge Repair

•

•

- Vernotto McMillan
  - NASA/MSFC
  - Mailstop: C030
- Huntsville, AL 35812
  - (256) 544-2615

•

The Successful Transfer of Space Derived Convergent Spray Technology (TM): An Application for Industrial Roof coatings and Interstate Bridge Repair

The NASA MSFC Technology Transfer Office has Eight Mission Areas:

- Technology Deployment Partnerships
- Technology Development Partnerships
- Small Business Innovation Research and Small Business Technology Transfer Research
- Facilities Commercialization
- New Technology Reporting
- National, Regional and Local Strategic Alliances
- Technology and Software Commercialization
- Technology Education and Outreach Projects

Note: The two subject projects were Technology Deployment Partnerships

The Successful Transfer of Space Derived Convergent Spray Technology (TM): An Application for Industrial Roof coatings and Interstate Bridge Repair

Introduction:

A Technology Deployment Partnership was formed among NASA's Marshall Space Flight Center (MSFC), the Environmental Protection Agency (EPA), and United Technologies USBI Company to develop, demonstrate, and evaluate a technology that uses a solvent-less spray process for depositing a lightweight, highly filled roof coating on low sloped commercial roofs.

A second partnership was formed among MSFC, the Federal Highway Administration, Alabama Department of Transportation, and USBI Company for the purpose of developing and demonstrating the Convergent Spray Technology (TM) as a method of applying a skid resistant coating to interstate roads and concrete bridge deckings. Again, different materials and coatings were evaluated and tested before the final selection of ground flint and resin were demonstrated on Interstate 65 near Huntsville, Al and the Mobile Bankhead Tunnel.

The Successful Transfer of Space Derived Convergent Spray Technology (TM): An Application for Industrial Roof coatings and Interstate Bridge Repair

Purpose:

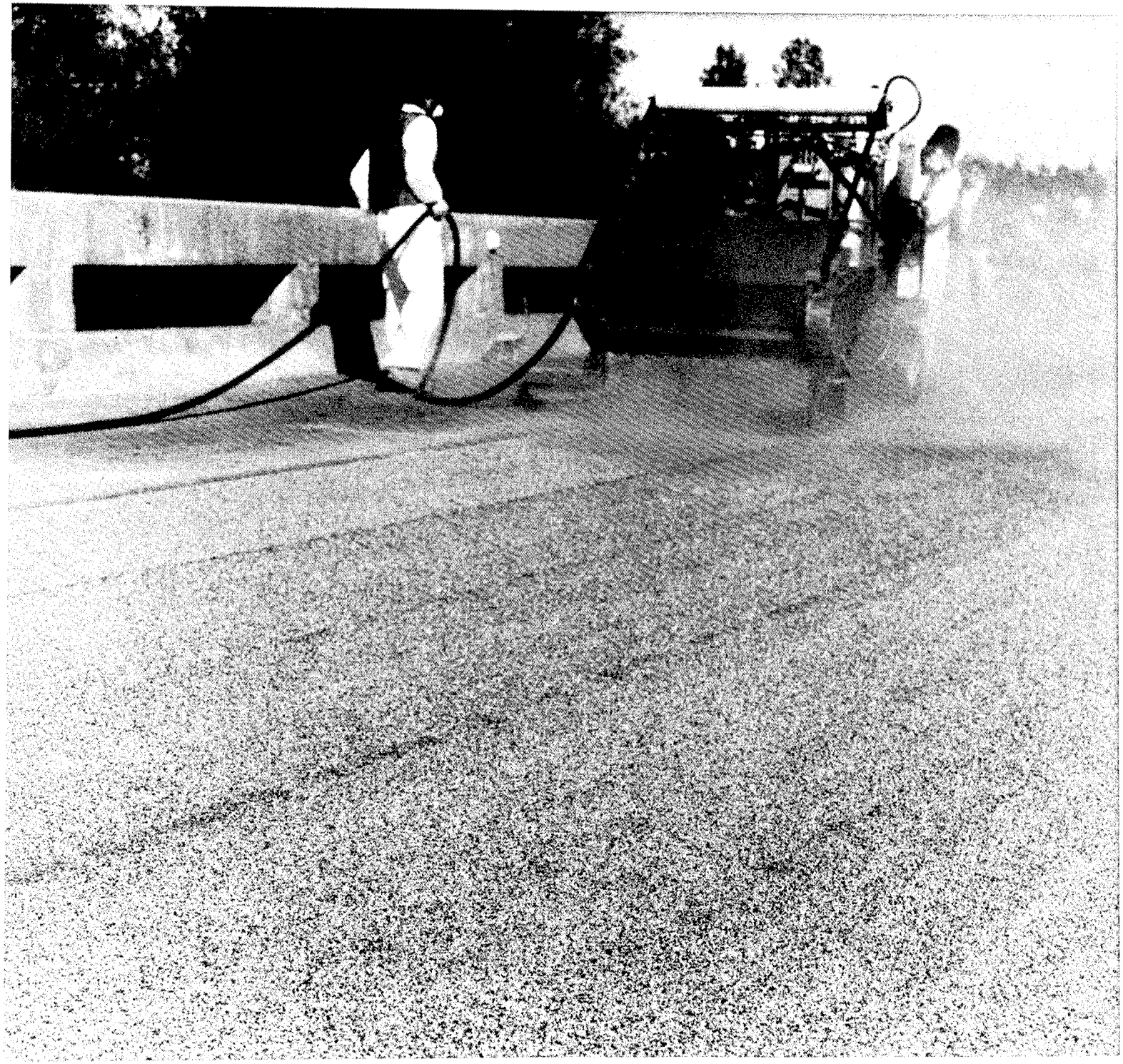
Although the levels of volatile organic compound (VOC) emissions from industrial roof coatings and paint operations have been reduced in recent years, the roof coating partnership was an effort to further reduce VOC emission levels and to also demonstrate the use of reclaimed automobile tire rubber as a filler material in roof coating systems. Different materials and coatings were evaluated and tested before the final selection was used to coat the roofs of two small buildings at NASA's MSFC during fiscal year 1997.

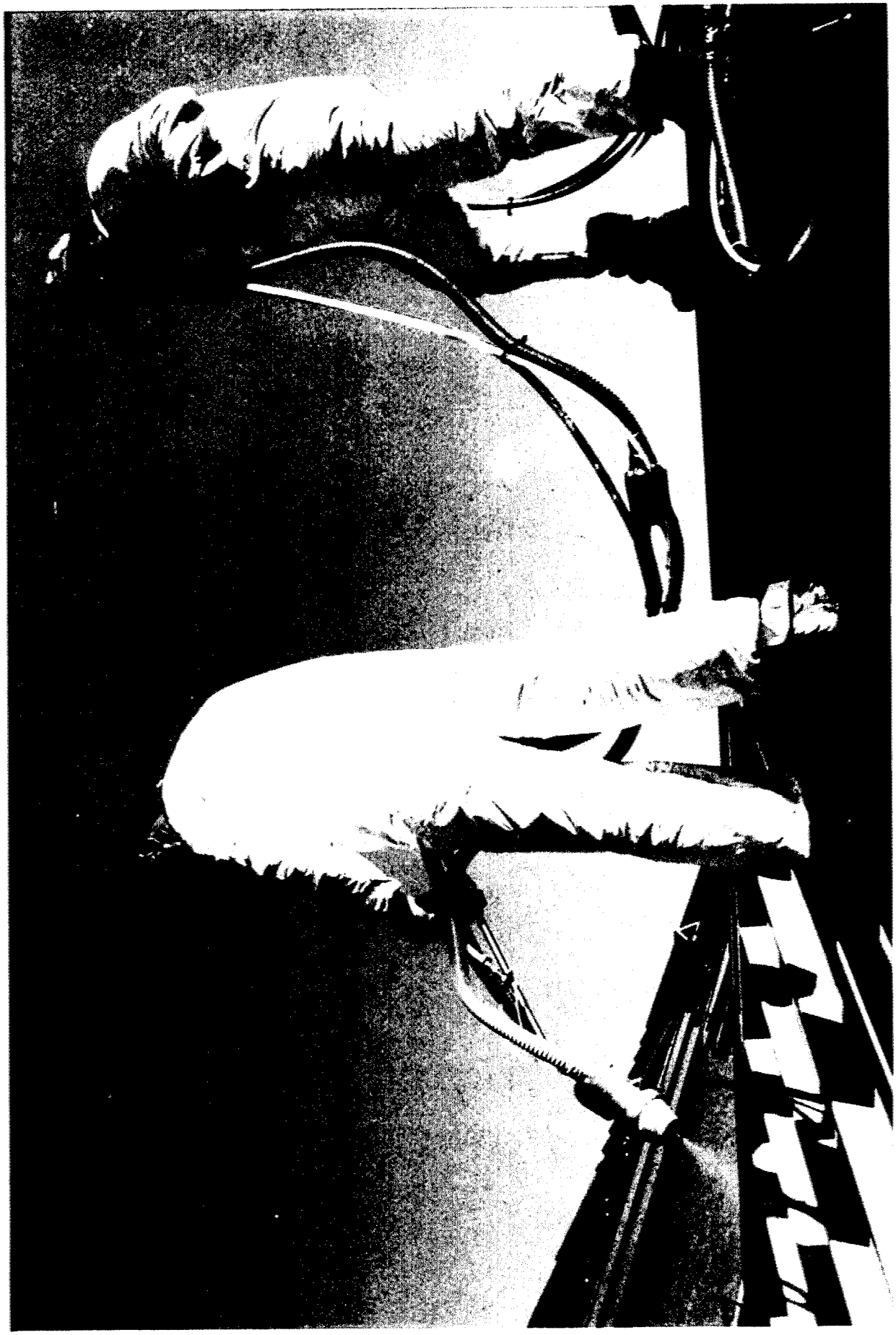
The primary objective of the Bridge repair partnership was to strategically leverage public and private sector funds for the purpose of developing a bridge repair process that was cheaper, better, and faster than conventional methods. It was also, imperative that this process be environmentally friendly and capable of performing under extreme conditions for a period of not less than 2 years.

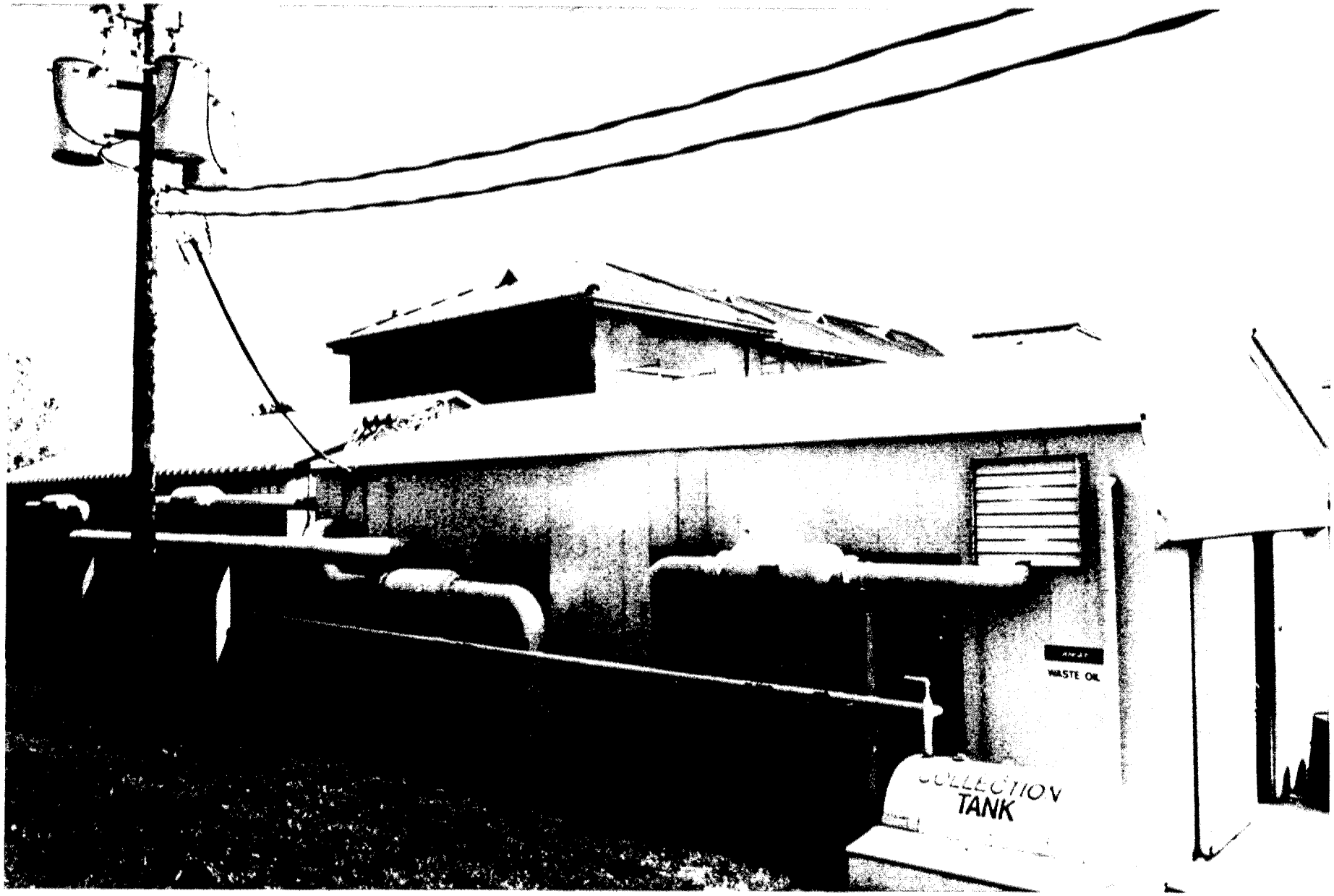
The Successful Transfer of Space Derived Convergent Spray Technology (TM): An Application for Industrial Roof coatings and Interstate Bridge Repair

The roof coating project successfully leveraged the investment of NASA, EPA, and private sector resources to demonstrate a pre-commercial roof coating process. The process utilized the Convergent Spray Technologies (TM) process, which was initially developed by USBI to apply highly filled,thermal protection coatings to the Space Shuttle Solid Rocket Boosters.

The bridge repair partnership afforded a cheaper, better, faster method of applying a skid resistant coating to bridge deckings and interstate roads. The project successfully leveraged the investment of NASA, Federal Highway Administration, the Alabama Department of Transportation, and private sector funding. December of 1998 will mark the end of a two year evaluation period that the Department of Transportation will be assessing the coating's performance. Once certified, the coating and process could revolutionize the way road surfaces are repaired throughout the country.






WASTE OIL
COLLECTION
TANK

Newer Cleaning Processes: Steam, CO2, Plasma, and Maximal Solvent Containment

Barbara Kanegsberg
BFK Solutions
16924 Livorno Drive
Pacific Palisades, CA 90272
310-459-3614
email: bkanegsberg@compuserve.com

and

Don Paquin
Metroline Incorporated
2464 Tripaldi Way
Hayward, CA 94545 – 5017
510-780-1070

Introduction

In evaluating and implementing new cleaning processes, components manufacturers are typically faced with juggling the requirements for consistent performance, affordable cost, worker safety, and a host of conflicting local, national, and global environmental and safety regulations. The political trend, and in many cases the economically astute trend, is toward self-contained, so-called zero-discharge processes which eliminate ozone depleting chemicals (ODC's) control volatile organic compounds (VOC's), and minimize the release of air toxics. The importance of cradle to grave responsibility for the chemicals has led to increasing costs of training, record-keeping, and disposal. Regulatory considerations, combined with ever-increasing contamination control requirements and increasingly close tolerances and miniaturization, has lead to the concept of cleaning by design.

Cleaning by design can mean extra care in choosing the correct cleaning agent, be it aqueous or organic solvent. It can also mean looking at what have been considered as non-traditional cleaning approaches and incorporating them into the build process. In the final analysis, cleaning by design implies stepping back and looking at the entire assembly process to devise more efficient, effective, environmentally sound approaches to manufacturing.

Some examples of non-traditional approaches will be discussed.

Plasma Cleaning

Dry plasma cleaning has long been recognized as a sensible, effective alternative to wet chemicals (4). In plasma processing, surface contamination is removed by electrically excited gas molecules at low temperature (50 degrees C or less) in a vacuum chamber. Relatively safe, inexpensive gases are used and only small quantities of typically non-toxic gases are generated in the process. The cleaning process medium is generated in-situ. The principle advantage of plasma cleaning is that gases can reach inaccessible places and react without leaving a residue. By-products of the process are pumped away. In addition, the volume of material exhausted is orders of magnitude less than from the typical traditional wet chemistry process, for example, the fumes generated by the typical wet etch bath. Considering the high cost of wet chemical treatment and disposal, plasma offers clear advantages.

Plasma cleaning is now becoming standard procedure as a final clean step in applications where extreme cleanliness, consistency, and residue-free surfaces are required. Typical plasma cleaning processes take from thirty seconds to ten minutes. Systems for small components and for fairly large industrial part have been designed.

It should be remembered that plasma cleaning is a final cleaning process It is not designed for the bulk removal of large amounts of soil The parts to be cleaned are already fairly clean to begin with In addition, variables must be optimized for the site-specific application Once those variables have been set, however, the plasma process is likely to need less monitoring than does a traditional wet chemistry process (unless gross unforeseen variables are introduced) Plasma cleaning can also produce surface modification Many engineers have used traditional cleaning agents to introduce subtle surface modification for years; plasma cleaning can enhance the effect This property of surface modification can be a double-edged sword With proper control, surface modification can improve performance, for example, by improving adhesion of coatings or potting compounds to a metal or glass surface Obviously, one wants to avoid unplanned, undesirable modification The best approach is, as always, test before implementing

Case study: plasma, semiconductor

Charlie Young of Fujitsu has successfully adopted a microwave-type off-the-shelf plasma system for cleaning semiconductor dice prior to wire bonding The group had had a contamination problem, probably organic, which had not responded to a variety of approaches, both typical and esoteric The group was reluctant to adopt solvent cleaning due to contractual and specification constraints Using a plasma/O2 system, they were able to solve the contamination problem

Case study: plasma, biomedical

A large biomedical company adopted a plasma system to replace a traditional wet chemistry cleaning system for final cleaning of suture needles with very fine (22 to 50 mil), tapered points Bulk organic contamination (oils and soaps) was removed during initial processing, including high temperature heat treatment and aging Plasma oxidation was used for final cleaning, to remove BS 60 oil, a lubricant containing sulfur and phosphorus A number of factors were varied in optimizing the process including the electric field, gas flow, gas mixture (O2 versus He/O2), pressure, and time An acceptable process was developed, as judged by appearance after electropolishing

Steam Cleaning

Steam cleaning is often thought of as a low technology, low cost process Steam cleaning has been used for years in the food industry, for bulk cleaning of equipment In the military, steam cleaning may be used in field repair operations, including munitions Steam cleaning is relatively low in cost The units are compact Cleaning is accomplished with de-ionized water In some instances, cleaning effectiveness is enhanced by spot-cleaning with aqueous cleaning agents Increasingly, steam cleaning is finding applicability for more critical cleaning processes

Steam cleaning involves a compact, relatively low-cost unit Steam cleaning is an aqueous process, but typically the surface is left clean and dry It can remove hardened, dried soils, including cleaning agent residue In many respects, steam cleaning is environmentally-preferred, because it uses deionized water and generates only very low levels of waste One needs to remember that steam cleaning is a "line-of-sight" cleaning process This means it will not clean around corners In addition, containment hoods or cabinets are preferred to avoid having soil blasting into operators faces The smaller steam systems are meant for benchtop applications They are slow for very large surfaces Steam cleaning requires some employee training/education to achieve consistent application Steam cleaning is not universally effective In one particular instance, steam cleaning was judged ineffective for reliable removal of light oil from a flat metal surface; the steam cleaner simply moved the oil around to different positions on the substrate

Other groups, however, have found steam cleaning to be very effective

Case study, precision flux removal

Richard Yabuki, an assembly engineer at National Semiconductor, has adopted a precision steam cleaning system from Vatran for removing organic acid flux from low-temperature co-fired ceramics Several thousand components, both production and proof of design, are processed monthly The steam cleaner has successfully removed soil from fairly closed-spaced components: 20 mil pitch and as close as 2 3 mil standoff The steam cleaning system replaced a batch cleaner with deionized water During rework, it was apparent that flux had not

been removed with the batch system, because visible flux was present. In addition, spurious measurements (noise) were observed during test (the product is 100% tested). The new system has resulted improved flux removal and better product performance.

Some of the features which Mr. Yabuki has found to have been helpful at National Semiconductor include:
- ease of implementation
- non-complex cleaning agent: deionized water is heated; steam is generated
- very low process waste
- compact unit (4 ft by 4 ft)

Richard evaluated a number of processes. Another group had adopted a jet agitation aqueous washer. There were problems in fixturing, and the footprint was unacceptably large. They investigated ultrasonic cleaning, but were concerned about possible product damage.

Initially, there were problems with solder leaching during cleaning. After modifying the solder reflow process and adjusting the pressure and positioning of the steam nozzle (150 psi and 0.25 inches to 75 psi at 2 inches), the problems were resolved. Overall, the new process was adopted with no problems.

Case study, final cleaning subassemblies

Steam cleaning was also adopted by B/E Aerospace, Galley Products Group. B/E Aerospace, Galley Products Group, produces 90% of aircraft galley refrigeration equipment. Initially, a PDQ Min/Max system with a cleaning cabinet was purchased for gross cleaning during repair of compressor parts after an electrical burnout. At this point, it was discovered that "off-the-shelf" means ready to use – but not yet. There was initial employee reluctance to even try the new equipment. It could not be used for sustained cleaning. The initial model needed some design modifications; the modifications are now standard on new steam cleaners. Ultimately, the unit was transferred to an assembly department. Employees discovered that it is very useful for final cleaning after aqueous cleaning. It removes traces of cleaning agent residue, other undefined soils, and oxides. This is important, because there can be variable and often unknown soils due to changes in sub-vendor processes. Steam cleaning was adopted as a final process to produce a clean, dry surface (5,6).

CO2 Cleaning

CO2 cleaning covers a wide range of processes, including solid CO2 snow, liquid (subcritical CO2), and super-cricital CO2.

CO2 snow is a relatively inexpensive line-of-sight cleaning process. Without automation, it tends to be used for low-throughput benchtop type cleaning. It is typically used for final particulate removal, where there is a very low level of soil. With CO2 cleaning, is important to avoid re-contamination, either by redepositing dust from the air or by condensing water. Therefore, a cleaning cabinet or micro-clean room with a heated stand for the part to prevent condensation is often used. In addition, the CO2 itself must be of high purity. CO2 snow guns vary in type. With low-velocity soft snow, particles, not organics are removed. It is very mild, rather like an air-knife. There are also higher-velocity guns which remove both particles and low levels of organics; cleaning could be described as mildly aggressive. CO2 dry ice pellets, with a compressed air boost, can provide very aggressive cleaning/blasting. Such systems are more costly and are typically useful for industrial, general cleaning applciations.

Liquid CO2, or sub-critical CO2, is useful for light hydrocarbon contamination, not for inorganics or particulates. It is a batch process, and is less costly than supercritical. In one application tested, it did not appear to remove low levels of mixed oils; the supercritical process was prohibitively expensive for the application under consideration. It should be noted that soils are often mixed (particulates and organics). Supercritical CO2 cleaning is above the critical temperature and pressure (-31 degrees C and 72.7 atmosphere). It is costly, and is most useful for high-precision cleaning applications. It is for oils, and organics, not for particles or inorganics. The cost is high; the footprint is large. It is very application specific; and one must design the process to protect the components.

Solvent Cleaning

Solvent Cleaning is often still desirable Solvency provide a cleaning for a range of soils There is low residue Vapor phase cleaning allows final cleaning in freshly-distilled solvent, avoiding redeposition of soils and issues of soil loading of the cleaning agent Airtight and airless system allow use of proven solvent technology, while minimizing environmental and worker safety issues Parts are processed in as sealed, controlled system The system is automated to allow efficient handling of parts and more consistent process control Lower solvent usage means lower costs (solvent and regulatory recordkeeping), as well as decreased liability and environmental concerns In fact, there are indications that airless systems can release significantly lower VOC's than even aqueous cleaning systems using 50 g/L VOC cleaning agents (1)

There are a number of considerations in adopting the newer cleaning systems The first is cost There is a significant up-front capital investment There is also a large footprint, a fixed chamber size, and typically longer process times than with traditional degreasers Specialized fixturing is required, and there is a definite learning curve Worker training and education are essential In addition, careful maintenance is needed, and solvent must be monitored to assure that there is no build-up of acid The extent of this problem varies markedly with the application under consideration

Case Study: Airtight Cleaning System, Complex Metal Parts

Bell Industries has adopted a Pero airtight system with trichloroethylene for removing oils from a variety of stamped metal parts Bell has a high-throughput, high product mix application There are many metals and alloys; and many of the parts have complex, intricate shapes Aqueous systems were tested extensively; none could be adopted for technical and economic reasons As a consultant to Bell Industries, it is apparent to Barbara Kanegsberg that Martin Wesley of Bell Industries evaluated a number of cleaning systems prior to choosing the Pero There was an initial learning curve: choosing fixturing, optimizing cleaning programs, and choosing and educating the most suitable employees to operate the system Except for regular maintenance, this system has been in continuous operation for an extremely high-volume application This application has been discussed extensively (3)

Case study: Airless Cleaning System, Honeycomb:

B F. Goodrich Aerospace has successfully replaced 1,1,1-trichloroethane (TCA), a Class I ODC, in a traditional open-top degreaser B F. Goodrich Aerospace implemented a fully-enclosed, airless, vacuum cleaning system , the Serec System, to clean aluminum honeycomb core using perchloroethylene (PCE). Mr Ron Thompson, Team Leader in the Environmental Health and Safety Department at B. F. Goodrich, has found that, in general terms, the equipment works very well It does a good job of cleaning, and the up time is high The group was able to continue to use proven, solvent-based cleaning technology without the costs and uncertainty of attempting to implement a drastically different approach to cleaning

Mr Thompson reports that there was a learning curve For one thing, B. F. Goodrich Aerospace purchased one of the earlier units and that some design modifications were necessary. At the same time, B. F. Goodrich Aerospace had some operator education issues in terms of optimizing the solvent to be used and assuring that the equipment was used to clean the appropriate product B F. Goodrich had to consider issues of temperature sensitivity, vacuum deformation, and part size

For example, one of the products melted during the cleaning process .. The failure was the result of an unintentional attempt to clean a Nomex core, a composite which melted at the boiling point of perchloroethylene The older, original degreaser had been filed w tca – was not attention to degrease TCA has a boiling point of 74 degrees C and a Kauri butanol (KB) number of 124, whereas PCE has a much higher boiling point of 121 degrees C and a KB number of 90. In general, the higher the KB number, the more aggressive the solvency. While the KB number of PCE is significantly lower than that of TCA, because PCE has a higher boiling point, the two factors generally balance out in degreasing operations Nomex is not cleaned, it is kept clean as received They expect that all build will be worked in a Clean Room; this will decrease degreaser usage in general. The general approach for the future will be to avoid degreasing where possible

Vacuum deformation can also be a problem. They were aware that it could be a problem; testing was performed with the manufacturer prior to implementation. The parts had been bonded to a metal skin & would begin to deform, the issue is the foam adhesives which can have air pockets. Degreasing in a vacuum minimizes solvent loss and employee exposure; some very delicate components can be damaged. Mr. Thompson reports that the vacuum deformation problem was avoided by fixturing the parts. This approach is working successfully. Groups contemplating purchase of vacuum equipment are well-advised to perform preliminary tests with the manufacturer of the cleaning equipment.

The size and shape of the parts to be cleaned is more restricted, less forgiving, with an enclosed airless or airtight system. In the traditional, open-top degreaser, because it has an open top, the occasional out-sized component, can be cleaned one end at a time with a portion of the part extending out of the top of the degreaser. A situation which Mr. Thompson notes is not a particularly desirable work practice. With an airless system, the part must fit inside a cleaning chamber which is of fixed size and then sealed before cleaning can begin. The situation is akin to packing items into hard-sided luggage prior to an airline flight versus placing them in the trunk of a car. In your car, you can even occasionally allow items to jut out of the trunk. Mr. Thompson notes that B. F. Goodrich has accommodated the situation by avoiding soiling the out-sized parts . Mr. Thompson adds that if such components were ever soiled, they would have to be cleaned in a larger airless system, or in a traditional open-top degreaser. A 1.25 inch thick metal chamber with a system which is designed not to start unless the system is sealed limits the configuration of parts to those which can be fitted into the chamber. The fixturing or rack may further limit the size.

Equipment maintenance is more complex than with traditional degreasers. A traditional degreaser is fairly simple; it is basically a box with a heater for the solvent and perhaps ultrasonics, and cooling coils to condense the solvent. Airless systems are more sophisticated and require greater care in operation and more careful maintenance. In terms of maintenance, Mr. Thompson notes that while the up-time is very high, when a breakdown occurs, airless systems take a bit longer to repair and require skilled repair people with the appropriate technical expertise. The equipment has been in operation for two years. Mr. Thompson expects the next major repair to be a rebuild of the vacuum pump assembly.

Mr. Thompson estimates that with the currently-available Serec systems, training and implementation should require approximately one month. During the first year of operation, there was a shake-down period. The equipment manufacturer replaced pump seals and sensors. B. F. Goodrich found that operators could circumvent the interlock system, allowing them to pull out samples before cleaning and drying was completed. The problem was solved with programming changes, now standard on all Serec systems. Barbara Kanegsberg observes that, while many operators may show an initial reluctance to learn about the newer, computerized cleaning systems, they are often surprisingly adept at perhaps inadvertently circumventing the system, short-cutting the cleaning process and removing parts prior to completion of cleaning. She has observed this problem with many of the newer cleaning systems. It is often very profitable for the components manufacturer to work with the cleaning equipment manufacturer during initial operation to be sure that technicians cannot make unwarranted program changes

Overall, adopting the Serec airless system resulted in a number of benefits. The cleaning process has been simplified, and there is reduced exposure of employees and the community to the solvent. The production person loads the samples, pushes a button, and then goes off to perform other tasks until a light flashes to signal that cleaning is complete. The software included in the newer automated system will simplify required record-keeping; they are looking to upgrade. Solvent usage has dropped dramatically. Solvent disposal ; there is the potential for exposure, but it is readily controlled by normal employee training; may be easier than open top because of plumbed connections.

The company has reduced solvent costs over continuing with TCA and has reduced exposure of employees and those in the surrounding community to PCE. PCE is regulated throughout the U.S. by the NESHAP; it is regulated even more stringently throughout the State of California (by AB 2588). While the open-top degreaser was permitted by local regulators for TCA, TCE (trichloroethylene), or PCE, state-wide regulations would have made it difficult to use chlorinated solvents.

In a normal work schedule for the Serec system consists of five to six loads per day (over two eight hour shift), with a cycle time of thirty minutes to one hour. The cycle time, although longer than with an open-top degreaser, has not been the limiting factor. More time is spent on paperwork and on racking parts than in cleaning components

Conclusions

Advanced cleaning encompasses a variety of techniques. It has often been said that there is no universal cleaning agent. There is also no universal cleaning process (2). The advanced cleaning techniques discussed above represent a range of processes, from the supposedly simple to the more sophisticated

Based on the case studies, successful implementation depends on a number of factors. Matching the process to the application is crucial. This involves a clear understanding of the limitations of any particular process. Partnering, then, becomes important. This means partnering with both the equipment manufacturer and with the production people or assemblers. It is often difficult to visualize a full process from one demonstration. Working with the equipment manufacturer allows design which suits the process to be changed.

Production people can make or break any new process. This is particularly true when the new process is seen as very unfamiliar; it is often viewed with skepticism. Getting the production people involved right away can help in terms of the comfort level. In addition, cleaning processes are used in the context of a production environmental. The assemblers and production people are usually the ones with the most expertise in meshing the new cleaning techniques with the total cleaning process

Some advice adopting any innovative technique: maintain a sense of adventure, be observant, and maintain a sense of humor. The result can be profitable, environmentally sound processes.

Acknowledgments:

The authors are responsible for the contents of this article. The authors are grateful to those who agreed to discuss their case studies. In addition, we wish to thank Jim Sloan of Vatran, Robert Sherman of Applied Surface Technology, Martin Wesley of Bell Industries, and Karyn Igar and Peter Gebhard III of Serec Corporation.

References:

(1) Gebhard, P, personal communication

(2) Kanegsberg, B., "Cleaning Options for Degreasing & Surface Preparation,", Plating & Surface Finishing, January, 1998, 48 – 50

(3) Mertens, J., "Cleaning Conversion Comes Full Circle," scheduled: Parts Cleaning Magazine, June, 1998.

(4) O'Kane, D F. and Mittal, K. L., "Plasma Cleaning of Metal Surfaces," J. Vac. Technol, 11 (3), May/June, 1974, 567 – 569.

(5) Petrulio, R., and Kanegsberg, B., "Back to Basics: The Care and Feeding of a Vapor Degreaser with New Solvents," Nepcon West '98, March, 1998

(6) Petrulio, R., and Kanegsberg, B., "Practical Solutions to Cleaning and Flushing Problems," CleanTech '98 Proceedings, May, 1998, 362 – 373.

Alabama Rapid Prototyping and Manufacturing Alliance (ARPAMA)

John A. Cranston
University of Alabama in Huntsville
CAR RI-A5
Huntsville, Al. 35899

Alabama Rapid Prototyping Advanced Manufacturing Alliance (ARPAMA)

Introduction: Through strategic partnering the Alliance delivers rapid production tooling, coatings, advanced manufacturing, and composite technology. Spearheaded by John Cranston of UAH and Roger Herdy of Micro Craft the University of Alabama in Huntsville (UAH), NASA's Marshall Space Flight Center (NASA/MSFC), Oak Ridge Centers for Manufacturing Technology (ORCMT), Southern Technology Applications Center (STAC), The Alabama Technology Network (ATN/MEP), and regional industries have teamed to offer industry a unique technology transfer opportunity. The alliance facilitates technology transfer between and out from these organizations. Technical, business, and economic assistance are made available through the Alliance. The Alliance showcases the technologies to system manufacturers, service bureaus and industry users. Alliance members have direct access to these advanced technologies and expertise within MSFC, ORCMT, UAH, and the technology companies. Development projects go through the Alliance until such time a new venture is formed. Then the new venture contracts with outside clients for commercial sales. See Fig. 1.

The initial focus of this Alliance is on four advanced manufacturing technologies: a vacuum arc vapor deposition process capable of thin, uniform coatings with minimal heating of the coated part patented by NASA and developed by Vacuum Arc Technologies, (VAT), surface transformation treatments capable of tailoring a surface to an alloy composition developed by University of Tennessee Space Institute and licensed by Surface Treatment Technologies, a spin-off company of Micro Craft,(MC), thermal spray coatings of metallic and non-metallic materials developed by Plasma Processes Inc. (PPI). Lastly a tooling foam, (developed by UAH), used for tools, mandrels, and molds for elevated temperatures. The combination of these technologies has created technology to build metal tooling and parts near-net. Pressure vessels, rocket engines, tooling, and molds have been fabricated. Some of the metals used to date include aluminum, copper, steel and inconel.

Researchers from UAH, MSFC, and the Alliance are jointly developing hardware that will lead to advanced manufacturing systems. These systems will incorporate advanced deposition technologies, CAD-CAM, robotics, CMM, analysis software tools and reverse engineering to produce a virtual product development system.

The concept of "virtual product development" is defined as an integrated approach to utilizing developmental tools such as CAD models, analysis software, and CAM to produce components in a virtual environment to reduce the development cycle time. This approach, coupled with advanced manufacturing technologies, would create a superior-manufacturing atmosphere that would showcase and facilitate commercialization of emerging technologies.

In Phase 1 the Alliance put together three demonstration projects for potential applications. Project #1 was between UAH/PPI/NASA/MSFC to build thin metal liners for composite wound Liquid Oxygen, (LOX), tanks. Project # 2 was between UAH/MicroCraft/Navy to develop a 21" one-step urethane molded simulation target. Project #3 was to develop a temperature tolerant foam tooling system for large composite parts, (human powered submarine). UAH developed this as an internal project. As the applications are defined the companies will form new ventures to commercialize the products. Project #1 has led to one such venture, Pressure Vessels Inc. The pressure vessel technology combines three of the technologies in the Alliance to manufacture rapid production tooling and pressure vessels without seams or welds. Project #2 has delivered 23 parts to the Navy that has been tested in the Gulf of Mexico last fall. Finally after Project #3 the UAH foam technology was licensed to a local commercial company, Alpha Products. New demonstration projects are being reviewed.

The potential for this alliance is exciting. It is a proactive move to help industry access cutting edge technology and assistance to enable them to be competitive in the global market place. The Alliance team approach offers industry the best of worlds, cutting edge technology and the expertise and support structure to commercialize that technology.

ARPAMA's VISION: Provide a model, a method and an infrastructure for Technology Infusion to foster economic growth and global competitiveness for Alabama companies with emerging technologies.

TECHNOLOGY INFUSION MODEL

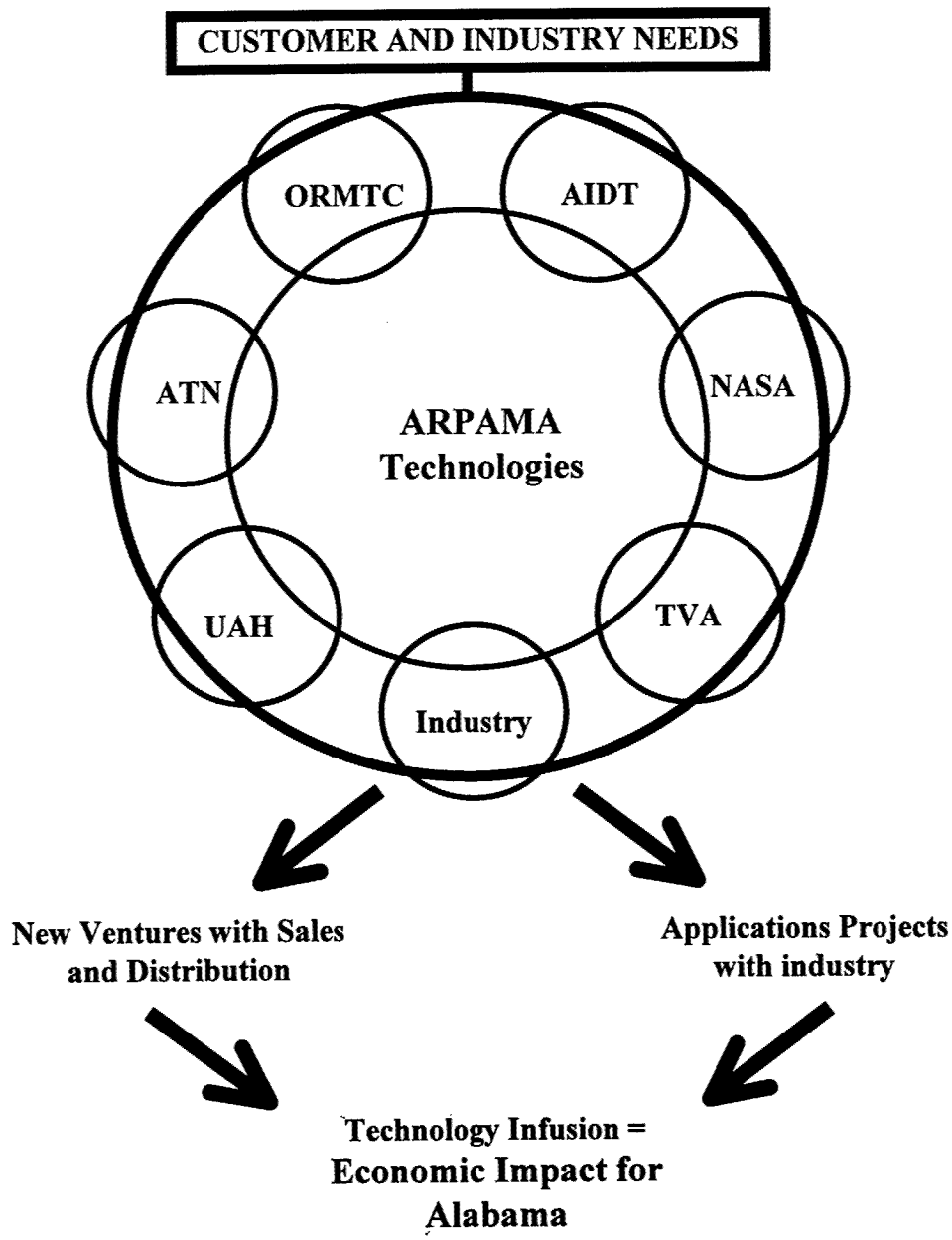


Fig. 1

The mission statements of the organizations listed became the central theme for the creation of the alliance approach. All of these organizations were interested in the transfer of technology and economic impact for the state of Alabama. Read the following excerpts from their literature;

AIDT - Alabama Industrial Development Training - Business Process Reengineering and Technology Integration - "AIDT's Business process and Reengineering and Technology Integration service helps a company figure out how its processes work or don't work, why the company uses those processes, and what improvement options are available. Our membership in the Alliance for Technology Transfer allows us to provide you access to national labs and other industries that can share experiences to help you solve problems. Our support includes manufacturing, logistics, networking, product development, systems integration, support functions, and integrating people and technology." Ref. AIDT literature.

ATN/MEP - Alabama Technology Network / Manufacturing Extension Partnership - "MEP centers are designed to help link sources of improved manufacturing technology and modern business practices with the small and mid-sized companies needing assistance." Ref. US Dept. of Commerce News, 10/3/95.

NASA/MSFC - "The Productivity Enhancement Complex is operated by the Materials and Processes Laboratory at Marshall Space Flight Center (MSFC). Here, NASA and industry work together to develop new materials, processes, and assembly techniques." Ref. Focus on the Future.

TVA - "**Mission**: To invest in economic development opportunities that result in the generation of high value jobs in the Tennessee Valley Region. Goals: Create high value jobs, leverage financial resources, improve business and workforce productivity. Primary Business Area: Business development, Industrial development, Community development, Technology development, and Technical services." TVA Economic Development Handout, Freddie Hogan, 1995.

UAH - "The University of Alabama in Huntsville is one of sixty Manufacturing Extension Partnerships, (MEP), Centers in the US funded by the US Department of Commerce. The MEP Centers are dedicated to helping manufacturers improve their competitiveness through the adoption of modern manufacturing technologies and business practices." Ref. UAH handout.

Micro Craft - New Business Incubator, "Our Business enterprise is focused on turning today's ideas into tomorrow's products. They have a three-fold approach to new products and services: Identify and develop innovative technologies to enhance our core products and services; Leverage our skills and products developed in the aerospace marketplace into non-aerospace markets; Create an "incubator environment to allow entrepreneurial ideas to be fostered, developed, and transitioned to the marketplace." Ref. Micro Craft business literature.

This was the organizational side, technology outreach. On the other you have industry looking for solutions to manufacturing problems, technology need. Their problem was where to go to get assistance for new technical solutions. The competition wasn't going to give it to them and if they had the answers they wouldn't be looking. . The way I was taught to transfer federal and university technology was to first, find their need or identify a technology opportunity, tell them where to get the technology, go on to the next

transfer, and report my successes. This match maker approach was not proving to be successful. Pointing to the technology was not enough so there needed to be a mechanism to carry the process through to the use of the technology.

Five and one-half years experience in technology transfer had taught me that most successful transfers occurred when there was management buy in and a company champion to carry the project to completion. Therefore I came to the conclusion that something different needed to be done to increase the likelihood of successful transfers for the organizations I was representing, NASA/MSFC, the Southern Technology Applications Center, and the UAH Manufacturing Extension Partnership, MEP.

The start of the Alabama Advanced Manufacturing Alliance, AAMA was a meeting held at the offices of the Alabama Industrial Development and Training, AIDT, August 22, 1996. The co-founder, Mr. Roger Herdy, of Micro Craft became an important industry ally for the alliance. Roger and I had tried to work several technology projects with little success. So the two of us invited approximately 30 people to that first meeting to see if there was interest in our idea of an alliance approach to foster successful transfer of technology. They represented the federal, state, local governments, universities, colleges, and industry.

The central ideas of the alliance approach were first to focus on a couple of key technologies that would impact a very large part of the manufacturing sector. Market those technologies at trade shows and conferences. Develop projects with industry to prove the use of the technology for their specific application. Determine commercial viability and go commercialize. This would be through partnerships that would generate shared equity, licenses, royalties, and agreements that were win-win. It was agreed that the alliance approach had merit and three pilot projects were suggested.

On December 2, 1996 the Alliance became official. The UAH Engineering Foundation became the fiscal agent for the alliance and partner with four companies; Micro Craft, Plasma Processes, Inc., Space America, Inc. and Vacuum Arc Technologies, Inc. The name changed to the Alabama Rapid Prototyping and Advanced Manufacturing Alliance, ARPAMA. Since its beginning the alliance has helped spinout three companies and incubates a fourth.

Startup 1: **Pressure Vessels Inc.,** (PVI), formed when PPI, SAI, and UAH had a story written about their seamless weld-free pressure vessels in Aviation Week, February, 1997, Industry Outlook section. After approximately 2 dozen inquiries from major companies across the country it was apparent that the team had something. On November 6, 1997 the company formed. PVI would take a three-phase approach to building its business. First sell rapid tooling using proprietary UAH technology. Second, develop the process further to manufacture metal molds, and tooling, and third, manufacture seamless, thin-walled metal-lined pressure vessels for commercial space application.

Startup 2: **Surface Treatment Technologies, Inc.**, (ST2), was formed to commercialize a University of Tennessee Space Institute technology named Laser Induced Surface Improvement, LISI. The company was getting off to a very slow start with no marketing. Micro Craft and ST2 saw the alliance as a much-needed marketing arm for their LISI process. Since their involvement Roger Herdy has brought several projects to the alliance and formed a partnership with one of the other alliance partners, VATI. LISI is an alternative to chrome plating, as well as a treatment for surfaces. Roger Herdy of Micro Craft volunteered to chair a working committee that would pursue an effort, which would initially focus on two projects: An injection molding tooling production cost analysis, and a comparison of wind tunnel model

manufacturing techniques with test results to an established database. Wind tunnel models have been fabricated and coated. Testing is expected in the following months.

Startup 3: **Alpha Products, Inc.** was formed in January 1998. A local company was looking to diversify and heard of the opportunity to license technology at UAH. Since the company had a complete lab facilities and familiarity with chemical handling and formulating it was a natural fit. A license was obtained for the manufacture of two of the university's formulations. These are both tooling foam formulations specially developed for temperature tolerance and stability. Several markets were identified by the university researcher that helped establish a customer base. The university and PVI are currently customers.

Incubator 1: **Vacuum Arc Technologies, Inc.** had already formed but did not have a marketing department. As a partner in the alliance and one of the key emerging technologies they found the marketing support they needed to get the news out about their technology. VATI had a patented technology that would make the chrome process entirely green. These coatings were amorphous and very dense. A key factor too was the ability to coat almost any substrate with metal. This is because the process did not require the use of preheating the target as in most other deposition processes that laid dense coatings. VATI and UAH are partnering to build a commercial unit at UAH for development projects with industry. Once a project has proven successful VATI will contract with the company to build them a unit at their facility. The university will continue materials characterization studies and projects for fee with industry.

The Alliance: **ARPAMA** has created a synergy for its partners. Together each organization meets its individual goals, i.e., mission statements. The university brought business management expertise, labs, faculty and students to help in the projects. The companies brought entreprenuership, money and customers for their technology. Together they got participation from NASA/MSFC, ORMTC, and the ATN/MEP to help identify technology transfer opportunities. The local chamber of commerce also saw the potential of the alliance as a marketer of Huntsville technology. So, several companies seeking technology have been referred to ARPAMA for follow-up. Recently the chamber arranged for ARPAMA representatives to meet with two companies from Israel. It is this kind of cooperation and focused technology marketing that has made for the rapid success of the Alabama Rapid Prototyping and Manufacturing Alliance.

The future looks bright for ARPAMA. In the past two months alliance partners won a Phase I SBIR from NASA. Several companies have partnered with ARPAMA members to go for state research funds through joint proposals. Just recently ARPAMA members have been asked to be on several NASA, DoD, and DoE SBIR proposals. The alliance is not just going after government funding. It has commercial customers they are partnering with to commercialize these technologies. Several of the partner companies have developed commercial sales. The main focus of the technology companies in the alliance has been to fully characterize the materials and processes. Once this is accomplished the marketing can proceed quickly.

Conclusion: Technology transfer does not have to be left to chance and serendipity. Target marketing and partnerships have proven to be a successful method of getting needed technology to Alabama industry. Sharing the costs through university sponsored projects has helped bring industry to the table. Cutting-edge technology from the university and its partners has also peeked the interest of industry and other organizations; Jet Propulsion Labs, Oak Ridge National Lab, the Office of Naval Research, and Sandia to name a few. Large corporations like Boeing, Pressure Technology Division of Carleton, Alliant, Mac Donald Douglas, and Summa are asking about ARPAMA technologies and seeking teaming

arrangements. Small companies are inquiring looking for a competitive edge in a niche market. We believe this alliance method could be successfully used for other technologies. The success of ARPAMA comes directly from the commitment of its partners to deliver needed technology through partnerships that last until the technology is adopted.

Acknowledgements: Thank you to Dr. Bernie Schroer acting V.P. of the Research Institute at the University of Alabama in Huntsville for his years of support for the Alliance activities. To Ms. Sally Little and the NASA/MSFC Technology Transfer Office and Mrs. Carol Ann Dykes of the Southern Technology Applications Center, thank you for your support with technology opportunities, information, referrals, and facility access.

Chemical Fingerprinting of ODC Replacement Solvents for Acceptance Criteria

By
William H. McClennen and Bart L. Weber
Thiokol Propulsion
P.O. Box 707 - M/S 245
Brigham City, UT 84302

Topic areas: Chemical fingerprinting, database development, instrumental analysis, acceptance criteria

Abstract

Qualification and implementation of ODC replacement materials requires carefully defined acceptance criteria and stability information for proper quality control. Chemical fingerprinting by powerful instrumental analysis techniques can be an essential aspect of these criteria and is currently being mandated by NASA as part of performance enhancement programs. However, a major challenge to the utility of chemical fingerprinting is the development of a database which is both versatile and efficient enough to facilitate materials data retrieval, examination and approval for a broad range of scientific and engineering backgrounds and requirements. This paper discusses the planned uses, system requirements, current approach and capabilities of our chemical fingerprinting database using preliminary examples of GC, GC/MS and FTIR data from a terpene in hydrocarbon ODC replacement solvent.

Introduction

The known ozone depleting chemical (ODC) 1,1,1-trichloroethane (TCA) has previously seen wide use in RSRM applications such as vapor degreaser bathes, rubber bonding surface activation and various hand wiping operations. The bulk degreaser uses are being replaced by aqueous based procedures as discussed in other presentations of this conference. Some of the bonding surface activation applications of TCA will continue under essential use exemptions, while other hand wiping operations are being taken over by alternative non-ODC organic solvents including terpene mixtures (e.g., PF Degreaser) and alcohols (e.g., IONOX BC) (1). Because small deviations in composition of critical RSRM materials have led to problems in the past, the qualification and implementation of these ODC replacement materials as well as the limited continuing use of TCA require carefully defined acceptance criteria and storage stability information for proper quality control consistent with use in the manned space flight program.

Chemical fingerprinting by powerful instrumental analysis techniques can be an essential aspect of these criteria and is currently being mandated by NASA as part of Enhanced Sustaining Engineering programs at Thiokol. The basic objective of chemical fingerprinting is to enable a more detailed understanding of the makeup of RSRM materials so that we can better detect subtle changes in composition which might not be detected by current acceptance tests, but could still have an impact on performance. These solvents are among the simplest materials that are being analyzed in the fingerprinting program, but serve as examples for the development and documentation of procedures and the general database structure.

A major challenge to the utility of chemical fingerprinting is the development of a database which is both versatile and efficient enough to facilitate materials data retrieval, examination and approval by personnel with a broad range of scientific and engineering backgrounds and requirements. This paper discusses the planned uses, system requirements, current approach and capabilities of our chemical fingerprinting database using preliminary examples of data from the chemical analysis of the ODC replacement solvent PF Degreaser.

Copyright '98 Cordant Technologies, Inc. All rights reserved.

Approach

The philosophical basis for Chemical Fingerprinting of raw materials as part of the RSRM technology enhancements program is that knowing the detailed chemical make up will enable us to more effectively assure materials quality and thus insure performance. The general approach is based on method development through four document levels, namely: a Preliminary Test Plan (PTP), a Laboratory Technical Procedure (LTP), a Standard Laboratory Procedure (SLP) and a final report. The PTP briefly reviews past work, outlines the most promising methods that will be evaluated and lists the types of samples that will be tested. An LTP is written for each successful method to include quality control procedures. The SLP will combine all of the essential LTPs in a format that can be implemented by the Quality Control Lab for routine application and the establishing of limits prior to possible incorporation into formal acceptance criteria.

The goal of the Chemical Fingerprinting database is to make readily available through desktop personal computers virtually everything an administrator, engineer, technician or chemist would want or need to know about a critical RSRM raw material. This includes everything from where and how it is properly used to the details of chemical composition that could impact performance. At the highest level would be information such as current stock and lot numbers, basic chemical properties, safe handling practices and responsible personnel. At the most detailed level the ideal system will enable a qualified chemist to immediately examine original chemical analysis data for the extremely small, but significant differences between the latest batch of material and previous good and bad samples. To facilitate the development of this system, commercially available hardware and software are being used as much as possible.

Experimental Procedures

PF Degreaser is a hydrocarbon solvent mixture consisting of decane, undecane, dodecane, tridecane and 6 - 10 percent of the terpene d-limonene. Current acceptance testing includes the determination of flashpoint, non-volatile residue (NVR) and density by ASTM procedures D 56, D 1353 and D 4052, respectively. Basically, the NVR is measured by placing 10 g of PF Degreaser in a platinum dish and heating in a vented oven at 105°C for several hours (usually overnight). The dishes are allowed to cool in a dessicator and reweighed. The samples are then heated for another hour, cooled and weighed repeatedly until a consistent weight is obtained. The d-Limonene content is determined by gas chromatography (GC) where its response is measured by comparison to a calibration curve.

The GC analysis can be and has been applied at several different levels between routine testing and comprehensive methods development. Current acceptance testing for d-limonene uses a Hewlett Packard 5890 or a Tracor 570 GC system with a flame ionization detector (FID) and a 5-percent phenyl methylsilicone (e.g., DB-5) capillary column. The sample is diluted to a final concentration of 5 percent V in dichloromethane (DCM) for injection of 1.0 μL with a 60:1 split. Standards of d-limonene were used to calculate its concentration.

The GC methods are generally developed based on the results of GC/MS analysis for column and temperature program parameters. These analyses were run with a Hewlett Packard 5890 series II GC system using a flame ionization detector (FID) and Perkin Elmer Turbochrom software. A 5-percent phenyl methylsilicone (e.g. DB-5) capillary column and a temperature program of initial hold at 150°C for 5 C/min, ramp to 210°C at 5°C/min and a 1 min hold were used. Samples were diluted to a final concentration of 5-percent V in methylene chloride (DCM) for injection of 1.0 μL with a 60:1 split for the determination of the main components and run neat (without dilution) for analysis of the tetradecane and BHT. Calibration standards included the five main compounds plus tetradecane and BHT to allow quantitation.

The GC/MS analysis utilized a Hewlett Packard 5890 series II GC system with a Hewlett Packard 5971 or 5972 Mass Selective Detector (MSD) with electron ionization. For these analyses, a 30m x 0.25mm x 0.25 µm film DB-5 GC column was used with similar temperature and flow conditions. When neat samples were run, the MSD was shut off during elution of the main components to avoid overloading the detector. For both the GC and GC/MS analyses, a set of method quality control (QC) procedures have been established to evaluate and maintain accuracy and precision standards. Method quality control procedures followed guidelines similar to those required by the Environmental Protection Agency.

Fourier transform infrared spectrometry (FTIR) has previously been used primarily for qualitative purposes on a variety of instruments. Those shown here were run on a Nicolet 750 Magna-IR Spectrometer with a 45 degree ZnSe flat, horizontal attenuated total reflectance (HATR) crystal in a out-of-compartment contact sampler. Typically the MCT detector was used with averaging of 32 scans and a resolution of 4 cm-1. The FTIR was used to analyze both neat samples of PF Degreaser and NVR samples that were transfered to the HATR crystal with chloroform.

A customized Chemical Fingerprinting data warehouse is still in the process of being designed and developed. Two of the main software components which are currently being used with a strong likelihood of eventual incorporation are a Laboratory Information Management System (LIMS) and a (nearly) universal spectroscopic and chromatographic data analysis system. The LIMS is an environmental database from Lab Vantage which takes individual quantitation reports from original instrument software and collects and compiles them into an Oracle based database which tracks analyses, generates reports on a variety of forms and monitors quality control results among other functions. The current spectroscopic and chromatographic data analysis system is GRAMS/32 from Galactic Industries which does enable viewing and manipulating of many different data types in one package with some strong comparative features, but without other capabilities of the original vendors software. Power Builder which also uses Oracle databases is currently being used to develop tools such as an electronic notebook front end for receiving and organizing data and the eventual data presentation shell. This shell will also manage and organize fingerprint information.

Results and Discussion

As mentioned above, acceptance testing involves the determination of flashpoint, density, non volatile residue (NVR) and amount of d-limonene by gas chromatography (GC). The first two tests are routinely done even though their results could be calculated from the comprehensive sample composition information available in the GC data. Figure 1 shows a chromatogram from the GC analysis of PF Degreaser similar to that currently used in acceptance testing. The d-limonene (d-Lim) peak area is integrated and compared to a standard calibration curve to determine its amount, but the rest of the GC data which could give the comprehensive composition of the sample is currently ignored. The NVR measurement provides unique information in that the GC analysis would not detect its high boiling compounds, i.e., the NVR is critical in demonstrating that the hand wipe solvent will not leave behind more residue than it is removing. Current specifications require 6 to 10% d-limonene and less than 100 parts per million (ppm) NVR in PF Degreaser. The goal of the chemical fingerprinting program is to determine if the current and additional critical information can be obtained more efficiently.

To be more efficient, current and future information must be organized for easy access. Table I lists in outline form an example of the Chemical Fingerprinting data warehouse organization. The outline mimics the hierarchy of access by placing the executive level on top followed by summary and detail levels. The list indicates both the main folder topics and examples of their contents including data files and specific applications which will be launched with appropriate initial parameters relative to the particular material and data type. Thus for example, a request for safety information would either open a simple bitmap copy of the material's MSDS or open the appropriate database software, e.g., the Aldrich Chemical MSDS database for the compound d-limonene.

The list is also similar to the current "tree-view" display except for the listing of files as well as folders. The first level of security is the fact that the directory list would only show the level for which the user was qualified. Thus someone with general network access would only view the executive level and would not be able to drill down into the more detailed levels whereas the material leader would view and be able to open all levels. Figure 2 shows a preliminary Detail Level view for PF Degreaser.

One of the original goals of the database was to make a broad range of information types more readily available. Figure 3 shows one step towards this goal in the form of a drawing to show exactly which critical surfaces PF Degreaser is qualified to clean. Bitmaps of photographs or even video clips demonstrating proper use procedures can also be made available in this one electronic source to augment conventional plan and procedural documents. For some of these possibilities data storage and access speed are real limitations requiring evaluation.

Figure 4 shows a second example of reference data that can be made readily accessible in folders such as "Past Problems". This is a comparison of the FTIR spectral data from a report on the analysis of good and bad PF Degreaser NVR samples. The good NVR spectrum indicates only the normal aliphatic hydrocarbon signals, whereas the bad sample shows the additional bands from the effects of oxidation and polymerization of the terpene. The ease of incorporating spectral or chromatographic data into reports via "the clipboard" has greatly widened the potential dissemination of data enabling more detailed comparison with new samples. If a chemist or technician obtains a high NVR amount, an FTIR spectrum could be run to visually compare to these previously reported spectra. The only limitation is that the traces cannot be easily overlaid for the most detailed comparison unless the original data files can be found in compatible formats.

Thus the next goal was to incorporate the facilities to access, display and manipulate the original chromatographic and spectral data files. Currently we are investigating the capabilities of the GRAMS/32 software as a platform for viewing data generated by a variety of instruments and vendors. The name stands for Graphic Relational Array Management System for 32 bit scientific data and in principle, the program will allow the material specialist to examine and re-examine data from many different sources without having to go back to the computer and software where the data originated.

For instance, unlike the simple bitmap form of the examples in Figures 1 and 4, this software would allow the chemist to zoom in on the data to look for very small peaks which may have been over-looked in previous examinations. Figure 5 shows an example of overlaid and expanded data from the GRAMS/32 software. This figure indicates the presence of the preservative BHT (buterated hydroxytoluene) in the "good" sample at a concentration of approximately 25 ppm while there is none detected in the sample that is starting to go bad (less than 1 ppm BHT). The initial identification and quantification of the BHT was performed on a GC system with mass spectrometry detection (GC/MS) in data which is also viewable in GRAMS/32.

This last example of BHT detection raises the issue of significant scientific findings via the chemical fingerprinting program. Previous work has reported on the need for oxidation inhibitors in a terpene ODC replacement solvent which was presumably pure d-limonene (2). However, there had been no mention of a stabilizer in this relatively dilute solution in the very stabile normal alkanes. Upon inquiring with the vendor, we learned that they would not accept their d-limonene without the BHT stabilizer and we were seeing it carried over into the PF Degreaser. The data for detected concentrations of BHT and NVR from several new (lots 21, 22 and 23) and old (bbss, hv and M-9 bb) PF Degreaser samples at Thiokol are shown in Figure 6. These results suggest that the BHT is essential for stability in the solvent and should be monitored in future lots of the material.

Summary and Conclusions

A NASA mandated Chemical Fingerprinting program at Thiokol has been described using the ODC replacement solvent PF Degreaser as an example. The detailed compositional data provided by powerful instrumental techniques has already improved our understanding of this material and suggested more efficient ways to evaluate the suitability of fresh or stored samples for use in critical applications. In particular, the detection of the simple stabilizer BHT and its potential role in preventing NVR formation has been a valuable contribution to its most effective use. Moreover, although the Chemical Fingerprinting program has been described through the example of this simple solvent, its greatest utility is expected to be in the analysis of the much more complex polymeric RSRM materials.

Acknowledgments

The authors acknowledge the assistance of all members of the fingerprinting team with special mention of Charles Whitworth, Dennis Fife and James Dietz for their vision of chemical fingerprinting and Bruce Lyons and Don Lee for their implementation of FP goals into the software development.

References

1. C. P. Clayton and M. P. Kovach, *Environmentally Compatible Hand Wipe Cleaning Solvents*, 1994 Aerospace Environmental Technology Conference at Huntsville, Alabama, NASA Conference Publication 3298, pp 491-497.

2. R. S. Gallagher, J. A. Purvis and W. W. Moran, *Prepsolv: The Optimum Alternative to 1,1,1-Trichloroethane and Methyl Ethyl Ketone for Hand-Wipe Cleaning of Aerospace Materials*, 1994 Aerospace Environmental Technology Conference at Huntsville, Alabama, NASA Conference Publication 3298, pp 187-197.

Table I. Generalized Example of Chemical Fingerprinting Data Organization (folder/file structure)

Material Folder

- General Material Information **Executive level**
    - Material Information [Word documents (.doc) and database links]
    - Where used [drawings or bitmaps (.bmp)]
    - Chemical structures [bitmaps or ChemDraw link]
    - Safety information [MSDS link]
- Formal Plans and Procedures
    - Current acceptance criteria [.doc]
    - PTP [.doc]
    - LTPs [.doc]
    - SLP [.doc]
- References
    - TWRs [.doc]
    - Background literature (refs)
    - Past problem reports
    - Other
- LTP Direct Support Data **Summary Level**
    - Data overview file/database
    - Method 1 (e.g. GC)
        - Examples [.bmp]
        - Selected data viewing [e.g. GRAMS/32 view link]
        - Raw data directories
            - Raw data files [e.g. GRAMS/32 .cgm]
            - Quantification files
    - Method 2 (e.g. NVR FTIR)
    - Method 3 (GC/MS)
- Controlled References **Detail Level**
- Additional Data
    - Electronic Notebook (database overview of experiments with eventual link to file path\name)
        - Method parameters
        - Method variations
            - Alternatives for special purposes
            - Failed efforts (lest they be tried again)
        - Sample variations
            - Lot to lot sample variation (good lots)
            - Bad lots
            - Aging studies
            - Related materials (e.g., old formulation)
    - Method 1 (e.g., GC)
        - Raw data directories
            - Viewer data [e.g. GRAMS/32 .cgm]
            - Original raw data files.
            - Quantification files
    - Method 2 (NVR FTIR)
    - Method 3 (GC/MS)
    - Method 4 (GC/MS 2, e.g., different instrument manufacturer)
    - Method 5 (NMR)
    - Method 6 (LC)

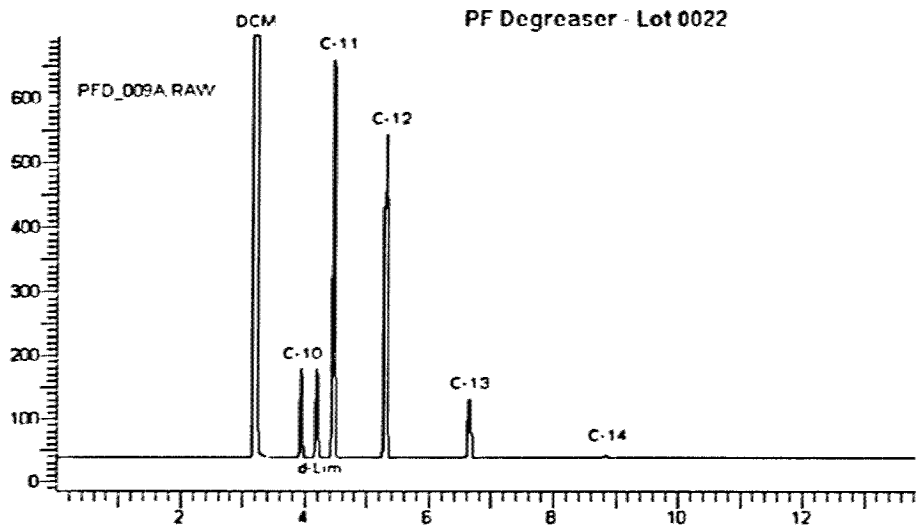


Figure 1. Basic GC Analysis of a PF Degreaser Sample in dichloromethane (DCM) Solvent

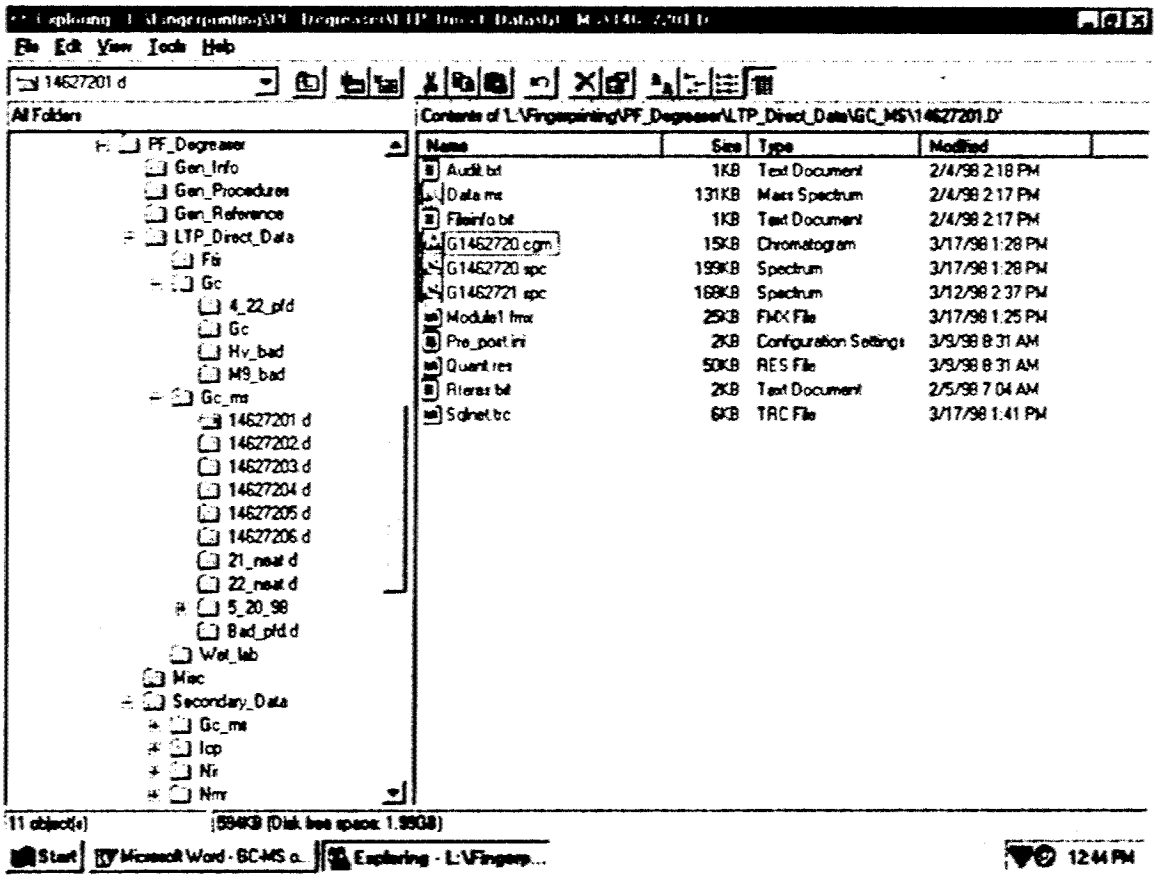


Figure 2. "Tree-View" of Accessible Folders for Detail Level Data of PF Degreaser

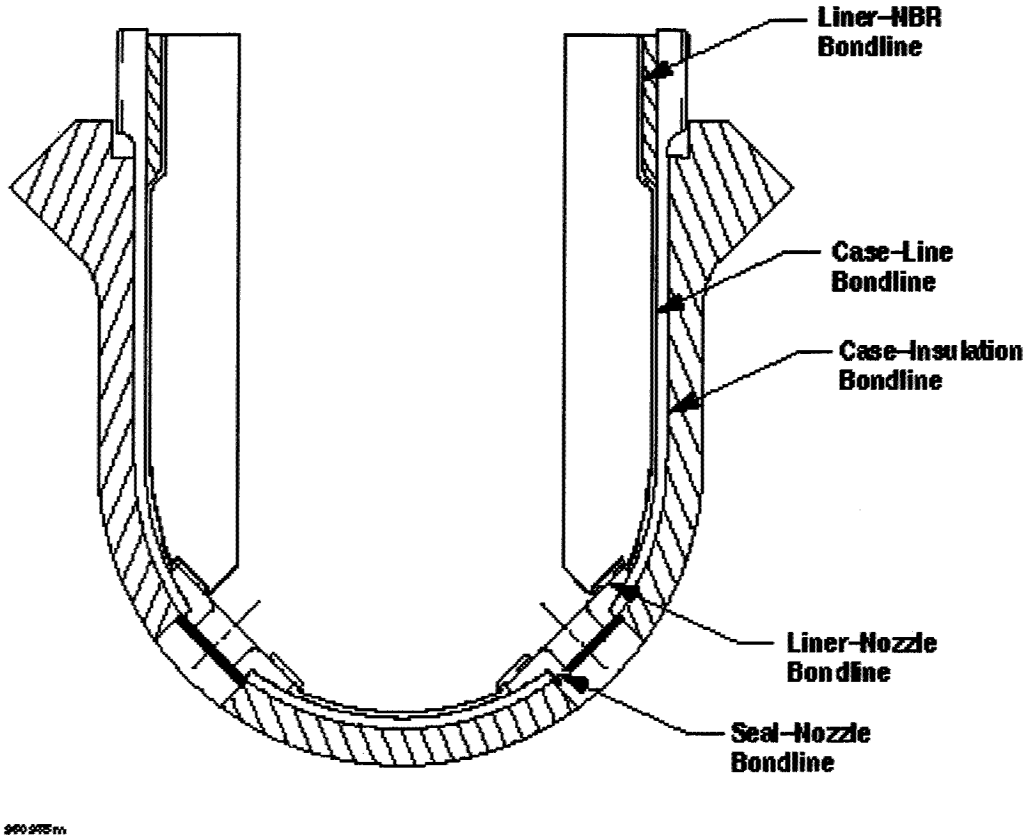


Figure 3. Schematic Showing Bondlines of the Igniter Initiator which are Cleaned with PF Degreaser

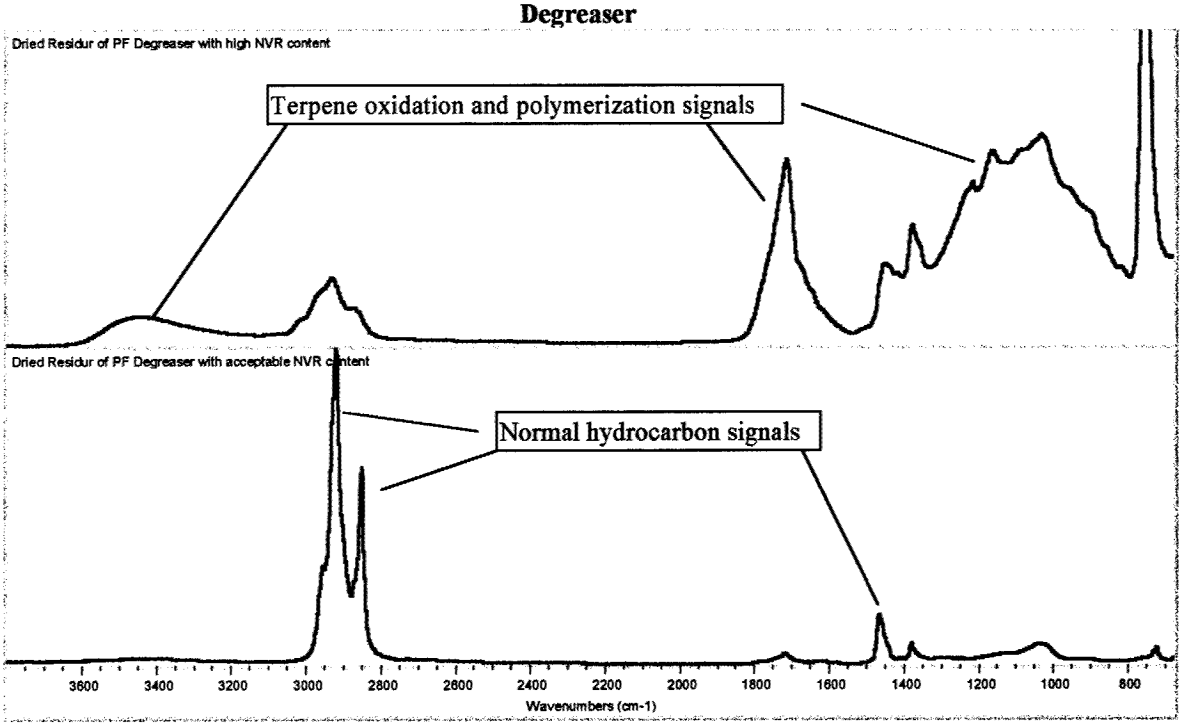


Figure 4. FTIR Analysis of NVR Samples from Bad (top) and Good (low NVR, bottom) PF Degreaser

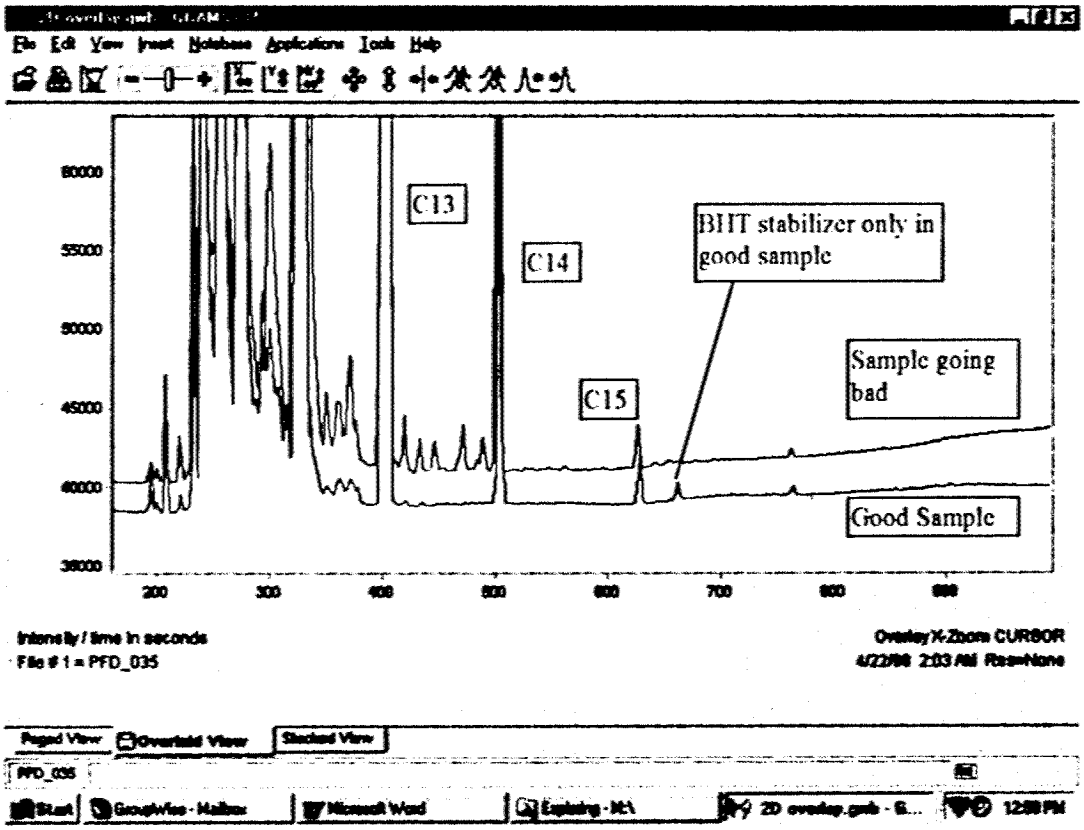


Figure 5. Comparison of GC Data from good sample and stored sample that is going bad. Copy of interactive screen in GRAMS/32 software allowing zooming in on detail of overlaid data

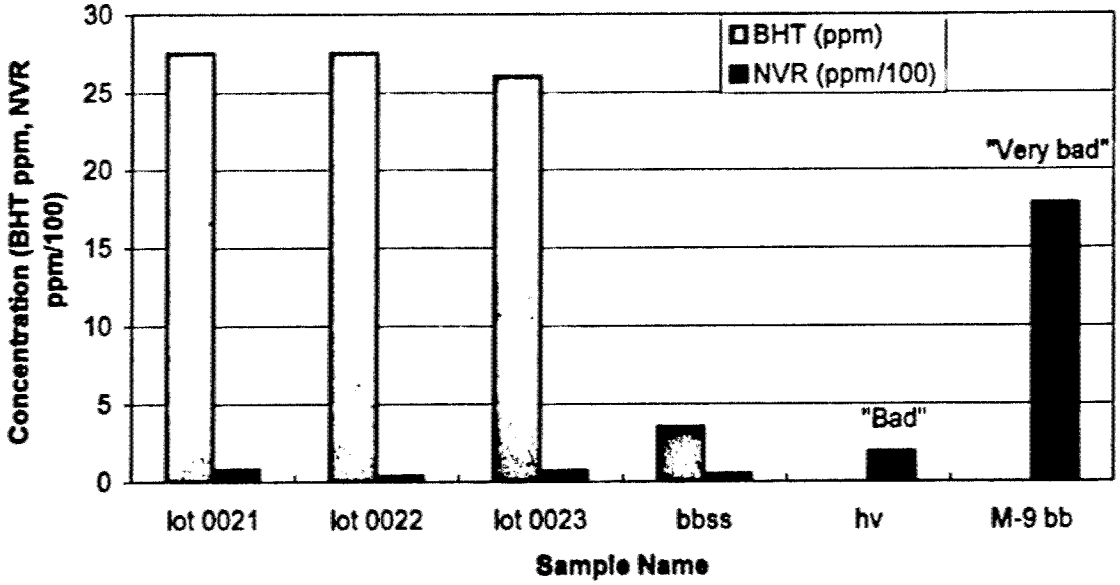


Figure 6. Comparison of BHT and NVR Concentrations in Terpene/Hydrocarbon Solvent Samples

Using Hazard Evaluation Techniques to Detect Potential Operational Risks Associated with Chemical Substitutions

John B. Mullen, Ph.D.
Senior Program Manager
ENSR Corporation
1220 Avenida Acaso
Camarillo, CA 93012

Rhonda Cardinal
Senior Environmental Engineer
The Boeing Company
5301 Bolsa Ave., H028-G111
Huntington Beach, CA 92647

Introduction

The Boeing Company (Boeing) in Huntington Beach, CA fabricates the liquid oxygen (LO_2) tanks of the Delta II launch vehicles on-site. After metal treatment, machining, welding and hydrotesting, the tanks go through a final cleaning process to remove any contamination.

Throughout most of the 1960's, trichloroethylene (TCE) was used for cleaning LO_2 tanks at the Huntington Beach facility. In 1968, Los Angeles County Rule 66 was adopted. This was a landmark rule aimed at reducing emissions of solvents, such as TCE, that contribute to the formation of photochemical smog, a major problem in Southern California. To replace TCE, the LO_2 tank degreasing system was modified and converted to 1,1,1 trichloroethane (TCA) which is not a smog precursor.

The Montreal Protocol, adopted in 1990 by the United States and many other nations, focused on eliminating solvents with potential for depleting the earth's ozone layer. Solvents with an ozone depleting potential (ODP) of 5 or above were originally targeted. TCA, with an ODP of 0.1, was far down on the list and was not expected to be heavily regulated until after the year 2000. In 1992, President George Bush issued an executive order to phase out production of TCA and other similar Class 1 ozone depleting compounds (ODCs) by 31 December 1995. Once again, a chemical substitution or new cleaning method for LO_2 tanks was required. The choices for LO_2 tank cleaning were limited.

Aqueous cleaning was briefly considered but immediately rejected. The qualification process that would be required to approve a new methodology for an existing system such as the Delta II was cost-prohibitive. It was also felt that the configuration of the LO_2 tank, with its inner isogrid structure and the many fayed surfaces, precluded effective rinsing and drying.

Three solvents were pre-qualified for cleaning the Delta II LO_2 tanks: TCA, TCE, and perchloroethylene (PCE). Since TCA was being phased out, the other two choices were TCE and PCE. After detailed evaluation, TCE was once again selected for use at Huntington Beach. Re-substituting TCE for TCA solved the ozone depletion problem, but it re-introduced a set of other environmental issues which had to be addressed: TCE was a volatile organic smog precursor, TCE was a carcinogen as defined by the State of California, it was a Hazardous Air Pollutant (HAP) under the Clean Air Act (1990), the degreasing system was subject to South Coast Air Quality Management District (SCAQMD) Rule 1122 for Vapor Degreasing Systems, TCE was subject to EPA's Halogen Solvent National Emission Standard, and the local fire department was very sensitive about how TCE was shipped and handled on-site.

To address all these issues, Boeing had a new TCE vapor degreasing system designed and constructed in 1997. In order to minimize emissions, the system was equipped with condensers, refrigeration systems and a dual carbon adsorber system, which in combination can recover more than 99.5% of the TCE. The system is permitted

by the SCAQMD to emit two pounds of TCE per month, which is sufficient to accommodate the production schedule. Cardinal (1997) provided a detailed description of the system and its operation.

The new TCE system makes the Delta II LO_2 tank being cleaned an integral component of the degreasing system. The tanks are approximately 12.8 meters (42 feet) in length and 2.4 meters (8 feet) in diameter. The overall system consists of a TCE supply tank, a vapor generator, the tank to be cleaned, condensers, the solvent recovery systems and a wastewater treatment system. Figure 1 is a simplified schematic of the system.

Before making the new system operational, Boeing wanted to review all aspects of system operations to anticipate any potential problems that may occur. This paper describes the hazard evaluation approach that was used to identify and prioritize these risks. The same methodology can be used for evaluating other chemical substitutions or process changes.

Identifying Operational Risks

During the hazard evaluation, potential accidents and operational failures were analyzed. These included events that could potentially cause TCE to be released, create safety hazards for personnel or cause damage to the system. The ultimate goal of Boeing was to develop a TCE risk management program that defined measures to reduce the frequency or severity of potential accidents and to insure that procedures and equipment were in place for handling accidents, if they did occur. An analysis was made based on the information provided by Boeing, their subcontractors and PPG Industries, the TCE manufacturer. The scope of the analysis was to speculate about potential operational and equipment failures and was not intended as an engineering validation of the system design parameters.

Based on the analysis and the system reviews, areas that needed improvement were identified, and recommendations were made concerning improvements that Boeing should consider implementing to reduce risks.

Methodology

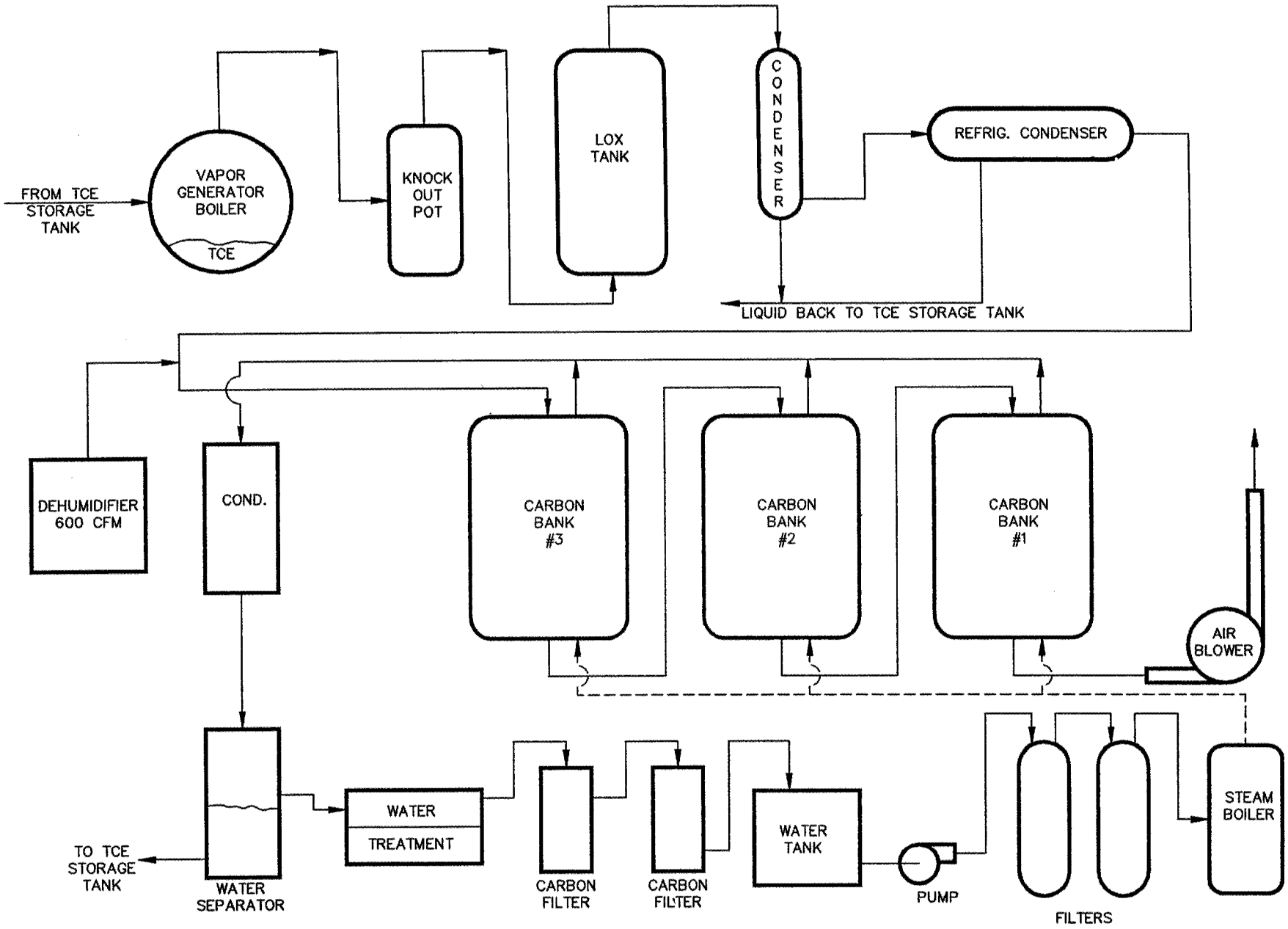
The technique used to evaluate the potential hazards was patterned after elements of the OSHA Process Safety Management (PSM) Program (OSHA, 1992) and the EPA Risk Management Program (RMP) (EPA, 1996). Although TCE is not a regulated substance (RS) under PSM or RMP, the techniques used in these programs for hazard evaluation offer a step by step systematic approach for identifying operational risks and their potential consequences.

The PSM and RMP regulations specify a number of different methodologies that can be used for conducting the hazard evaluation. These include: checklists, preliminary hazard analysis, "What If" analysis, Hazard and Operability (HAZOP) analysis, failure modes and effects analysis, fault tree analysis, event tree analysis, and combinations of the preceding.

A combination of the What If approach and the HAZOP approach was used for the Boeing TCE evaluation. Both the What If and the HAZOP approaches (along with the other hazard evaluation approaches mentioned above) are described in the American Institute of Chemical Engineers (AIChE) document titled "Guidelines for Hazard Evaluation Procedures" (AIChE, 1992). The What If and HAZOP approaches are discussed in more detail below.

To conduct the hazard evaluation, a multidisciplinary team was formed to identify potential adverse risks. The team included someone familiar with hazard evaluation procedures to guide the overall process. Other team members included a representative of management, a person familiar with the overall degreasing process, a person familiar with the equipment design, a person knowledgeable of field service and system installation, a maintenance person, a person from operations who will run the system, a controls engineer, representatives of environmental, health and safety, the TCE supplier, and someone who actually will handle the TCE (unload, transfer, refill and dispose of it when it is replaced).

FIGURE 1 BASIC BLOCK DIAGRAM FOR LO_2 TANK CLEANING



The team examined the TCE systems from the design drawings and "as constructed," and speculated about what types of deviations from the design intents could occur. The deviations that were evaluated included potential equipment failures due to mishandling, accidents and wear, and potential operational failures due to human errors of omission or commission.

Break the System into Smaller Pieces

The first step of the hazard evaluation required that the TCE system be broken up into its various modes of operation and, within each operating mode, into its respective major operations and components. A total of seven separate operating modes were considered for the different phases of operation of the Delta II system. These consisted of the following:

1. Receiving TCE and filling the solvent supply tank
2. Charging the vapor degreasing system with TCE prior to running
3. Running the vapor degreasing cycle to clean the propellant tank
4. Propellant tank drying cycle
5. Desorbing of the carbon adsorbers to recover TCE and cool down of the adsorbers
6. Cook down of the degreasing system to remove TCE from the vapor generator
7. Pit pot pump down to recover condensed TCE prior to lock down

For each of the above operating modes, the system was broken into logical pieces for analysis. The pieces are called segments and represent separate portions of the system that can be analyzed individually. The segments were developed by reviewing the system operating sequences and Piping and Instrumentation Drawings (P&IDs) for those parts of the system that are active during any operating mode.

Analyzing the Segments

The "What If" approach looks at the various segments and asks " What If " questions. For example, during Operating Mode 1, "Receiving TCE and filling the solvent supply tank", the question was asked, "What If the tanker truck hose ruptures while off-loading TCE to the supply tank?" The team was asked to speculate about how this might happen, how often it might happen and what the consequences might be if it did happen. Then, the team discussed methods to prevent the occurrence of the accident or to minimize the consequences if it does occur.

The HAZOP approach uses "Guide Words" to stimulate thinking. Guide Words are simple words to qualify or quantify the intention of each part of the system. The Guide Words are used in conjunction with various system parameters to help identify potential deviations. For this study, the parameters considered were Level, Pressure, Temperature, Flow Rate and Contents. The Guide Words applied to these parameters were High, Low, No, As Well As, and Other Than. System deviations were then considered by combining parameters with appropriate Guide Words, for example Pressure/High, and then evaluating all the reasons why the pressure might be high in a particular portion of the TCE system and what the consequences of that might be.

(Note: The analysis of system components that involve pressure, temperature, flow rates and the like are most easily analyzed with HAZOP techniques using the Guide Word approach. For operational elements, such as the unloading and transferring of chemicals, the hook-up and disconnection of equipment and the failure of safety systems or electronic components, the What-If approach is more useful).

Table 1 is an example of a worksheet that was used to record both the What If and the HAZOP information for Operating Mode 1, "Receiving TCE". The HAZOP worksheets were designed for the Guide Word approach but can also be used for the What If approach. When used for What If analysis, the What If condition is paraphrased in the "Immediate Cause" column. For example, "What If the truck hose leaks during TCE unloading?" could be stated in the Immediate Cause column as if the event occurred, "Truck hose leaks". The team would then speculate about the consequences of a cracked hose, any mitigating measures that might be in place to make TCE unloading operations safer, the qualitative frequency and severity of such an event, and would complete as many other

Table 1. Shortened Example of Delta II HAZOP Worksheet - Receiving TCE (Operating Mode 1)

Segment: 1 Bulk delivery of TCE and quick fill connections from tank truck to solvent supply tank

Item	Param/ Guide Words	Deviation	Immediate Cause	Contributing Causes	Consequences	Safety Systems/ Proceed	Probability	Severity	Notes
1-1 Truck connect to refill	Not Applicable (NA)	Chemical spill	Truck hose leaks	Faulty hose, poor inspection/ Maintenance	Exposure of workers in loading area	Flow restrictors/ emergency shutoff	Frequent	Slight	Emergency shut down can happen in about 30 seconds (maximum of 20 gallon spill). Hose frequently leaks a few drops at the truck.
1-2 Truck Connect to Refill	NA	Chemical spill	Truck hose bad hookup/ Connection	Poor SOP, poor training, no cross check, not follow SOP	Exposure of workers in loading area	Emergency shutoff switch at air padding.	Frequent	Slight	If gasket is cracked or worn out, connection can drip. Bucket is usually placed under connection to catch drips. Truck should be off-loaded on concrete.
1-3 Truck connect to refill	Flow Rate/ Reverse	Chemical spill	No shutoff when disconnect	No check valve, bad SOPs	Exposure of workers in loading area	Flow restrictors, emergency shutoff, quick connector	Frequent/ Periodic	Slight (a few drops)/ Moderate (a few gallons)	An adapter should be installed to accommodate a quick connector that can be disconnected without spilling. (Boeing to consider).
1-4 Hose/ piping to supply tank	NA	Chemical spill	Truck hose rupture	Truck drives off with hose connected, hose fails	Exposure of workers in loading area, spill outside of containment	Signage, SOPs, cross checks, trucks are chocked, two people required for off-load	Occasional	Moderate/ Severe	Not a likely scenario considering the number of observers that will witness the first fill up.

Parameters - Level, Press, Temp, Flow Rate, Contents Guide Words – High, Low, No, As Well As, Other Than

Probability

Frequent - 0 to 1 years (more than once per year)
Periodic - 1 to 10 years (once per decade)
Occasional- 10 to 100 years (during facility life)
Possible - 100 to 10,000 years
Remote - not likely to occur at all

Severity

Catastrophic - death or damage and production loss > $1M
Severe - multiple injury or loss from $100K to $1M
Moderate - single injury or loss from $10K to $100K
Slight - operational problems only or loss < $10K

columns on the worksheet as possible. (The example shown is for Segment 1: Bulk delivery of TCE..... To conserve space, the worksheet has been shortened. It is typically two pages or more in length for each segment.)

The process hazard analysis was conducted separately for each of the operating modes. When conducting the hazard analysis for a particular mode, those parts of the system that contain TCE were broken into their major components. This was done by tracing what happens to the TCE from the moment the mode starts until the mode is completed. This involves examining operational steps, such as setting initial valve positions, verifying temperature and pressure settings, and initiating start-up; system hardware components, such as valves, piping, hoses, vent lines, the tank, the vaporizer, condensers, accumulators and carbon adsorption equipment; and, support systems, such as instrumentation, measurement gauges, alarms, relief devices, and program logic controllers (PLCs). The P&IDs and operating modes were used to identify the system components that are utilized during each mode of operation.

The frequency of occurrence is broken into five categories: Frequent, Periodic, Occasional, Possible and Remote. Frequent is qualitatively defined to be more than once per year (occurrence in 0 to 1 year). Periodic is defined as once per decade (occurrence in 1 to 10 years). Occasional is qualitatively defined as during the facility lifetime (occurrence in 10 to 100 years). Possible is something that may occur in the broad range of 100 to 10,000 years. Remote is defined as not likely at all.

The severity is broken into four categories: Catastrophic, Severe, Moderate and Slight. These are loosely defined in terms of human injuries and monetary loss. Catastrophic is defined in terms of death or production loss greater than one million dollars. Severe is defined as multiple injuries or losses from 100 thousand to one million dollars. Moderate is defined as single injury or loss from 10 thousand to 100 thousand dollars. Slight is defined as operational problems only or losses less than 10 thousand dollars.

When the HAZOP worksheets were completed, the Immediate Cause of each potential adverse risk identified on the worksheets was then placed on a criticality matrix (Table 2). (Table 2 shows the matrix for Operating Mode 1 "Receiving TCE and has been shortened to save space). The criticality matrix ranks these potential adverse risks based on frequency of occurrence and severity. (The frequency and severity are the qualitative assessments that were discussed above. These were made by the PHA team for each potential event and represent a consensus of the team members). Each item on the matrix is followed by a numerical code in parentheses. The designation (1-1-1) or (1-1-4) corresponds to the information on the HAZOP worksheets. The designation (1-1-1) represents Operating Mode 1 (Receiving TCE), Segment 1 (Bulk delivery of TCE and quick fill connections from tank truck to solvent supply tank), and the first row of information on the Segment 1 table (Truck connect to refill). Similarly, the designation (1-1-4) corresponds to the information for Operating Mode 1, Segment 1, and the fourth row on the Segment 1 table.

In the upper left hand corner of each box on the criticality matrix is a single number that is the criticality score for the box. The scores range from 1 to 4. A score of 1 (Critical) indicates that a facility is frequently encountering catastrophic or serious situations (not a viable operating mode for any organization). A score of 2 indicates an undesirable operating mode which must be addressed. A score of 3 means that the situations described are acceptable with controls (but are obvious areas for improvement). A score of 4 indicates that the situations are acceptable (but are still candidates for consideration in the interest of continuous process improvement).

The next step taken by the team was to examine all the risks identified on the criticality matrix and to define what types of mitigation measures would be required to reduce or eliminate the risks. As part of this review process, the team compared the required measures with the systems, procedures and training that Boeing had in place. Based on this comparison, areas that needed improvement or required development were identified. The team first concentrated on all items on the matrix with a criticality score of 1, 2 or 3. Also included for mitigation consideration were any risks with a criticality score of 4, which have "Moderate" consequences and "Occasional" frequency. All other items on the matrix were identified as items that are candidates for continuous process improvement but not for required mitigation. The same selection process was used for all operating modes.

Table 2. Criticality Matrix

Operating Mode 1 - Receiving TCE

Frequency /Severity	Frequent	Periodic	Occasional	Possible	Remote
Catastrophic	(1)	(1)	(1)	(2)	(4)
Severe	(1) Hook up wrong tanker to unloading port (1-1-6) Incompatible material added to tank (1-2-6)	(2) Tank rupture (1-2-3)	(3) Truck hose rupture, piping damage (1-1-4)	(3)	(4)
Moderate	(2)	(3) No shutoff when disconnect (1-1-3)	(4) Truck hose rupture, piping damage (1-1-4) Valve closed when truck pumps (1-1-8) Tank truck accident (1-1-9) Tank split seam (1-2-4) Spark/fire source ignites combustible material or incompatible material starts bed fire (1-6-7)	(4) Fire in containment area (1-2-10) Pipe failure (1-4-3)	(4)
Slight	(4) Truck hose leaks (1-1-1) Truck hose bad hookup/ connection (1-1-2) No shutoff when disconnect (1-1-3)	(4) Leaking valves, leaking flange (1-1-5), (1-4-1), (1-4-7), (1-5-1), (1-5-7) Impurities in the TCE, system dirty (1-1-7), (1-3-1) Bottom valve leaks, line or flange leaks, drain opened (1-2-2) Contaminated material added to storage tank (1-2-5), (1-4-4), 1-5-4) Level gauge failure (1-2-7) Unit fails (1-2-8), (1-2-9) Inappropriate valve setting (1-3-4) Entering chill water too warm, water flow rate too low (1-4-9), (1-5-9)	(4) Operator adds too much chemical to tank (1-2-1) Pipe failure - minor (1-3-2) Adsorber fittings or containment shell leaks (1-6-2) Inappropriate valve settings (1-6-6) Downstream valve closed (1-7-3) Compressor not active, pneumatic lines leaking or rupture (1-8-1) No signal from PLC (1-8-2)	(4) Pipe failure (1-4-2), (1-5-2), 1-5-3) Incompatible chemical added to cooler (1-4-5), (1-5-5) Cooler rupture (1-4-6), (1-5-6) Cooler split seam, corrode through (1-4-8), Condenser split seam, corrode through (1-5-8)	(4)

Parameters - Level, Press, Temp, Flow Rate, Contents Guide Words - High, Low, No, As Well As, Other Than

Probability
Frequent - 0 to 1 years (more than once per year)
Periodic - 1 to 10 years (once per decade)
Occasional- 10 to 100 years (during facility life)
Possible - 100 to 10,000 years
Remote - not likely to occur at all

Severity
Catastrophic - death or damage and production loss > $1M
Severe - multiple injury or loss from $100K to $1M
Moderate - single injury or loss from $10K to $100K
Slight - operational problems only or loss < $10K

Score
(1) Critical
(2) Undesirable
(3) Acceptable with controls
(4) Acceptable

The potential adverse risks noted on the criticality matrices all involved vapor or liquid releases due to the following generic types of occurrences:

- Leaking fittings, valves, hoses or connections;
- Cracks in hoses fittings and casings;
- Cracks in piping, tanks, separators, accumulators, condensers or coolers due to mishandling and defects;
- Ruptures in piping, tanks, separators, accumulators, condensers or coolers due to accidents or external events (e.g., earthquake, vehicle accidents);
- Failure of safety or control systems;
- Damage to hardware due to operational errors; and,
- Fires or explosions

Boeing has addressed the major risks detected by this process and corrective procedures have been established. Table 3 is an example of some of the typical risks that were identified and the mitigation measures that have been instituted. (A much more extensive list was prepared but requires specific knowledge of the system components to interpret).

In addition, a list of lower priority process improvement recommendations was developed during the hazard analysis. Table 4 is an example of the type of recommendations that were made.

Table 3. Partial Summary Of Mitigation Measures

Risk	Mitigation	Status/Recommended Actions
Adding incompatible material to the TCE tank	A procedure should be established to control replenishing of TCE	Boeing established a new sign off procedure for replenishing TCE. The procedure defines who is authorized to add make-up materials to the supply tank.
Rupture of the tank, vapor generator, separator, receiver or accumulator	A major spill (up to 1200 gallons of TCE) due to a rupture can be controlled by a containment dike with sufficient volume. Emergency response teams can be activated to clean up the spill.	1) Boeing has verified that the containment capacity of the dike in the equipment area is sufficient. 2) An emergency response plan has been established for evacuation of the immediate area and recovery and clean up of TCE
Fast cool down of LOX tank causes vacuum	A vacuum break can prevent a damaging pressure differential.	A vacuum break and pressurization system are in place. Boeing verified the methodology used to size all relief devices.
Not enough TCE sensing locations in the pit	Currently there is one sensing location in the pit. Additional sensing tubes can expand the coverage area and improve the detection response time.	The analyzer has one remaining sensing port. Boeing will install sampling tubing for that port in a new location in the pit.
Truck hose rupture, piping damage	Signage, SOPs for truck filling operations, chocks for trucks, two people check off-system.	1) Boeing has established procedures requiring trucks to be parked on concrete and chocked, with check-off by Boeing required for verification of truck contents, proper hookup, valve settings, tank levels, off-load operations, disconnect and drive-off.
Tank truck accident	SOPs for on-site vehicle operations and delivery routes, enforced speed limits, and SOPs for truck back up.	1) In plant vehicle speed limits and safety procedures are strictly enforced. 2) Boeing personnel supervise and direct truck operations in the vicinity of TCE equipment.

Table 3. Partial Summary Of Mitigation Measures (continued)

Risk	Mitigation	Status/Recommended Actions
External fire source or bed fire	Fire suppression systems, removal of flammable materials, no contamination of carbon beds	No flammable materials are currently stored in the area. Boeing established SOPs to insure TCE quality for deliveries that insure that incompatible materials will not contaminate the carbon.
Valve closed in error	A checklist that specifies the proper manual valve positions for each operating mode can safeguard against human errors.	The O&M manual provides a checklist for all manual valves in each sequence of system operation to insure that the manual valves are properly set before the operations begin.
Water tubes rupture/leak-Condenser	Flooding by water could cause TCE to be spilled from the system. SOPs to isolate the water systems when the TCE system is not operating can prevent accidents when the system is unattended.	Boeing should establish a procedure that requires that the water supply to the condensers be blocked in when not in use. This can prevent unattended flooding of the system when not in operation.
Inappropriate valve settings	Inappropriate valve setting can be prevented by detailed checklists.	Checklists have been prepared for all valve positions for each operational cycle.

Table 4. Summary of Typical Process Improvement Recommendations

Additional Recommendations
1. Establish a procedure that TCE trucks are positioned over concrete, not asphalt, during unloading and that drip pans be positioned to catch small leaks.
2. Inspect TCE truck hose gaskets before hook-up.
3. Verify that all system drain valves are plugged to prevent spills due to accidental drain valve opening.
4. Perform emergency response exercises on at least an annual basis.
5. Regularly test the condition of the TCE stabilizers to make sure that the solvent is not susceptible to breakdown by contaminants such as acids, alkalis, metal chips and fines and exposure to oxygen, light and heat.
6. Establish a procedure for opening downstream valves that may have been accidentally closed to protect pumps and filters from sudden pressurization.
7. Insulate hot pipes and surfaces to a height of seven feet above grade.
8. Warn personnel about potential steam hazards and hot piping hazards in the skid area.
9. Inspect the gaskets of all flexible connections to the LOX tank for integrity at each hook-up. Verify proper grounding pathways after connection.
10. Insure that all personnel assigned to the degreasing system are properly trained regarding what they are expected or not expected to do.
11. Obtain data on the maximum blocked-in pump head for the wastewater treatment pumps and determine whether the carbon drums could be ruptured if blocked-in.
12. Determine whether check valves should be installed in the piping to the pit pump cooler to prevent water flow to the vapor generator and pit pump in the event of a water tube rupture.

Conclusions

This paper briefly describes a methodology that has proven very useful in past studies that were performed for a wide variety of chemicals and processes. Although these techniques were originally devised for studying acutely hazardous materials, they are also useful for defining potential operational risks that may be encountered any time a chemical substitution, a increase in chemical usage, a process change or a hardware modification is made.

The best approach for conducting a hazard evaluation is to put together a diverse and knowledgeable team, to break the system into logical pieces and to follow the hazardous materials from they moment they arrive and are accepted until they are consumed in the process or disposed.

The analysis of portions of a system that involve pressure, temperature, flow rates and the like are most easily analyzed with HAZOP techniques using the Guide Word approach. For operational elements, such as the unloading and transferring of chemicals, the hook-up and disconnection of equipment and the failure of safety systems or electronic components, the What-If approach is more useful. The HAZOP forms demonstrated in Table 1 are useful for both Guide Words analysis and the What-If analysis.

Some complex systems have several operating modes where certain portions of the system may be in operation and other portions are dormant. Also, the operating parameters (pressure, temperature, flow rates, etc.) of the active portions of these systems may vary in different modes of operation. Under such circumstances, it is best to conduct a separate hazard evaluation for each operating mode, as if it were a separate system.

References

Cardinal, R., "Cleaning Liquid Oxygen Tanks With Trichloroethylene in Southern California - A Technical and Environmental Challenge", Proceedings of the 1997 Aerospace Hazardous Materials Management Conference, Palm Beach, FL, August 1997, Technology 4 Section.

Center for Chemical Process Safety, "Guidelines for Hazard Evaluation Procedures; Second Edition with Worked Examples", Am. Inst. of Chem. Engr., 1992.

Department of Labor, Occupational Safety and Health Administration, 29 CFR 1910, "Process Safety Management of Highly Hazardous Chemicals; Explosives and Blasting Agents; Final Rule, Federal Register, February 24, 1992 pp6356-6416.

Environmental Protection Agency, 40 CFR Part 69, "Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act Final Rules and Notice", Federal Register, June 20, 1996 pp31668-31730.

REMOVAL OF EMULSIFIED OIL AND AFFF USING AIR-SPARGED HYDROCYCLONE TECHNOLOGY

Presented By:

1Lt Dennis O'Sullivan
Environmental Engineering Project Officer
Air Force Research Laboratory
Airbase and Environmental Technology Division (AFRL/MLQ)
Tyndall AFB, Florida 32403-5323
dennis.o'sullivan@ccmail.aleq.tyndall.af.mil

Ye Yi, Ph.D.
Advanced Processing Technologies, Inc. (APT)
P.O. Box 58131
Salt Lake City, Utah 84158-0131
aptash@aol.com

INTRODUCTION:

A range of Air Force (AF) activities generate wastewater containing suspended solids, petroleum, oil, and lubricant (POL) products, emulsion stabilizing agents, and aqueous film forming-foam (AFFF) liquids. These contaminants may pose a nuisance to federal or civilian industrial wastewater treatment plant (IWTP) operations or actually force the effluent stream to be out of compliance with local discharge limits. These concerns have been identified as Environment, Safety, and Occupational Health (ESOH) Needs #912, "New Treatment Technologies for Removing Low-Level Emulsified Oils in Contaminated Wastewater from Point and Non-Point Sources (High Priority)," #1414, "Pollution Controls for Aircraft Wash Racks (High Priority)," and #1609, "Methods to Mitigate Problems Associated with the Release of AFFF From the Flooding of Hangars as a Fire Suppressant (Low Priority)" (HSC/XRE, 1997). More information on these needs and the entire ESOH needs process can be found at the USAF Human Systems Center Environmental Planning Directorate's (HSC/XRE) Environment, Safety, and Occupational Health Technical Planning Integrated Product Team (ESOH TPIPT) website: http://xre22.brooks.af.mil.

Conventional wastewater pre-treatment processes are either ineffective or too costly to treat emulsified oils caused by the use of soaps and detergents and AFFF releases. Gravity oil/water (O/W) separators are not able to separate the chemically stabilized O/W emulsions that exit from aircraft and vehicle wash racks. Separators incorporating coalescing media provide only a marginal improvement in separation efficiency (Acurex, 1997). Other pre-treatment unit operations, such as thermal treatment, chemical demulsification, depth filtration, and combinations thereof, are capital intensive and usually have high operation and maintenance costs. Wastewaters containing AFFF need pre-treatment before being released to federally or privately owned treatment works (FOTW, POTW) due to its persistent foaming and high biochemical oxygen demand (BOD). Biological degradation may be economically successful if containment facilities and aeration equipment are available; otherwise, large capital expenditures are necessary. Also, long residence time, sludge removal, and intermittent flow may be barriers to an effective biodegradation process.

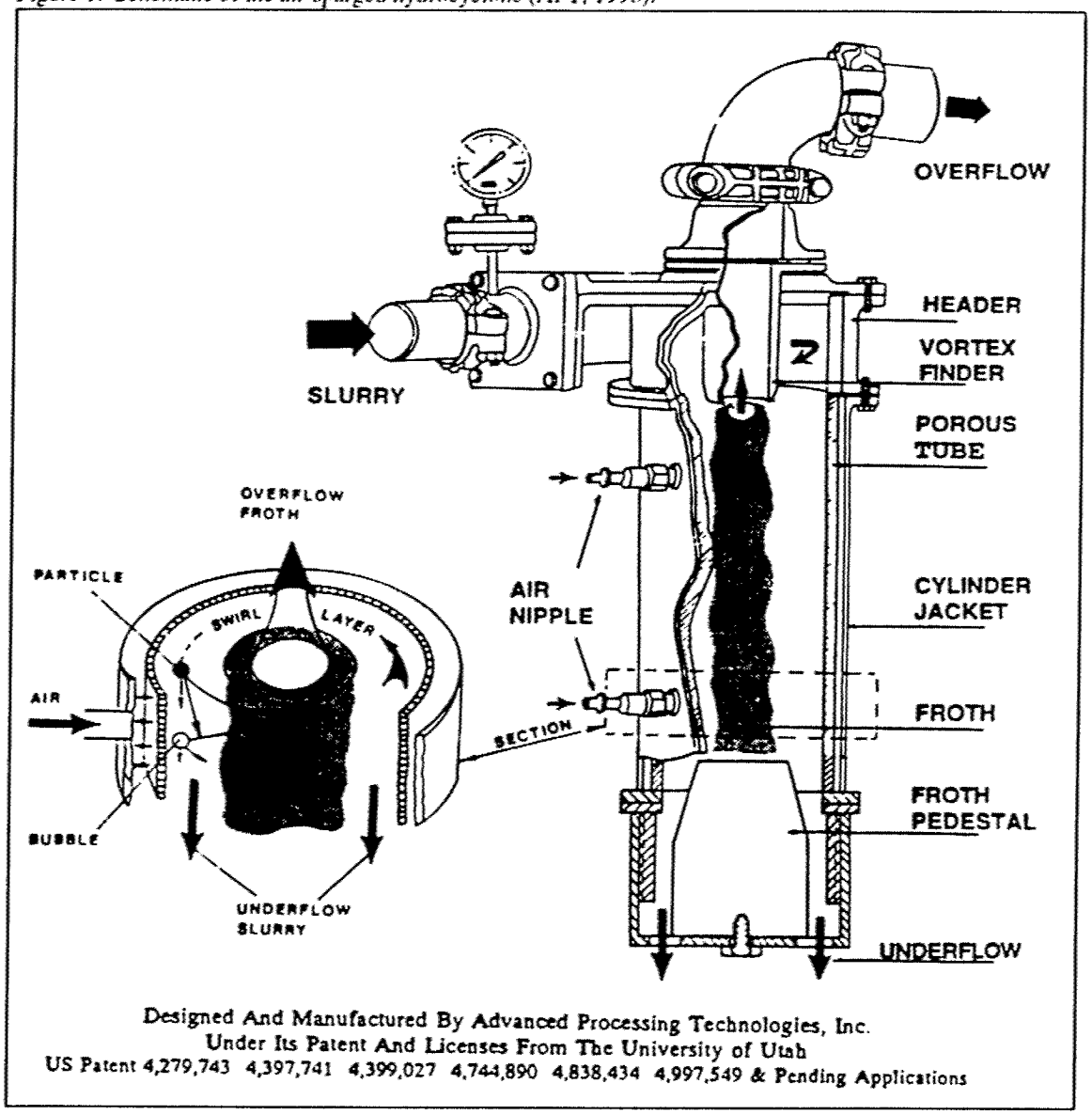
Air-sparged hydrocyclone (ASH) technology presents a low-cost, highly efficient treatment option for emulsified oil and AFFF waste streams. By combining chemical coagulation, hydrocyclone, and air flotation principles into one unit operation, an ASH unit can provide adequate pre-treatment, and often final treatment, of these effluents. It has a very large throughput while maintaining a small footprint. ASH technology also provides operational flexibility. It can be installed as a fixed process to provide continuous or batch treatment or placed on a small, standard sized trailer to treat geographically separated sources. This paper will present test data accumulated by AFRL/MLQ and APT during a Small Business Innovative Research (SBIR) Phase II research and development effort. The treatment studies were conducted on various waste streams at six different AF bases. Results from commercial treatability tests on textile printing and food processing waste streams are available but will not be presented in this paper.

BODY:

AIR-SPARGED HYDROCYCLONE OPERATION

The air-sparged hydrocyclone unit removes hydrophobic solid particles or liquid droplets, including chemically emulsified oils, from wastewater. It consists of a jacketed, right-vertical, porous tube, a conventional cyclone header with a mounted vortex finder, and a froth pedestal/underflow structure that is centered on the cyclone axis at the bottom of the porous tube. See Figure 1. Wastewater is fed tangentially through the cyclone header to develop a swirl flow inside the porous tube. Pressurized air passes through the jacketed porous tube wall and is sheared into numerous fine bubbles by the high-velocity swirl flow of the suspension. Hydrophobic particles/oil droplets (or particles rendered hydrophobic by a chemical reagent) in the suspension collide with these bubbles, and, after bubble/particle attachment, are significantly reduced in their tangential velocity and transported radially into a froth phase which forms on the cylindrical axis. The froth phase is supported and constrained by the froth pedestal and thus moves towards the vortex finder of the cyclone header, being discharged as an overflow product. Cleaned water remains in swirl motion and is discharged as an underflow product through the annulus between the porous tube wall and the froth pedestal.

Figure 1. Schematic of the air-sparged hydrocyclone (APT, 1996).



The design features of the ASH system improve the removal of fine particles in three ways. Firstly, a strong centrifugal force field is developed; the magnitude of the field is determined and controlled by the tangential velocity of the suspension and the cyclone diameter. This centrifugal force field results in increased inertia of fine particles and hence facilitates their collision and attachment to air bubbles. Secondly, the high-speed swirl flow exerts a considerable shear force at the porous tube inner surface wall. This, coupled with the fact that the air phase is introduced through extremely fine pores (35 - 140 microns), results in the generation of numerous fine air bubbles with average bubble diameter at about 100 microns. These small air bubbles are directed in the radial direction, orthogonal to the motion of particles contained in the swirl flowing water. As a result, the probability of collision of air bubbles with particles is significantly increased so that the collision event is no longer a rate determining process. Finally, the wastewater inside the ASH has two basic motions. One is the swirl motion along the circular inner surface of the porous tube, and another is an axial downward motion toward the bottom of the ASH. For a 2-inch inner diameter ASH 20 inches in length, any particular reference point in the influent wastewater may have approximately 9570 chances to collide with a freshly generated air bubble before it is discharged from the unit. It is these features that enable the ASH system to have a specific processing capacity (gallons processed per unit volume of the equipment) 100 - 500 times of any other conventional equipment. The ASH test unit used in all testing processed 20 gallons per minute (gpm). At that rate, each liter of wastewater resides in the ASH reactor (2.0-in. inside diameter, 24-in. long) for less than 0.25 seconds.

USAF SBIR PHASE II TEST RESULTS

At each test location, the wastewater for each test run was usually pulled from the o/w separator, floor sump, or containment structure that serviced the facility. Effluent characterization was determined from a one-liter grab sample collected adjacent to where the ASH feed pump was placed. The quality of the treated water was determined from a one-liter sample collected from the ASH discharge line after approximately ten minutes of operation. Independent laboratories conducted all chemical analyses, except AFFF concentrations, which were determined by APT. Quantitative values for total suspended solids (TSS), oil and grease (O&G), and total petroleum hydrocarbon (TPH) were obtained by EPA 160.2, EPA 413.1 or SM18 5520-B, and SW846 8015-M methodologies, respectively. Presently, there is no standard method to determine AFFF concentration in solution. APT developed two semi-quantitative methods to determine AFFF removal from firefighting training pit effluents: foam height (FH) and surface tension (ST) measurements. In the first method, air is passed through a specific volume of AFFF solution until the produced foam layer breaks and rises no higher. Surface tension measurements were made with a Kruss K10T Digital Ring Tensionometer. Calibration curves were produced for each method as a function of AFFF concentration. Measurements of the untreated and ASH treated solutions were plotted on the respective calibration curves to determine AFFF concentrations. The FH and ST calibration curves will not return an absolute AFFF concentration for a specific sample; however, they clearly bracket an range of AFFF removal

Nellis AFB, Nevada

Testing at Nellis AFB base was conducted from 31Jan-6Feb 1997. The vehicle maintenance facility (VMF) provides repair and maintenance services to over 2800 AF vehicles. The majority of the waste stream results from the washing of vehicles and parts, both before and after repair work. Occasionally, empty oil and fuel tanks are washed clean. Contaminants in the stream include engine oil, transmission and hydraulic fluids, gasoline, diesel fuel, solids, and detergents (in this case, mostly Simple Green). The ASH feed pump was submerged about two feet below the surface of the water in the primary chamber of the exterior floor sump, which acts as a simple O/W separator.

The Nellis AFB jet engine test cell facility (JETC) generates wastewater from the washing of jet engine parts and floor washing. The flow is low; yet, contains a relatively high amount of oil and fuel. Wastewater is piped to an exterior, below grade, O/W separator. The first chamber of the separator was almost entirely full of fuel and oil. Therefore, the ASH feed pump was placed in the second chamber. Visual inspection of a grab sample indicated at least 5% fuel and oil content. A low volume of wastewater in the separator dictated that only one test could be conducted. Total suspended solids (TSS), oil and grease (O&G), and total petroleum hydrocarbon (TPH) contents of the wastewater from each facility, before and after ASH treatment, are presented in Tables 1, 2, and 3, respectively (APT, Feb. 97). It was also noted that approximately 60-90% of the heavy metals in these waste streams was removed. The cost to treat the motor pool wastewater would be approximately $0.42 for every 1000 gallons processed, while the jet engine test cell effluent would cost $0.72/1000 gallons (APT, Feb 97).

Table 1. Total Suspended Solids Analyses for Nellis AFB

Stream	Test #	Influent (ppm)	Effluent (ppm)	% Removal
Vehicle Maintenance	1	60	43	28
	2	302	83	73
	3	105	37	65
	4	9250	77	99
Engine Test Cell	1	>5000	37	>99

Table 2. Oil & Grease Analyses for Nellis AFB

Stream	Test #	Influent (ppm)	Effluent (ppm)	% Removal
Vehicle Maintenance	1	104	21	80
	2	663	34	95
	3	40	26	35
	4	4360	34	99
Engine Test Cell	1	>5%	11	>99.9

Table 3. Total Petroleum Hydrocarbon Analyses for Nellis AFB

Stream	Test #	Influent (ppm)	Effluent (ppm)	% Removal
Vehicle Maintenance	2	549	52	91
Engine Test Cell	1	>5%	19	>99.9

Other Air Force Bases

Similar tests were conducted at Tinker AFB, OK (24-25 Mar 97), Tyndall AFB, FL (3 Apr 97), Eglin AFB, FL (5 Apr 97), and Goodfellow AFB, TX (19-22 Nov 97). The results of these tests are in Table 4 (APT, Dec 97). Aircraft wash rack effluents (ACWR) tested at Tyndall AFB were obtained from the primary chamber of the servicing O/W separator. The AFFF contaminated effluents from firefighting training exercises at Tyndall AFB are collected in a lined lagoon after passing through an O/W separator used to reclaim free phase fuel. The fire training pit (FTP) lagoon water, which is presently being treated by an aerobic biological process to reduce TPH and BOD, is used as make-up water for the fire pits or metered into the sanitary sewer. This lagoon water was used in the ASH test. At Goodfellow AFB, FTP effluents are gravity fed to a lift station where they are pumped to a 500,000-gallon holding tank without any treatment. Water from the bottom of the tank is metered to the sanitary sewer, used for fire pit make-up water, or reutilized in the firefighting pump trucks. Water for the Goodfellow test was taken from the lift station. The cost to treat Goodfellow AFB FTP wastewater was estimated to be $0.34-$0.44/1000 gal (APT, Dec 97).

Table 4. ASH Treatment of Various AFB Waste Streams.

Stream	Test / Sample	Influent (ppm)	Effluent (ppm)	% Removal
Tinker-JETC	TSS-1	26	7	73
	TSS-2	120	7	94
	O&G-1	8700	ND*	100
	O&G-2	5200	ND	100
	O&G-3	13	ND	100
	O&G-4	3120	6	99
	O&G-5	7470	ND	100
Tyndall-ACWR	O&G-1	2090	ND	100
	TPH-1	2340	ND	100

* ND – Non Detect

Table 4 (cont.). ASH Treatment of Various AFB Waste Streams.

Stream	Test / Sample	Influent (ppm)	Effluent (ppm)	% Removal
Tyndall-FTP	TSS-1	53	4	93
	O&G-1	94	6	94
	AFFF(FH)-1	800	100	94
	AFFF(ST)-1	100	12	88
Eglin-VMF	O&G-1	5250	31	99
Goodfellow-FTP	TSS-1	390	3	99
	O&G-1	1850	6	99
	TPH-1	1120	ND	100
	AFFF-1			80-90

* ND – Non Detect

CONCLUSIONS:

Through extensive testing on AF waste streams containing suspended solids, emulsified fuels and oils, metals, and AFFF liquids, air-sparged hydrocyclone technology has provided a high level of contaminant removal at very low cost. With the construction flexibility of fixed or mobile configurations, ASH technology could be utilized in a wide variety of AF applications. System attributes such as low capital cost, operation and maintenance expenses of only $0.40-$1.10/1000 gallons, high throughput, process flexibility, and high contaminant removal rates, make the ASH an unbeatable value when designing wastewater treatment processes for AF waste streams. At the present time, a mobile ASH treatment system is being constructed for the 325 CES Environmental Flight, Tyndall AFB, Florida. In addition, a fixed ASH system is being purchased by AFRL/MLQC (Airbase Technology Development Branch) for installation at the 823 Civil Engineering Red Horse – Detachment 1, Silver Flag Fire Training Facility, Tyndall AFB, Florida. Also, a large, fixed ASH system is being considered for installation at the DoD Firefighting Training School, Goodfellow AFB, Texas.

REFERENCES:

1. Acurex Environmental Corp., Draft report, "Testing of New Technologies for Oil/Water Separation at Dover AFB," USAF Contract # F0863-95-D6003/DO5302, December 1997.
2. Advanced Processing Technologies, Inc., Third Quarterly Progress Report, USAF SBIR Phase II Contract F41624-96-C0003, 17 February 1997.
3. Advanced Processing Technologies, Inc., Sixth Quarterly Progress Report, USAF SBIR Phase II Contract F41624-96-C0003, 28 December 1997.
4. Advanced Processing Technologies, Inc., December 1996.
5. HSC/XRE Website at http://xre22.brooks.af.mil, 12 January 97.

Meeting the 50 Percent Reduction Mandate: Progress at MSFC

Sharon D. Belser, CH2M HILL
J.P. Martin, P.E., CH2M HILL
Nannette C. Woods, P.E., CH2M HILL

Introduction

"... The Federal Government should become a leader in the field of pollution prevention through the management of its facilities, its acquisition practices, and in supporting the development of innovative pollution prevention programs and technologies..." (Executive Order 12856)

The federal government is the nation's largest consumer of raw materials, power, water, and products (EPA, 1994). This consumption can generate potentially harmful releases (air, water, and soil) and wastes that might adversely affect public health or the environment. In addition, high costs are associated with managing waste at current facilities and cleaning up contaminated facilities.

To demonstrate leadership in environmental stewardship, President Clinton issued several executive orders requiring federal facilities to comply with pollution prevention efforts. The orders deal with reducing pollution at its source, recycling and procuring recycled goods, setting targets for reducing the release and offsite transfers of toxic chemicals, and reporting toxic chemical releases and offsite transfers above threshold values. This paper presents the efforts of the George C. Marshall Space Flight Center (MSFC) to comply with Executive Order (EO) 12856, which requires facilities to voluntarily reduce the release and offsite transfer of toxic chemicals by 50 percent by December 31, 1999.

MSFC's primary goal is to achieve a 50 percent reduction in total reportable toxic chemical releases and offsite transfers under Section 313 of the Superfund Amendments and Reauthorization Act (SARA), using the 1994 Toxic Chemical Release Inventory (TRI) baseline for comparison (NASA/MSFC, June 1995). In addition, MSFC will apply the reduction goal to new chemical substitutions that may occur (such as trichloroethylene for Freon 113) even though this is not required by EO 12856. MSFC's secondary goals are to reduce significant general toxic chemical releases by 50 percent; to control the use of toxic chemicals in any existing or new processes, to the extent feasible; and to find non-toxic substances for the replacement chemicals.

This technical paper has been prepared to document MSFC's progress toward meeting these goals. The focus of this paper is only on reportable and general toxic chemical usage, although EO 12856 addresses other areas, such as solid waste, energy, and water use. The progress toward meeting the 50 percent reduction goal is documented by evaluating the projects completed and by identifying additional pollution prevention projects to help meet the reduction goals. The objectives of this paper include documenting the following:

- Progress made toward meeting the 50 percent reduction goal for reportable chemicals
- Status toward meeting secondary goals for general toxic chemicals
- Pollution prevention projects completed to date and those planned for implementation
- Projected status toward meeting the 50 percent reduction goal by December 31, 1999, based on implementation of proposed projects

Summary of Baseline and 1996 Chemical Use

A baseline survey was conducted in 1994 for the initial reporting year. Chemical use was classified into two primary categories for the baseline survey: (1) reportable toxic chemicals and (2) general toxic chemicals. The reportable toxic chemicals are those that must be reported under the requirements of the Emergency Planning and Community Right-to-Know Act (EPCRA) (also known as Title III of SARA) and that have an annual use of more than 10,000 pounds. At MSFC, these chemicals are:

- Perchloroethylene (PCE)
- 1,1,1-trichloroethane (TCA)

- Diphenylmethane-4,4'-diisocyante (MDI)
- 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)

These reportable chemicals are addressed by EO 12856. General toxic chemicals were chemicals that were used at less than the reportable quantity of 10,000 pounds. Although these chemicals are not included in the goals of EO 12856, MSFC seeks to reduce the use and release of the general toxic chemicals as much as practical.

The 1994 baseline reportable chemical release was 131,860 pounds. In 1996, MSFC had a reportable chemical release of 100,400 pounds; in other words, MSFC has accomplished a 24 percent reduction in reportable toxic chemical releases from the baseline year. The implementation of proposed pollution prevention projects and the phase-out of Freon 113 and TCA use will allow MSFC to meet the 50 percent reduction goal by December 31, 1999.

As for general toxic chemicals, the 1996 chemical data indicate that the use of three general toxic chemicals (methyl ethyl ketone [MEK], methylene chloride, and HCFC 141b) almost reached the 10,000 lbs/yr threshold level for reporting requirements. MSFC's secondary goal is to control the use of these substances in new and existing processes and to maintain their use below threshold levels. An ongoing effort is taking place to identify substitute solvents for the general toxic chemicals.

Summary of Chemical Release History and Projections

Total releases of the four reportable toxic chemicals were developed as part of the 1994 TRI Report (NASA/MSFC, June 1995). Total baseline releases for the four reportable chemicals were estimated to be 131,860 pounds. A comparison of baseline (1994), 1995, and 1996 toxic chemical releases, as well as projected releases for 1997 and 1998 for each reportable chemical, is provided as Exhibit 1. A comparison of MSFC's progress toward the 50 percent reduction goal based on baseline releases and projected chemical use reductions is provided as Exhibit 2.

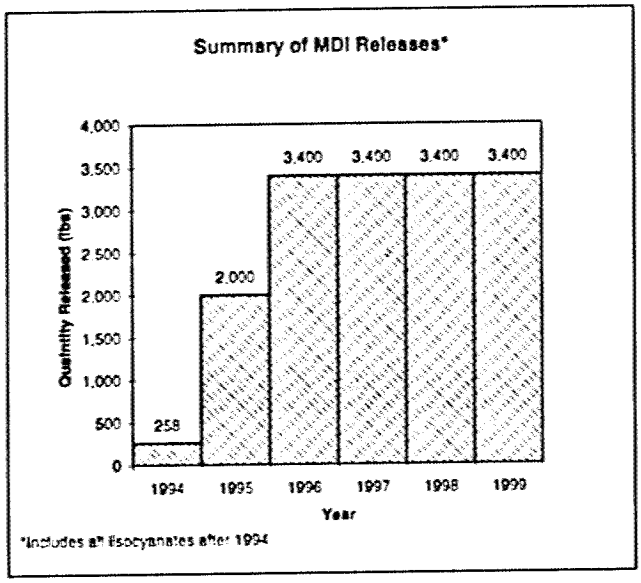
The 1996 releases indicate that MSFC has achieved a 24 percent reduction in reportable releases and offsite transfers. However, as shown in Exhibit 2, it is expected MSFC will near the 50 percent chemical release reduction goal by the end of 1998. Most of this reduction probably will be a result of reduced PCE releases, which should decrease by 40 percent annually once the two vapor degreasers located in the plating shop are modified. It is assumed that in 1998 the facility will only realize a 30 percent reduction in PCE releases since the vapor degreaser modifications were completed in April 1998.

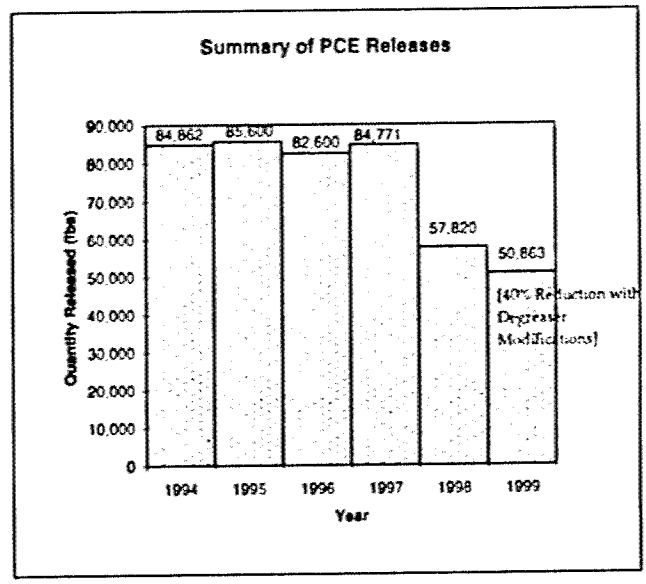
Other significant reductions should result from the discontinued use of Freon 113 and TCA, which have been banned from production. MSFC originally anticipated discontinuing the use of Freon 113 by December 1996. However, it is likely that Freon 113 will continue to be recycled and used at the facility until 1999. There has not been a date scheduled to discontinue the use of TCA at the facility. Currently, some operations have been granted exemptions to continue using TCA for cleaning purposes. Nonetheless, there is an ongoing effort to find appropriate nonreportable substitutes for TCA. If the estimated releases of Freon 113 and TCA are reduced to zero by 1999, MSFC will report at least a 65 percent reduction in toxic chemical releases from baseline levels.

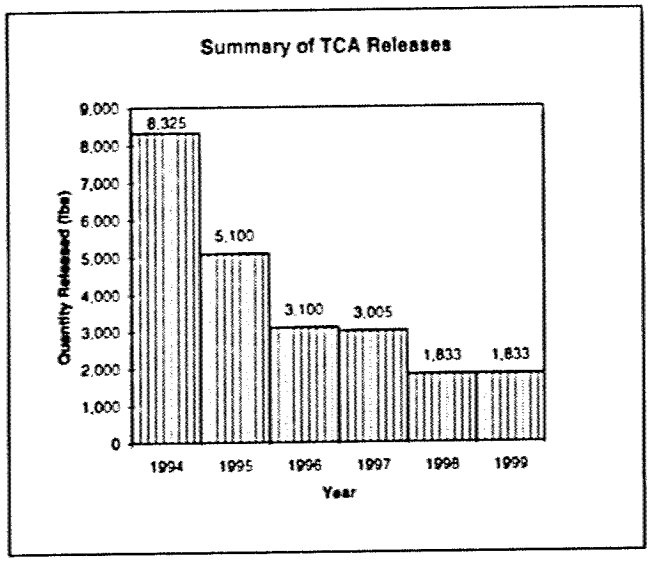
Note that the releases of diisocyanate compounds actually have increased since the baseline year. For the baseline year of 1994, only the release of the diisocyanate compound MDI was required to be reported on the TRI report. In 1995 this requirement was modified, and MDI is now reported in a group of diisocyanate compounds. Most of these compounds are being used at the spray-on foam insulation (SOFI) process, and most of the diisocyanate compound releases are releases to land or energy recovery. Diisocyanate compounds are disposed of as hazardous waste after use in the SOFI process; occasionally, the shelf life of the materials expires due to overstocking and subsequently these materials are sold as excess.

Pollution Prevention Projects – Reportable Toxic Chemicals

Pollution prevention projects that have been implemented and those proposed for implementation for MSFC's reportable toxic chemicals are described below. Implementation of these projects will assist MSFC in meeting the reduction goal.







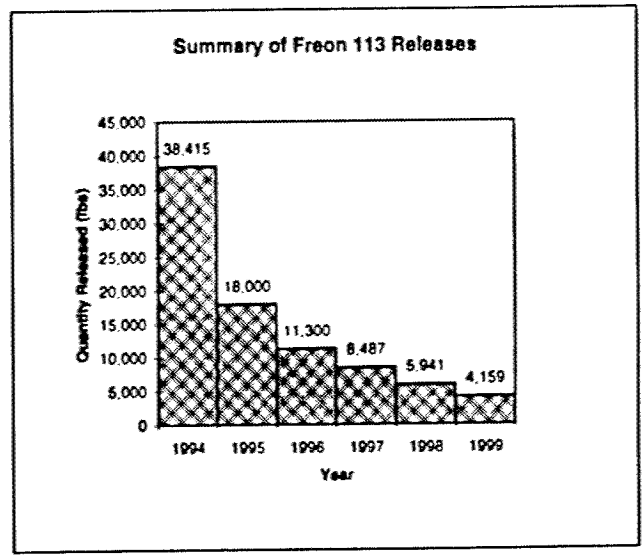


EXHIBIT 1. Historic and Projected Reportable Chemical Releases (1994-1999)

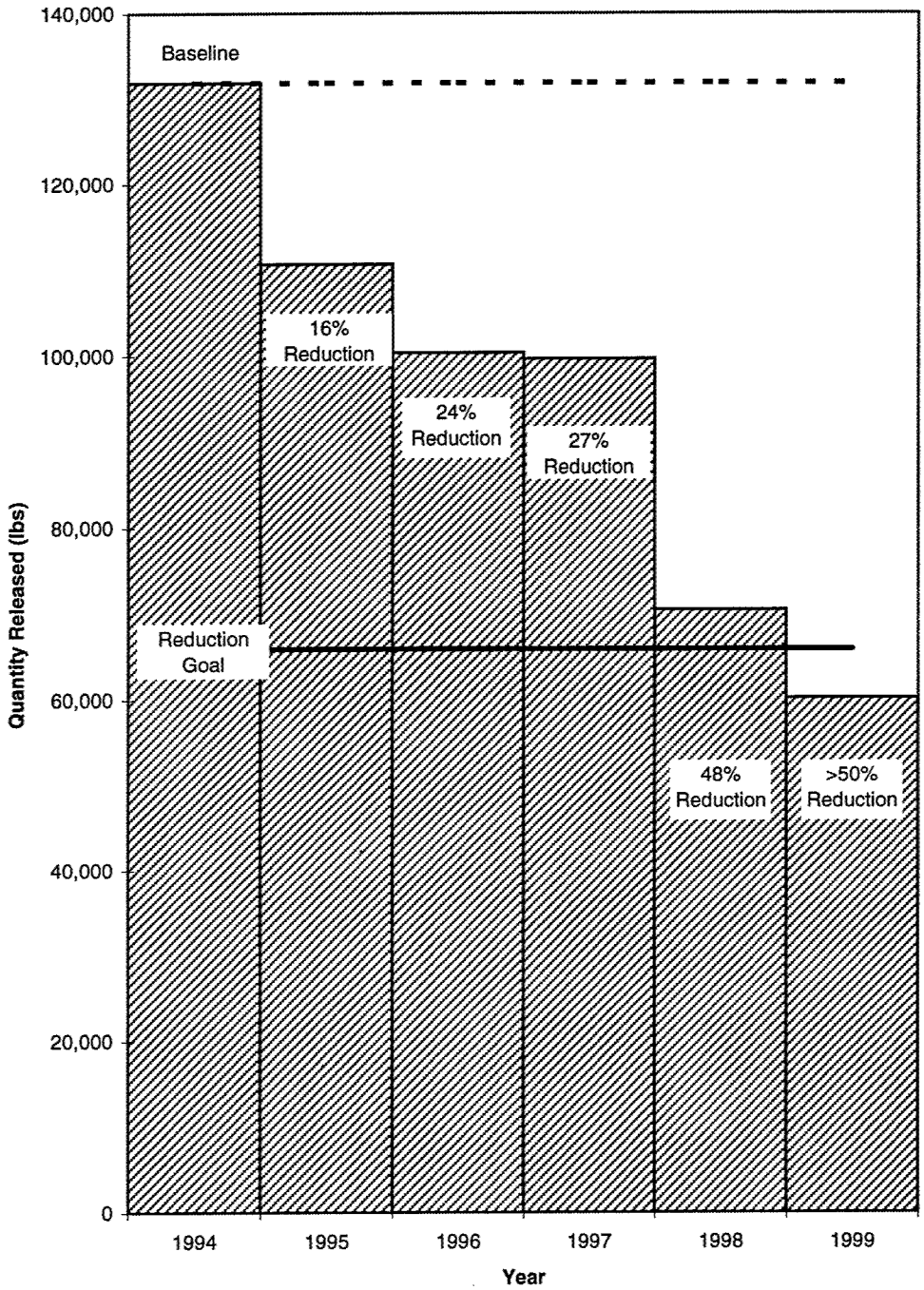


EXHIBIT 2. Summary of Reportable Chemical Releases

Vapor Degreasing. Four vapor degreasers previously were evaluated for pollution prevention activities because of the significant usage amounts of PCE and TCA. Currently, one of the smaller vapor degreasers has an exemption from the federal government to continue using TCA as a cleaning solvent. An estimated 18 percent potential pollution reduction of reportable toxic chemicals could be achieved by discontinuing the use of TCA in this degreaser. This reduction will not be realized until an appropriate substitute is found for TCA in the degreaser.

MSFC has two large PCE degreasers that account for the majority of PCE usage at the facility. The vapor degreasers were retrofitted with an increased freeboard area and refrigerated cooling coils in early 1998. The freeboard area in the degreasers has been increased 75 to 80 percent. In addition, the vapor degreasers were retrofitted with sub-zero degree Fahrenheit (°F) refrigeration coils that were added above the water jacket. According to manufacturers of vapor degreasers, retrofitting an existing degreaser with refrigerated cooling coils and increasing the freeboard area will reduce degreasing emissions by approximately 40 percent (this is a conservative estimate). Once the degreasers are retrofitted, a potential pollution reduction of approximately 27 percent for reportable toxic chemicals is anticipated.

Parts Cleaning. Two pollution prevention activities have taken place for the parts cleaners used in maintenance activities. The parts cleaners are covered when not in use to reduce air emissions from evaporative losses, and the TCA-based solvent has been replaced. Previously, the cleaning solvent used in the parts cleaners was Saf-Sol 20/20, which is approximately 40 percent TCA. Use of an alternative, terpene-based solvent for cleaning and the discontinued use of TCA are expected to result in a potential pollution reduction of approximately 2 percent for reportable chemicals.

Sitewide Pipe Cleaning/LOX Equipment Cleaning. TCE and Freon 113 are being used for verification testing of liquid oxygen (LOX) equipment. To limit the use of TCE and Freon 113, AK225 could be used for verification testing. Input from operators at the precision cleaning facility indicates that AK225 provides acceptable performance but has a strong odor and causes minor physical irritation when inhaled. This problem can be corrected easily by mandating that operators use proper personal protective equipment when using AK225 for verification testing.

Manual Cleaning. Pollution prevention activities are ongoing in implementing alternative cleaners or alternative application methods for hand-wipe cleaning operations. Toxic solvents, such as MEK, acetone, toluene, and isopropyl alcohol, are currently being used for hand-wipe cleaning. Numerous replacement cleaners are being investigated to identify a nonhazardous replacement cleaner.

At the test stands, the Freon 113 currently used for hand-wipe cleaning will be replaced with AK225. In other areas, cleaning solvents are issued only in squeeze bottles. This packaging helps reduce use and therefore reduces waste and emissions.

When the use of Freon 113, TCA, and other SARA 313 reportable chemicals is discontinued in manual and hand-wipe cleaning operations, a potential pollution reduction of 6.6 percent for reportable chemicals is anticipated.

Pollution Prevention Projects—General Toxic Chemicals

Additional pollution prevention projects have been implemented or proposed for reduction of general toxic chemical usage. These projects are described below.

Paint Booths. Pollution prevention activities have been implemented and are ongoing at the water wall paint booths to reduce the use and release of general toxic chemicals, such as MEK, methyl isobutyl ketone (MIBK), xylene, ethyl benzene, and toluene. These activities include the following:

- **High-Volume, Low-Pressure (HVLP) Spray Guns**. HVLP paint guns reduce the amount of airborne paint from overspray during the painting process. HVLP spray guns have transfer efficiencies of between 30 and 60 percent, whereas conventional paint spray guns have transfer efficiencies of between 15 and 40 percent.

- **Low Volatile Organic Compound (VOC) Paints**. Low-VOC paints generate less air emissions during painting and drying.

- **Sign Decals**. Using decals reduces the amount of painting deeded to generate a sign and improves the quality and durability of the signs.
- **Automatic Paint Spray Gun Washers**. According to manufacturer's data, the use of automatic paint spray gun washers can reduce solvent use for spray gun cleaning by 70 to 90 percent.
- **Activated Carbon Filters**. Use of activated carbon filters for treatment of the water in the water wall reduces the quantity of wastewater that is discharged.
- **Separate Paint Guns for Specialty Applications**. Providing additional paint guns allows painting of flight hardware with a paint gun that requires MEK cleaning and painting of non-flight hardware with a separate system that can be used with terpene-based solvents.

Fuel Use. MSFC is planning to install a Stage II Vapor Recovery System at the facility fueling station. In previous pollution prevention efforts at the facility's fueling station, some underground storage tanks (USTs) were replaced with aboveground storage tanks (ASTs) to decrease losses of gasoline and diesel fuel from spills and leaks associated with fuel storage.

Additional pollution prevention activities associated with reducing fuel usage and releases require reducing the testing and maintenance schedule for emergency backup generators located at the facility. MSFC has approximately 60 backup generators. Each generator is tested for approximately ½ hour per month to verify proper working order and for maintenance purposes. Currently, there is no standard procedure for testing the generators at MSFC. The facility will develop a new maintenance schedule for generator testing to reduce generator testing for emergency generators that can experience some downtime.

HVAC and Refrigeration System Operation. Pollution prevention activities associated with the heating, ventilating, and air conditioning (HVAC) and refrigeration systems include a refrigerant recycling machine, non-chlorofluorocarbon (CFC) refrigerants in new equipment, and preventive maintenance. Another project that will reduce Freon 11 releases is the installation of high efficiency purge units on numerous chillers.

Chemical Distribution. MSFC is currently working on implementing the Fingerprint software program for tracking of the facility chemical inventory and chemical purchases, particularly with respect to TRI reportable chemicals. MSFC plans to begin implementation of the tracking system with reportable toxic chemicals purchased through the facility substore. A listing of the chemicals purchased from the substore is maintained and will be entered into the database quarterly. For inventory reporting, department personnel will be provided with a listing of their substore purchases and will be asked to report how many containers they have remaining. This procedure will greatly improve chemical purchase tracking and inventory reporting.

Once the tracking system described above is successfully implemented, it is recommended that MSFC implement the bar-coded tracking system provided through Fingerprint. This will allow tracking of products as they come in such that individual containers can be tracked throughout the facility from entry at the substore, to purchase by the activity, through use of the product and turn-in of the empty container. Tracking of the product through the bar-coding system will eliminate some of the manual entries into the database for product tracking.

Summary

Through 1996, the facility has accomplished a 24 percent reduction of reportable toxic chemical releases. The greatest contributor to the reduction is Freon 113, for which releases decreased by 30 percent from those reported in the baseline year. Since the pollution prevention project for vapor degreasers was completed in April 1998, it is expected that chemical releases will be reduced by 42 percent from the baseline amounts. Furthermore, once the use of Freon 113 has totally diminished, the facility should reduce chemical releases by approximately 70 percent when compared to the baseline releases.

MSFC is expected to achieve the 50 percent reduction goal through the implementation of pollution projects, such as retrofitting the vapor degreasers, and projects planned for implementation, such as painting gun cleaners, segregating paint gun systems, and using low-VOC paints.

References

NASA/MSFC. 1994 Toxic Chemical Release Inventory Reporting. Prepared by CH2M HILL for Marshall Space Flight Center. June 1995.

U.S. Environmental Protection Agency. Federal Facility Pollution Prevention Planning Guide. Office of Enforcement and Compliance Assurance. EPA 300-B-94-013. Washington, D.C. December 1994.

Development of an Environmental and Health Risk Assessment Tool for Materials and Processes

Laurence Weinberg, Roark Doubt, and Denis Bourcier,
Environmental Engineering, Environmental Affairs
Boeing Information, Space & Defense Systems,
I&CS, Mailstop 4H-26, P.O. Box 3707
Seattle, WA 98124

Executive Summary

This paper describes a risk assessment tool developed at Boeing to permit the analysis of human health, environmental and regulatory risk associated with the use of hazardous chemicals in the processes employed by an aerospace manufacturer. Risk is evaluated from both a chemical hazard and a regulatory aspect, using existing health and environmental regulations and definitions while taking into account the process characteristics and the quantity of material being used. The risk is computed as a function of innate material properties adjusted for such factors as process exposure potential and amount of material used in the process. The material properties are chosen to be reasonably accessible in the literature, in order to facilitate use by organizations that do not possess toxicological investigative resources or capabilities.

Information from the risk analysis can be used to compare chemicals and processes. Such comparisons are useful in determining where to concentrate resources in order to reduce risk and in evaluating proposed alternatives from a risk standpoint. Various functions of the quantity of material used, such as log base x, are examined. The health and environmental portions of the analysis are separate, allowing the health and environmental aspects to treated by themselves as well as in a combined fashion. By adjusting the final tabulation formula, the weights assigned to health and to environment can be altered.

This risk analysis tool represents a compromise between the time and resources required for a detailed scientific investigation and the need for a tool that can be efficiently applied to numerous combinations of processes and materials by an organization that wishes to examine potential risk to human health and the environment. It is constructed so that it can be modified as new health and environmental factors are identified.

Introduction

The use of chemicals at an industrial site presents a range of risks that management must take into account as part of its overall management system. These risks include hazards to employee health and safety, potential threats to the physical environment, legal risks associated with physical hazards either from the common law or statutory/regulatory law, business risks related to competitiveness, and financial risks associated with the costs of chemical management. While no one tool may be able to address all of these risks, it is desirable to measure relative risk between various materials and processes in order to make better business decisions. It is useful at this point to note that there are several meanings that can be given to the term 'risk assessment' and to note what is meant by that term in this paper. To the toxicologist, risk assessment is the study and determination of chemical pathways in the environment, exposure, dose, and effect. In an insurance context, risk assessment is an examination of probabilities and potential damages to determine policy premiums. In this paper we are concerned with management risk assessment. Here we are looking at potential impediments to meeting management objectives such as quality, cost and schedule.

Large, integrated manufacturers of aerospace and electronic products face several challenges with respect to the use of chemicals, particularly those that are considered hazardous. Considerations of competitiveness, quality, stewardship, cost, and regulatory compliance require that the company constantly examine its use of chemicals to minimize and control risk. In order to better manage chemical risk, a method for ranking and prioritizing this risk is desirable. Risk ranking allows for targeting certain materials for reduction or elimination. Boeing has in place a Comprehensive Chemical Reduction (CCR) Program that seeks to reduce or eliminate the use of hazardous chemicals at company sites. When an alternative material substitution or a complete new process replacement has been identified for an existing process, it is useful to have a basis for comparing the risk associated with the existing,

baseline process with that associated with the replacement process. It is important to determine if the new approach will truly reduce risk.

This paper focuses on the development of a tool to measure certain risks associated with chemical usage in processes. The tool attempts to take into account human health and environmental impacts as well as regulatory considerations. In order to provide an approach that is usable, useful and used in a manufacturing setting utilizing thousands of chemicals in hundreds of processes; several attributes need to be possessed by the tool:

1. Existing chemical health and environmental data should form the basis of the analysis; and when data is unavailable, the tool should permit reasonable estimates to be employed in a straight-forward manner. The data itself should be relatively easy to obtain. Use of the tool should not require laboratory analysis by the user if at all possible.

2. Regulatory risk should be determined in a simple fashion.

3. Process-specific information needs to be taken into account to reflect that the same material used in several different processes may present different risks for each process. The process characteristics should be broadly stated so that hundreds of different processes can be accommodated with a relatively simple criteria.

4. Quantity of use should be taken into account in a manner that balances chemical/process hazard with amount of use so that neither term dominates the other.

5. The tool should lend itself to modifications as additional information about the chemicals is obtained and as new health and environmental hazards are identified. The tool should be able to separate health risk from environmental risk so that different weighting could be assigned to these two areas if considered appropriate by the user.

6. The results of a risk analysis using the tool should lend themselves to ease of communication to management and other interested stakeholders.

Although other attributes could be envisioned, for the application at Boeing the attributes listed above provided a framework to construct the tool described in more detail below.

The available literature on similar risk comparisons was found to be somewhat limited, generally focusing on evaluation of either health or environmental risk, rather than both. An approach for evaluating substitute materials was presented by Goldschmidt for work place processes only and described examples of substitution using vapor hazard ratios (1). A review of the process of risk assessment for environmental and workplace chemicals was presented by Brown (2); however, a method for integrating the two types of hazards was lacking. Another review of risk assessment for chemicals authored by Paustenbach described quantitative risk assessment including dose-response and pharmacokinetic-based models, but again, very limited information was provided to allow multi-chemical comparisons and environmental and health risks were not evaluated simultaneously (3). Reinert, Weiler and Fava discuss a health and environmental regulatory and risk scoring index for products (4).

Tool Specifics

The tool described below is intended to model health and environmental impacts. It is not a cost model and does not measure financial risks or liabilities. The cost factors would be treated separately using life-cycle cost accounting or other financial measurement techniques. The tool does not explicitly yield regulatory risk as a separate number, but regulatory risk is built into the determination of the health and environmental aspects of the model.

The tool has been developed for use at a manufacturing site. It is not intended as a life-cycle tool, although others could utilize the same approach to examine chemicals and processes used in operation and maintenance of a product or facility. As with any model, this tool should always be evaluated against 'common-sense' analysis of risk; and application of the tool should be questioned when tool results yield risks that do not comport with the knowledge and experience of the user. This model does not include ordnance, nuclear or biological risks. It addresses the typical

chemical risks associated with manufacture of aerospace products, although it can be applied to a wider set of industries and activities.

Development

To meet the attributes noted above, it was decided that the risk would be expressed as a product of factors associated with chemical hazard, process release potential and quantity respectively. Thus for a particular chemical, C, used in Process P in the amount Q, the risk R would be calculated using an equation of the form:

$$R(C,P,Q) = [H_1(C)* H_2(P,C) + E_1(C)* E_2(P,C)]*F(Q) \quad (1)$$

where H_1, H_2, E_1, E_2 and F are functions to be determined. H_1 is a measure of the inherent health risk associated with the chemical and H_2 is multiplier that reflects the worker exposure potential of the process. E_1 and E_2 are the corresponding functions for the environmental impacts. F is the function that enables us to take into account the quantity of Chemical C used in the process. We assume that the same function, F, will reflect the effects of quantity for both the health and environmental impacts. This is an area that would benefit from further research and development. It is assumed that the effects of chemical, process and quantity can be separated in the manner shown. This model does not attempt to account directly for chemical reactions that might occur in the process. Thus, for a process P that uses n chemicals, C1, C2, ..., Cn, in respective quantities Q1, Q2, ..., Qn; the risk *R* associated with the process is given by:

$$\begin{aligned} R(P) &= R(P;C1,Q1, C2, Q2, ..., Cn,Qn) = \Sigma R_j(Cj, P,Qj) \\ &= \Sigma [H_1(C_j)* H_2(P,C_j) + E_1(C_j)* E_2(P,C_j)]*F(Q_j) \end{aligned} \quad (2)$$

where the summation is taken from j = 1, ..., n. This last equation assumes that the risk associated with a process can be expressed as a summation of the risks associated with the process chemicals. In those situations where a process *P* is comprised of a sequence of subprocesses P_1, P_2, ..., P_k; the risk associated with *P* is given by:

$$R(P) = \Sigma R(P_j) \quad (3)$$

where the summation is taken from j = 1, ..., k and the function *R* is of the form given by equation (2). The assumptions of linearity and independence from chemical reactions are simplifying assumptions to enable the model to meet attributes 1, 3, and 5 above and make the tool easier to use. These assumptions represent a trade-off between precision and usability in a manufacturing setting.

With the general tool format given in equation (1) above, it now becomes necessary to specify the functions H_1, H_2, E_1, E_2 and F.

Determination of Chemical Health, Environmental and Regulatory Risk

To determine the health, environmental and regulatory risk associated with a chemical it was decided to employ a point system, described below, that provided separate evaluations for health and environmental factors; realizing that in many instances the environmental and health effects are closely related. To take into account regulatory factors, the determination of the health and environmental factors was based on regulatory lists or definitions. This means that the regulatory risk is built into the health and environmental risk estimates. Regulatory risk does not appear as a distinct category, and there is no regulatory risk 'score.' The use of a point system will result in scores that are best used in a comparative mode to compare alternatives or rank materials and/or processes. The outcome is a pure number and the resulting risk number should not be interpreted as some sort of absolute score.

Under the model a maximum score of 10 points is possible for health risk and 10 points for environmental risk. These points are calculated using the algorithms specified in Table 1 for health and Table 2 for environmental impacts. Within the two categories there was no attempt to assign specific weights to specific factors. This certainly could be done; and for a particular application, weighting could be employed to better account for regulatory risk. Thus, higher weights could be assigned to factors that carry higher regulatory impact in the jurisdiction where the plant site is located.

The health factors that were selected are based on toxicity, carcinogenicity, reproductive effects, and fire and explosive hazards. The authors selected Volatile Organic Compounds (VOC's), Hazardous Air Pollutants (HAP's), Superfund Amendments and Reauthorization Act (SARA) 313 substances, water concerns, and a series of special concerns as environmental factors. The choices were made to facilitate the acquisition of the necessary data to carry out the risk calculation. As can be seen in Tables 1 and 2, the points are based in many instances on criteria developed by federal agencies. In the case of the environmental water concerns, allowance was made for local regulations. The scoring system would accommodate similar adjustments for local regulation in other categories if this was desired by the user. This would be valuable in instances where local authorities have adopted more stringent or additional requirements.

Allocation of Points for Health Risk

Area of Concern*	Points
Toxicity	
Listed under EPA guideline[a] as danger poison under multiple categories or chronic toxicity[b] without acute toxicity under EPA guidelines	4
Listed under EPA guideline[a] as danger poison under one category only or chronic toxicity[b] with acute toxicity under EPA guidelines	3
Listed under EPA guidelines[a] as warning or a sensitizer[c] or considered to be a strong corrosive (pH $\leq$ 2 or pH $\geq$ 12)	2
Listed under EPA guidelines[a] as caution or considered to be a weak corrosive (2 < pH < 12)	1
None of above categories	0
Carcinogen or Reproductive Hazard	
Listed by EPA[d] as human carcinogen or reproductive hazard[e]	4
Listed by EPA[d] as probable human carcinogen	2
Listed by EPA[d] as possible human carcinogen	1
None of the above categories	0
Fire/Explosion Hazard	
Regulated[f] as flammable or explosive	2
Regulated[f] as combustible	1
None of the above categories	0

* Source information for the definitions in the Table can be found in Appendix I.

Table 1

The function $H_i(C)$ is computed from Table 1 using the point allocation rules specified therein. In a similar manner $E_i(C)$ is computed from Table 2 using the point allocation rules specified in that table.

Allocation of Points for Environmental Risk

Area of Concern*	Points
Volatile Organic Compounds (VOC)	
EPA VOC[g] with vapor pressure $\geq$ 45 mm Hg	2
EPA VOC[g] with vapor pressure < 45 mm Hg	1
Not an EPA VOC	0
Hazardous Air Pollutant (HAP) or Superfund Amendments and Reauthorization Act, Section 313 (SARA 313) Listed	

Listed as a HAP[h] or SARA 313[i] substance by law or EPA	2
Not listed as a HAP[h] or SARA 313[i] substance by law or EPA	0
Regulated under Safe Drinking Water Act (SDWA) or by Local Wastewater Treatment Authority	
Regulated under SDWA[j] or by local treatment authority and a persistent chemical	2
Regulated under SDWA[j] or by local treatment authority and not persistent	1
Not regulated under SDWA or by local treatment authority	0
Special Concerns (maximum of 4 points)	
Classified as halogenated hydrocarbon[k]	1
Contains a heavy metal[l]	1
Classified as a glycol ether[m]	1
Classified as a Class I or II Ozone Depleting Compound (ODC)[n]	1
Rated fish toxicity[o] at $\leq$ 100 mg/l	1
Suspected endocrine disruptor[p]	1
Department of Transportation listed[q] hazardous material with RQ $\leq$ 10 pounds	1

* Source information for the definitions in the Table can be found in Appendix I.

Table 2

In those instances where information is not readily available in order to derive the points for a specific chemical, the user can allocate points on the basis of similar chemicals or classes of chemicals where data is known. If this is not possible; laboratory testing can be performed or a literature search carried out when feasible. Finally, as an option, points can be allocated in a conservative manner, assuming that the material displays the highest level of hazard for the category where data is lacking.

Determination of Process Exposure Potential

The next step is to derive the multipliers that reflect the process characteristics and the potential to release material to the workplace or the environment. Once again it was decided to use a point allocation system to model exposure potential. The allocation rules are given in Table 3 for health impacts ($H_2(P,C)$) and Table 4 ($E_2(P,C)$) for environmental impacts. The exposure factor is an integer between 1 and 5. When combined with the health and environmental impact factors discussed in the prior section, the potential score for a material used in a process is the range 0 to 100.

Allocation of Points for Health Exposure Potential

Exposure Potential Description*,**	Points
Chemical released to plant work area as a gas or dust during normal use or use of chemical requires Level A Personal Protective Equipment (PPE)[r]	5
Chemical released to plant work area as a liquid during normal use or use of chemical requires Level B PPE[r]	4
Chemical released to plant work area as a gas, dust or liquid during normal use if failure of control equipment or likely in the event of a spill or non-catastrophic accident	3
Use of chemical requires breathing or dermal protection, but at less than Level B PPE or chemical is used in more than 5 shops	2
or chemical is found in more than 10 storage locations	1
None of the above categories	
* If more than one category can be met, choose the category with the highest point allocation.	

** Source information for the definitions in the Table can be found in Appendix I.

Table 3

The reference to shops and storage locations in the next-to-last category (two points) for health exposure potential is intended to address common processes that may be found throughout a plant, such as wipe solvent cleaning.

Allocation of Points for Environmental Exposure Potential

Exposure Potential Description*	Points
Chemical released to outside air or water during normal use	5
Chemical released to outside air or water during normal use if failure of control equipment	4
Chemical normally becomes a hazardous constituent of hazardous waste stream or local industrial wastewater discharge	3
Chemical release to outside air or water is likely in event of a spill or non-catastrophic accident	2
None of the above categories	1
* If more than one category can be met, choose the category with the highest point allocation.	

Table 4

Determination of Chemical Quantity Multiplier

As noted above, under the algorithms for determining impact and exposure, the score associated with any one chemical used in any one process can range from 0 to 100. The quantity of material, however, can range from 0 to millions of pounds. If the final risk score is computed by a simple multiplication of the impact/exposure factor ($[H_1(C)*H_2(P,C) + E_1(C)*E_2(P,C)]$) by total use in the process, then those materials that are used in the greatest quantities will overwhelm possibly more dangerous materials that are used in smaller quantities. It was considered desirable that the factor for quantity be of the same order of magnitude as the impact/exposure factor. This represents an engineering judgment; and a choice of a different scaling, including the unadjusted quantity, would allow a shift in weight between impact/exposure and quantity. The function for the quantity multiplier was required to have the following properties:

$$F(0) = 0$$

$$F(10^6) \cong 100 \qquad (4)$$

$$F'(Q) \geq 0$$

where F′ is the first derivative of F. The last requirement insures that the risk will not decrease with increasing quantity, and it is this property that is important rather than the differentiability of F. Three functions were considered for F, and obviously there are more choices. These functions are shown in equations (5), (6) and (7). In addition the choice of F(Q) = Q was also examined to judge the results that simple multiplication by Q would yield.

The first function uses a linear relationship to yield F(0) = 0 and then smoothly matches the linear function to a $\log_{10}$ function to scale the relationship at larger values of Q.

$$F_1(Q) = \begin{cases} 2.6628Q & Q \leq e \\ 16.67\log_{10}(Q) & Q > e \end{cases} \qquad (5)$$

where e = the base for the natural log and is approximately equal to 2.7182818. The 16.67 is approximately 100/6 and provides the scaling that converts $\log_{10}(10^6)$ into 100. The number 2.6628 is the approximate value of $(100/6)*\log_{10}(e)*(1/e)$ and is chosen so that F is differentiable everywhere, including at e where the function definition changes. [Note that by adjusting the slope of the linear segment and by shifting the argument of the log function from Q to $Q - Q_0$, we can shift the quantity where we change from linear to log to the close vicinity of Q_0. Doing this will cause the slope to decrease as Q_0 increases from e. Thus, for $Q_0 = 1{,}000$, the slope of the straight line segment will be between .01 and .1.]

The second option uses a simple $\log_{10}$ function, with the argument shifted by 1 to ensure that F(0) = 0.

$$F_2(Q) = 16.67\log_{10}(Q + 1) \qquad (6)$$

where 16.67 is again the scaling factor.

The third function is more complicated, but has some interesting properties. It is a logistics function that is flat for small and high values of Q, but changes more rapidly in the intermediate values. The use of such a function reflects the observation that as you go from .001 pounds to .1 pounds or from 10^6 to 10^7 pounds the relative effects may not be as dramatic as when the quantity changes from say 100 to 10,000 pounds. At the lower levels there is not enough material available to create much impact; while at the higher levels, risk doesn't change as appreciably based on the rationale that if you can destroy the population of the earth 100 times, there doesn't seem to be much more risk if you have enough material on hand to destroy it 1000 times. The risk still increases with increasing quantity; just not as fast at the higher levels of quantity. The logistic equation is given by:

$$F_3(Q) = [101/(1 + 100e^{-aQ})] - 1 \qquad (7)$$

where a is chosen so that the logistic curve gains a specified percentage of its final value at a specified choice of Q. [*To illustrate this, suppose we wish that when Q = 10,000 pounds, F_3 should attain 60% of its final (actually asymptotic) value of 100. Setting $F_3(10,000) = 60$, yields $a = 5.0272 \cdot 10^{-4}$. Note that for this example, $F_3(1,000) = .64$ and $F_3(100,000) = 100$ (because of round-off). Hence from 0 to 1,000 pounds and from 100,000 pounds and up, there will be little if no change in the risk under a logistics model.*] The subtraction of 1 as the final term is done to give F(0) = 0. Unlike the first two functions, $F_3(Q)$ cannot exceed 100, no matter how large Q becomes. This is just a property of the logistics function.

All three functions meet the requirements shown under (5) above. For ease of use and for the examples shown in this paper, the multiplier function given by $F_2(Q)$ in equation (6) above has been chosen.

The Effect of Increased Production on Risk

Because of the way that the model is structured, it is possible to carry out some simple mathematical analysis using the first derivative to estimate the rate of change in the risk attributable to chemical usage as production through a process increases. From equation (2) above we have for the risk *R* associated with a simple process P the following equation:

$$R(P) = \Sigma\, [H_1(C_j) \cdot H_2(P,C_j) + E_1(C_j) \cdot E_2(P,C_j)] \cdot F(Q_j) \qquad (8)$$

where the summation is taken over the number of chemicals used in the process. For any particular level of production, the quantities Q_j for each of the j chemicals will be specified. The impact/exposure factor (the expression within the brackets, [ ], above) is independent of the quantity Q. Hence if the chemicals are held constant and the process is not altered, just scaled up or down for production changes; we can express the change in the risk due to a changes in quantity as:

$$\partial R(P)/\partial Q = \Sigma\, [H_1(C_j) \cdot H_2(P,C_j) + E_1(C_j) \cdot E_2(P,C_j)] \cdot dF(Q_j)/dQ \qquad (9)$$

For the simple logarithm model in equation (6), we dF/dQ given by:

$$dF/dQ = 16.67 \cdot \log_{10}e \cdot (1/(Q + 1)) \qquad (10)$$

From this expression we can see that the contribution to the rate of change is inversely proportional to the quantity. Assuming that a logarithm model is correct; this means that changes in the amount of small quantity materials, especially those that rate high in the impact/exposure point system, will have a disproportionate impact on the change in risk. Note that this does not mean they are the highest contributors to risk, only that they have a stronger effect with respect to change in risk.

If we use F(Q) = Q, then dF(Q)/dQ = 1 and the rate of change is a constant that depends on the chemical and process properties only. For the mixed, linear-log model, we will have an increase in risk that is proportional to the increase in quantity until we reach the point where we shift to the log function. At the shift point, the growth rate will be inversely proportional to the quantity. As might be expected the change in risk as Q varies for the logistic model will be considerably more complicated. Essentially, changes in Q for small quantities and large quantities will be close to zero, with larger effects observed for Q in the range where the logistic curve grows from near zero to its asymptotic limit.

Examples

Example 1. A wipe solvent process (WSP) is carried out in the main part of a plant using 1,000 pounds of Methyl Ethyl Ketone (MEK). The workers do not use any special personal protective equipment beyond gloves. The MEK is applied with a squeeze bottle and wiped off with a rag. There are no air pollution controls so that MEK evaporates into the plant air and from there can move to the outside atmosphere. What is the risk associated with wipe solvent cleaning using MEK under a logarithmic model?

For this situation we have:

$$H_1(MEK) = 4$$
$$H_2(WSP,MEK) = 2$$
$$E_1(MEK) = 4$$
$$E_2(WSP,MEK) = 5$$

with

$$F(1,000) = 16.67*\log_{10}(1001) = 50.02$$

and as a result:

$$R(MEK,WSP,1000) = [H_1(MEK)*H_2(WSP,MEK) + E_1(MEK)*E_2(WSP,MEK)]*F(1000)$$

$$= [4*2 + 4*5] *50.02$$
$$= 1400.56$$

Note that this number by itself conveys little information. It is useful; however, if we have an alternative process for wipe solvent cleaning or a new cleaner to replace the MEK. We can then compute risk for the alternative and compare MEK-cleaning to the new choice to determine if there is a significant change in the risk.

The corresponding risk figures for 100 pounds and 10,000 pounds are given by 935.54 and 1867.06, respectively. From this we see an increase of 900 pounds at the 100-pound level (from 100 pounds to 1,000 pounds) produced an increase of 465.02 in the risk score, while an increase of 9,000 pounds at the 1,000-pound level (from 1,000 pounds to 10,000 pounds) only produced a risk increase of 466.50. This illustrates the rate of change of risk as inversely proportional to the quantity for the logarithmic model.

Example 2. Consider a hypothetical process P_1 that uses four chemicals C_1, C_2, C_3, and C_4. The impact, exposure and quantity information is displayed in Table 5. Table 6 displays the computed risk for each material and for the process, using both the logarithmic function for F(Q) and F(Q) = Q. In addition the health and environmental components are displayed separately.

Process P_1 Data

Chemical	H_1	H_2	E_1	E_2	Q
C_1	6	3	4	2	100
C_2	3	2	2	1	100
C_3	7	3	6	2	1,000
C_4	2	2	4	3	1,000

Table 5

Process P_1 Risk Estimate

	$F(Q) = 16.67*\log_{10}(Q+1)$			$F(Q) = Q$		
	Hlth Risk	Env Risk	Ttl Risk	Hlth Risk	Env Risk	Ttl Risk
C_1	601	267	868	1,800	800	2,600
C_2	200	67	267	600	200	800
C_3	1,050	600	1,650	21,000	12,000	33,000
C_4	200	600	800	4,000	12,000	16,000
P_1	2,051	1,534	3,585	26,400	25,000	51,400

Table 6

Let us now suppose that an alternative process P_2 is under consideration. P_2 uses the same equipment, but with some changes in the chemicals. In particular chemicals C_1 and C_3 are used, but C_2 and C_4 are replaced by C_5, C_6 and C_7. The corresponding data for P_2 is displayed in Tables 7 and 8. From a health and environmental risk standpoint, we want to know if anything is gained by going to P_2 and eliminating P_1. Note that the quantities of C_1 and C_3 have changed in the alternative process.

Process P_2 Data

Chemical	H_1	H_2	E_1	E_2	Q
C_1	6	3	4	2	50
C_3	7	3	6	2	50
C_5	5	2	6	1	500
C_6	3	3	3	1	1,000
C_7	2	1	2	1	10,000

Table 7

Process P_2 Risk Estimate

	$F(Q) = 16.67*\log_{10}(Q+1)$			$F(Q) = Q$		
	Hlth Risk	Env Risk	Ttl Risk	Hlth Risk	Env Risk	Ttl Risk
C_1	512	228	740	900	400	1,300
C_3	598	342	940	1,050	600	1,650
C_5	450	270	720	5,000	3,000	8,000
C_6	450	150	600	9,000	3,000	12,000
C_7	133	133	266	20,000	20,000	40,000
P_2	2,143	1,123	3,266	39,100	28,800	67,900

Table 8

This example illustrates the effect of the choice of the function to model quantity impacts. The choice of a logarithm model indicates that Process 2 is the lower risk, while the selection of F(Q) = Q as the equation yields Process 1 as the preferred alternative from a risk standpoint. What has happened is fairly clear. The large quantity of a fairly benign hazardous material, C_7, has swamped the impact of the other materials. When the logarithm is used the multiplier associated with C_7 goes from 10,000 to 4, and the chemicals with a greater hazard have a greater relative influence on the final risk estimate.

Discussion

A usable, useful and used risk assessment tool must possess several attributes if it is to possess these characteristics. Further the risk assessment is only one factor in a multi-factor decision-making process. Considerations such as cost, schedule, performance, and worker and public perception must also be taken into account in selecting alternative manufacturing materials and processes. What the tool provides is a means of quantifying and comparing alternatives with respect to health and environmental risk. Although it provides a risk value, this result should not be taken as an absolute measure of risk. As noted, the value of the tool is in facilitating comparisons. It is not meant to be a substitute for life-cycle analysis or a cost accounting tool. It is not meant to be the only way to determine risk or the best way. What the risk estimator described in this paper does offer is a means of computing an integrated health, environmental and regulatory risk estimate for materials and processes used in a manufacturing setting.

Implicit in the model are values. The structure gives equal weighting to health and environment. Within these classifications, subfactors are given varying weights based on the judgment of the authors. Use of the logarithm function represents a value-judgment that quantity and 'hazard' should be of roughly equal magnitude in determining final results. Anyone contemplating the use of this or similar models should be alert to the underlying value assumptions that are built into the model and should determine if such assumptions are ones that are acceptable. Because regulatory considerations are integrated into the model, the user of a tool such as the one described herein may want to examine the weights given to various factors and adjust them to meet local regulatory considerations and emphasis.

REFERENCES

1. Goldschmidt, G.: An Analytical Approach for Reducing Workplace Health Hazards through Substitution, Am. Ind. Hyg. Assoc. J. 54, (1): 36-43 (1993).

2. Brown, S.L.: Quantitative Risk Assessment of Environmental Hazards, Ann. Rev. of Pub. Health, (1): 247-267 (1985).

3. Paustenbach, D.J: Health Risk Assessment and the Practice of Industrial Hygiene, Am. Ind. Hyg. Assoc. J. 51, (7): 339-351 (1990).

4. Reinert, K.H., Weiler, E.D., and Fava, J.A.: A New Health and Environmental Regulatory and Risk Scoring Index, Total Quality Environmental Management 5, (3): 25-36 (1996).

5. Biological Testing Methods, Part A, Static Fish Toxicity Test, WDOE 80-12, Washington State Department of Ecology, Revised 1996.

Please note, the authors regret that because of the space limitations of this paper, the Appendices are not included. The author can be contacted for further information and copies of the entire manuscript.

Characterization of an Environmentally Friendly Cleaning Process with Surface Analysis

Michael W. Lesley
Thiokol Propulsion
P.O. Box 707 - M/S 245
Brigham City, Utah 84302-0707

ABSTRACT

This paper describes the role of electron spectroscopy in support of the successful development and scale-up of an aqueous cleaning process for large metal parts. The results complement and explain trends in bonding data, and provide information on the causes of process anomalies such as corrosion. They also demonstrate equivalence of results between this process and a vapor degreasing process it replaced.

1.0 INTRODUCTION

About five years ago Thiokol Propulsion began a comprehensive effort to eliminate the use of 1,1,1-trichloroethane (TCA) for adhesive bonding surface preparation in the manufacture of NASA's Space Shuttle Reusable Solid Rocket Motor (RSRM). TCA is an ozone depleting chemical (ODC) whose production has been banned by international agreements.

TCA had been the solvent of choice for both vapor degreasing of large steel and aluminum rocket motor parts and handwipe cleaning of metal and polymer surfaces. Vapor degreasing of steel and aluminum parts has recently been replaced by a spray-in-air aqueous cleaning process using Brulin 1990 aqueous alkaline cleaner. An effort to eliminate TCA from handwipe cleaning is now underway.

This paper discusses how surface-sensitive spectroscopy was used to characterize the effects of this new environmentally compliant process on bonding surfaces and adhesive bond strengths. The focus is on the role these methods have played in aqueous cleaning process development.

2.0 EXPERIMENTAL

2.1 Description of Techniques

Most of the results presented here were acquired using the electron spectroscopy for chemical analysis (ESCA) technique. In ESCA, a sample is irradiated with X-rays that cause electron emission from core levels of the surface atoms. By measuring the kinetic energies of these emitted electrons, one can determine surface elemental compositions and information about the types of chemical compounds present. The average analysis depth of the technique is typically 30 - 50 Angstroms or about 10 - 15 atomic layers.

Some Auger electron spectroscopy (AES) results are also reported. In AES, a finely focused electron beam is used to stimulate secondary Auger electron emission. The kinetic energies of the emitted Auger electrons are measured. The advantage to AES is that it can be used to analyze very small surface features, on the order of microns in diameter. AES typically yields surface elemental composition data only. Its sampling depth is similar to that of ESCA.

2.2 Equipment and Analysis Procedures

Surface analysis data were collected on two different instruments. Data for the initial process/cleaner downselect (Section 3.2) and the subscale aqueous cleaner process development study (Section 3.3) were acquired at a commercial laboratory, Physical Electronics Laboratories in Eden Prairie, Minnesota. Data for the post-clean gritblast cleaning efficiency, full-scale aqueous cleaning evaluation,

and bath life studies (Sections 3.4, 3.5, 3.6) were acquired on an instrument located at Thiokol facilities in Brigham City, Utah.

The Physical Electronics Laboratories instrument was a Physical Electronics Model 5600 ESCA spectrometer equipped with a monochromatic Al Kα X-ray source. Quantitative elemental analyses were obtained from high resolution scans (approximately 20 eV pass energy) on one characteristic peak from each element. The analysis area in these experiments was approximately a 4 x 10 mm rectangle.

The Thiokol instrument was a Kratos XSAM 800 ESCA spectrometer/scanning Auger microprobe. The system was equipped with a dual anode X-ray source for ESCA and an electron gun for AES. Nonmonochromated Al Kα X-radiation was used for ESCA. The analysis area was about half that sampled by the Physical Electronics instrument. ESCA samples were analyzed by a procedure designed for rapid throughput. They were subjected to a medium-resolution (80 eV pass energy, 0.25 eV step size) survey scan, with one characteristic peak of each element integrated to provide quantitative analysis. For steel samples, the C (1s) and Fe (3p) regions were also scanned at high resolution (20 eV pass energy, 0.1 eV step) to provide organic functional group distributions and oxidation levels. For aluminum, the C (1s) and Al (2p) regions were scanned to provide this information.

AES samples were analyzed in fixed retarding ratio (FRR) mode with a retarding ratio of 2. A primary electron beam of 5 keV energy was used to stimulate Auger electron emission. Auger spectra are presented as the first derivative of electron emission. This is done to distinguish the relatively small Auger peaks from the large, slowly varying background upon which they are superimposed.

3.0 RESULTS AND DISCUSSION

3.1 Examples of Surface Spectra

Figures 1 - 4 show some examples of spectra obtained with the Thiokol equipment. Figure 1 is a survey scan (binding energy region above 750 eV omitted) of zirconium silicate gritblasted D6AC steel. This particular sample was gritblasted in a production facility, and immediately placed into the ultrahigh vacuum environment of the instrument. The surface contains mainly constituents of the steel and gritblast sand. There is also a small amount of "adventitious carbon" (which any real sample will have as a result of being exposed to an atmospheric pressure environment). Figure 2 shows a high resolution scan of the C (1s) region on this sample, showing the distribution of surface organic functional groups.

The top frame of Figure 3 shows a high resolution scan of the Fe (3p) region of the same freshly gritblasted steel sample as described by Figures 1 and 2. The oxide thickness is low enough to allow the underlying metal to be detected, indicating that it is thinner than the sampling depth in ESCA. The bottom frame in Figure 3 shows an Al (2p) spectrum of a zero time, freshly zirconium silicate gritblasted 7075 aluminum surface. These are typical of the surfaces as they come out of the gritblast equipment. Over time the surfaces will become increasingly oxidized as they are exposed to ambient environments. This process of oxide growth can be tracked by the oxide-to-metal ratios in Fe (3p) and Al (2p) spectra.

Figure 4 shows Auger spectra for a 100 micron (0.1 mm) diameter corrosion spot (top frame) and a noncorroded area (lower frame) on a sample of steel from an aqueous cleaning process. This showcases the main utility of AES, namely good lateral resolution. The unusual circumstances leading to the corrosion will be discussed later.

3.2 Initial Process /Cleaner Downselect for Vapor Degreaser Replacement

Surface analysis was very useful in understanding differences in surface chemistry produced by different types of cleaners and processes in the early phases of the ODC elimination effort. This understanding played a role in the initial selection of spray-in-air aqueous alkaline cleaning as the process

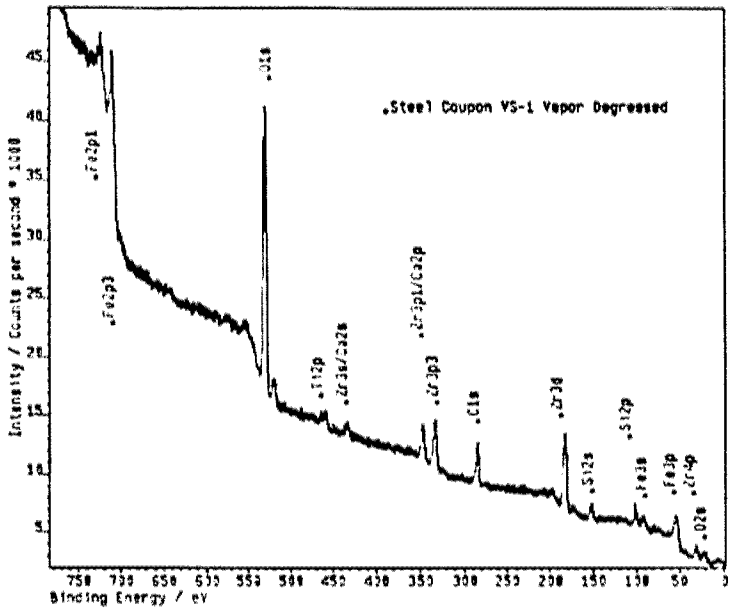


Figure 1. ESCA Survey Scan of Grit Blasted Steel

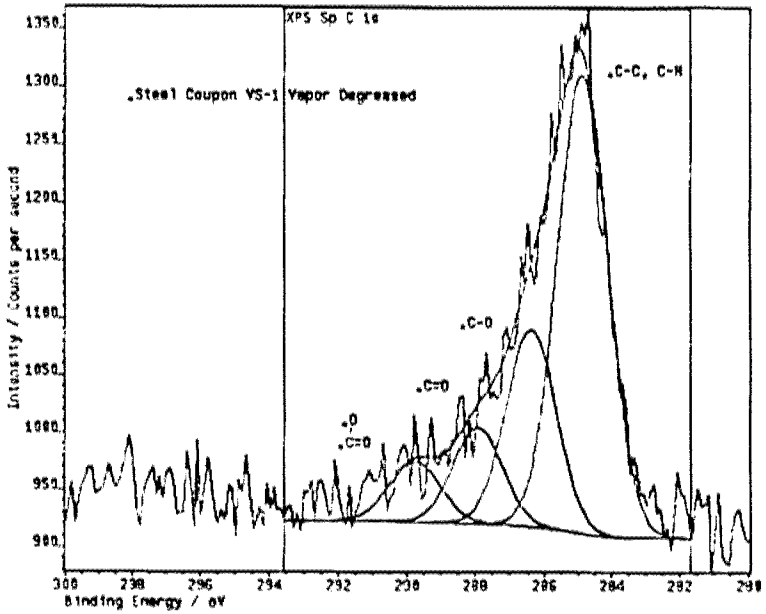


Figure 2. High Resolution Carbon (1s) ESCA Scan of Grit Blasted Steel

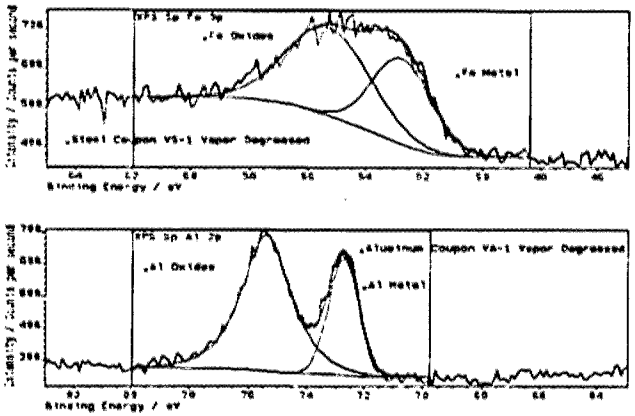


Figure 3. High Resolution Iron (3p) and Aluminum (2p) ESCA Scans of Steel and Aluminum

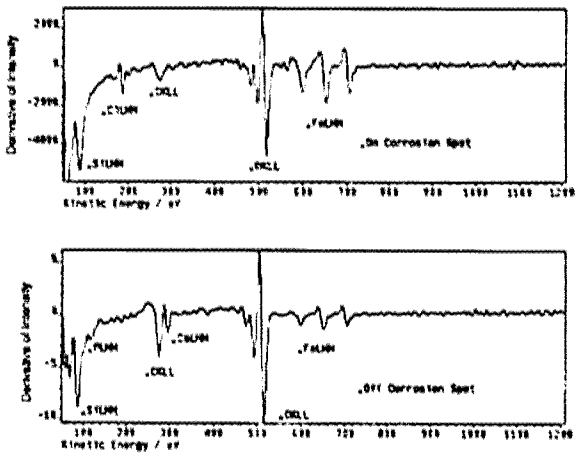


Figure 4. Auger Spectra of Corroded and Noncorroded Area on Steel Sample

of choice to replace TCA vapor degreasing of large metal parts. This history was documented in a paper presented in 1994 [1].

During that study it was determined that spray-in-air cleaning with aqueous alkaline cleaners produced better epoxy-to-metal bond strengths than cleaning with (neutral pH) semi-aqueous cleaners. The bond strengths were better than those obtained with the baseline TCA vapor degreasing process or even with freshly gritblasted steel or aluminum. Standard analytical techniques failed to show any differences between surfaces cleaned with the various cleaners. Obviously, the aqueous alkaline cleaners were modifying the surface in a way that enhanced bonding, but it was not obvious why this was occurring.

Analysis by surface techniques, including ESCA, readily provided an explanation for the difference in bond strengths. It was found that the aqueous alkaline cleaned surfaces were enriched in silicate. This excess silicate comes from a sodium metasilicate additive in the cleaners. The silicates appeared to be present as surface iron or aluminum silicate compounds. Contact angle testing showed that the enriched silicate surfaces were more polar than ordinary gritblasted surfaces. This enhances wettability of the surface by the epoxy adhesive and provides for better bonding.

Therefore, the aqueous alkaline cleaners offered the possibility of obtaining superior bond strengths, better than those provided by the baseline process, without having to resort to a post-clean gritblast. This provided an incentive, and part of the rationale, for selection of the aqueous alkaline cleaners for TCA cleaning process replacement. The surface analytical techniques provided the theoretical understanding of the reasons for bond enhancement.

3.3 Subscale Aqueous Cleaning Process Development for Steel and Aluminum Parts

ESCA methods were used in the early stages of cleaning process development. By this time, the program had settled on Brulin 1990 aqueous alkaline cleaner for use in the spray-in-air process.

A two-level fractional factorial test matrix, shown in Table I, was used in a subscale parts washer to evaluate the responses of bond strength, failure mode, and surface chemistry to changes in process variables. Bonding tests were conducted on steel and aluminum samples (tensile specimens and tapered double cantilever beams, or TDCBs) held together with Hysol EA-913NA epoxy adhesive. Experience has shown that gritblasted steel and aluminum bondlines involving this adhesive are very sensitive to contamination, much more so than other metal bondlines on the RSRM.

Sixteen coupons or "miniature witness panels" (1-1/2 - in. x 1-5/8 - in.) each of zirconium silicate gritblasted D6AC steel and 7075 aluminum were prepared and treated with common process contaminants. They were than cleaned according to the matrix of Table I. The discussion will concentrate on aluminum results. The aluminum coupons were contaminated with Conoco HD-2 preservative grease, which contains hydrocarbons and calcium bases, prior to cleaning.

Response variables used to evaluate cleaning performance and bond integrity included tensile strength, fracture energy and failure mode from the bonding tests. ESCA response variables included the atom percent carbon, a measure of residual HD-2 grease, and the Si/Zr atom ratio, a measure of surface silicates in excess of those contained in the gritblast sand, that are contributed by from the Brulin 1990 cleaner.

To show the effect of process parameters on surface chemistry and bond strength, "main effects" charts were prepared, with data analyzed by an analysis of variance method. To construct a main effects chart, the values of the response variable for the eight high and eight low levels of each process variable are averaged. These values are plotted and joined by a straight line. If the line extends beyond the dotted horizontal lines in the figure, the averaged main effect is significant at the 95 percent confidence level.

Figures 5 and 6 show example main effects charts for two of the bonding response variables, namely tensile adhesion strength and failure mode (expressed as percent cohesive in the adhesive) in the TDCB tests. Higher cleaner concentrations, cleaning temperatures, and flow rates produce better bonds. Higher wash nozzle pressures appeared to reduce some measures of bond integrity in this case. Prerinsing had a slight positive effect on aluminum tensile strength, but did not significantly improve results in other bonding response variables for steel and aluminum.

Table I. Process Development Study Test Matrix

Run	Cleaner Temp.	Cleaner Conc.	Wash Press.	Flow Rate	Wash Time	Pre Rinse	Rinse Time
1	-	-	-	-	-	-	-
2	+	-	-	-	+	-	+
3	-	+	-	-	+	+	-
4	+	+	-	-	-	+	+
5	-	-	+	-	+	+	+
6	+	-	+	-	-	+	-
7	-	+	+	-	-	-	+
8	+	+	+	-	+	-	-
9	-	-	-	+	-	+	+
10	+	-	-	+	+	+	-
11	-	+	-	+	+	-	+
12	+	+	-	+	-	-	-
13	-	-	+	+	+	-	-
14	+	-	+	+	-	-	+
15	-	+	+	+	-	+	-
16	+	+	+	+	+	+	+

Parameter Levels

	-	+
Wash Temperature	110 °F	180 °F
Cleaner Concentration	3 %	10 %
Cleaner Pressure	75 psi	225 psi
Flow Rate	1.5 gal/min	2.5 gal/min
Cleaning Time	3 minutes	6 minutes
Pre-wash rinse	No	Yes
Post-wash rinse time	3 minutes	6 minutes

Overall, for steel and aluminum testing, cleaner concentration and temperature were most significant variables, followed by wash pressure and flow rate. Other process variables had an effect on none or one of the response variables or gave contradictory results.

Figures 7 and 8 show parallel ESCA atom percent carbon and Si/Zr atom ratio response variable plots. These show that higher cleaner concentrations and temperatures increase cleaning efficiency and silicate levels, both of which would be expected to increase bond strength. Higher flow rates seem also to have the same effect but it is not strong enough to be statistically significant. These data show that the main trends observed in EA913 NA epoxy adhesive bond data (effect of cleaner temperature and concentration) reflect changes in surface chemistry.

The ESCA data in Figure 7 also indicate that wash nozzle pressure had a significant effect on grease levels, with higher pressures having somewhat higher cleaning efficiency. In contrast, the bond data indicate that the higher pressures reduce bond strength. This could indicate that the higher wash pressures change something else besides the surface chemistry, such as surface roughness or morphology.

Ultimately, based on process models derived from the two level fractional factorial matrix and facility considerations, a set of process variable levels was were recommended for the full-scale process.

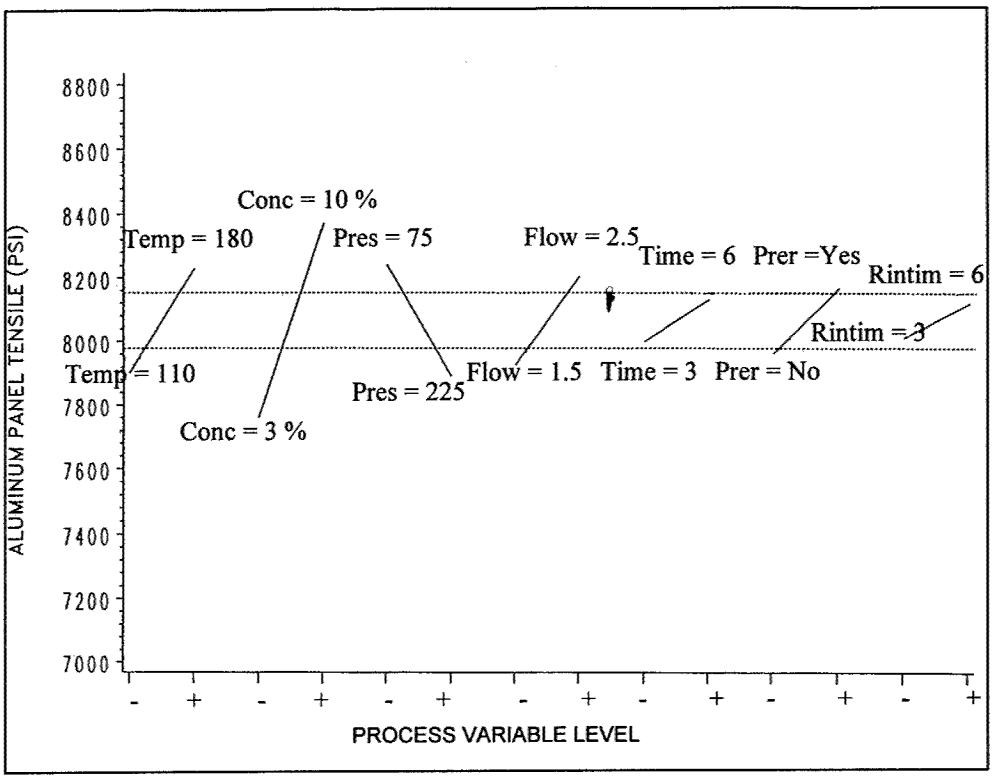


Figure 5. Main Effects Chart for Aluminum Tensile Bond Strength, Aqueous Cleaning Process Development Study

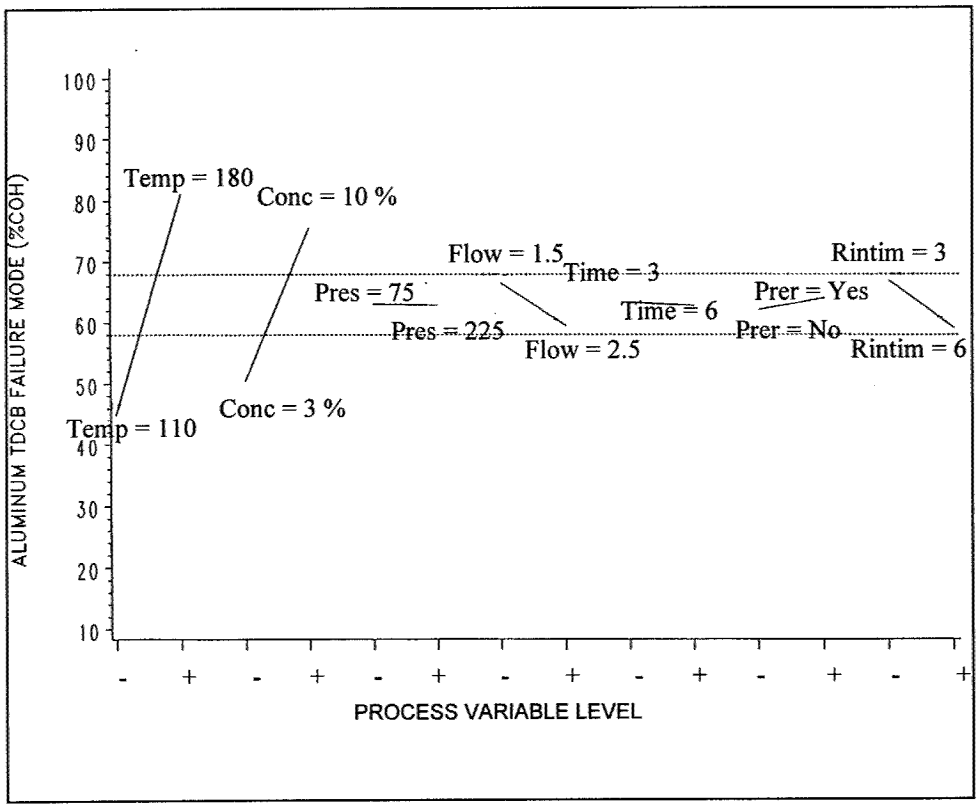


Figure 6. Main Effects Chart for Aluminum TDCB Failure Mode, Aqueous Cleaning Process Development Study

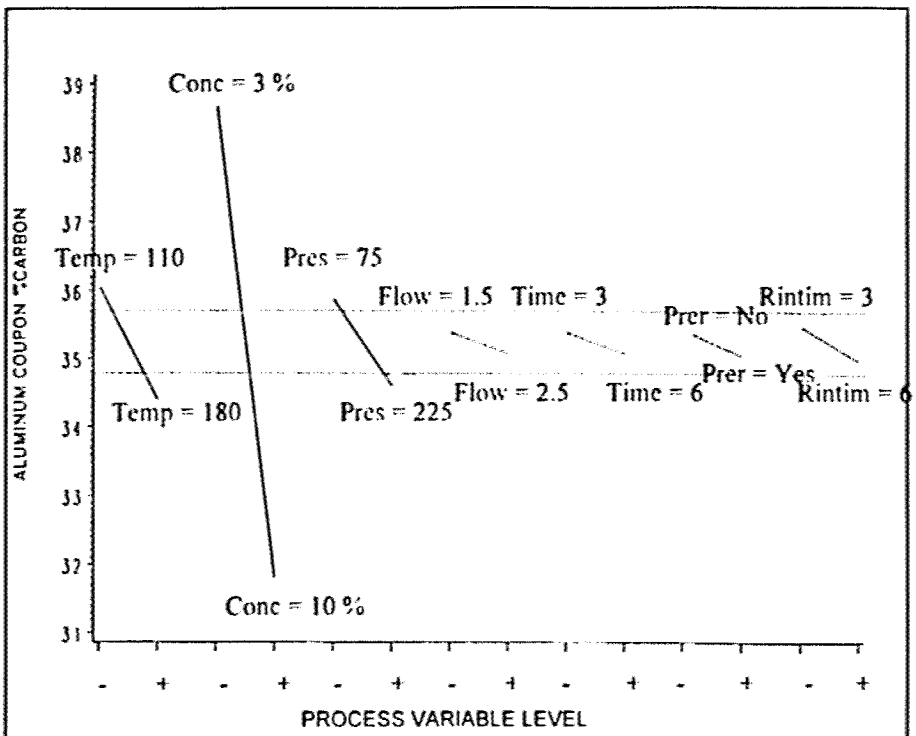


Figure 7. Main Effects Chart for Aluminum ESCA Carbon Level, Aqueous Cleaning Process Development Study

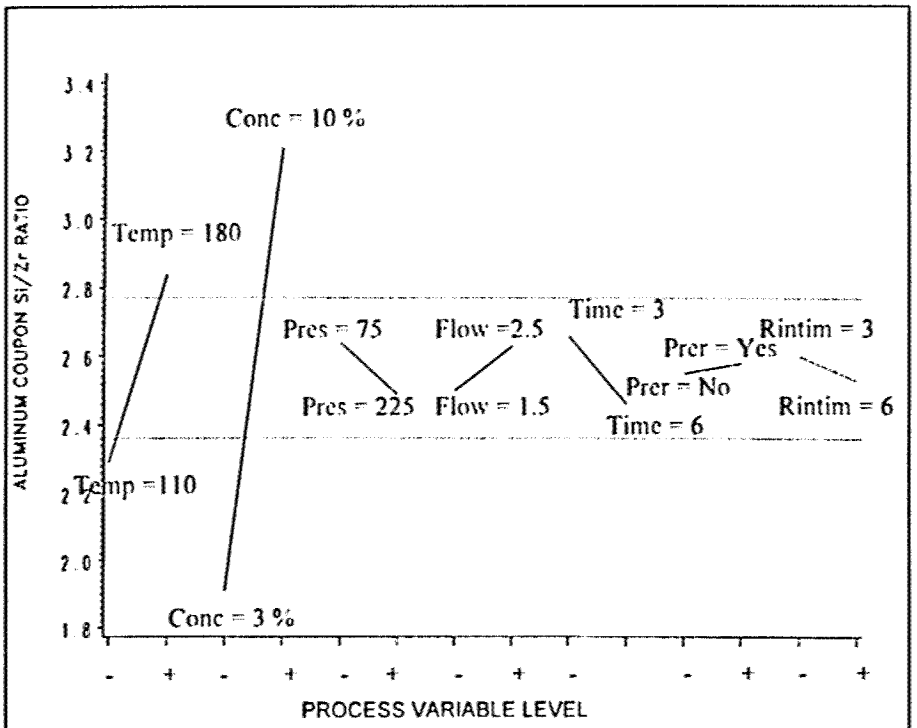


Figure 8. Main Effects Chart for Aluminum ESCA Si/Zr Atom Ratio, Aqueous Cleaning Process Development Study

These were: A cleaner concentration of 10 percent, a cleaner temperature of 150°F, a wash nozzle pressure of 70 psi, and a flow rate of 2.5 gallons per minute per nozzle.

3.4 Evaluation of Post-Clean Gritblasting Efficiency

Prior to implementation of the process, it was decided to follow aqueous cleaning with a post-clean gritblast before bonding of steel and aluminum parts. This decision was made in part because qualification of the new process would be facilitated if it could be shown that it produced surfaces with chemistry identical to that of the existing, qualified process. Also, the cosmetic gritblast removes minor surface blemishes such as the occasional superficial corrosion that sometimes occurs in real processes.

To verify that the new process was capable of yielding steel and aluminum surface chemistries comparable to the existing TCA process, ten steel and ten aluminum "miniature witness panels" were contaminated with HD-2 grease. Half of them were TCA vapor degreased in production facilities, while the other half were subjected to the optimized subscale aqueous cleaning process. Both sets were then gritblasted in production facilities and immediately afterward placed in the vacuum chamber of the surface analysis system. Statistical analyses (*t* tests) were performed on the resulting data sets to determine if there are differences that are statistically significant.

Tables II and III show the results of the study. Tabulated are indicators of HD-2 grease (C and Ca level), general surface cleanliness (Fe and Al level), silicate levels (Si/Zr atom ratio), and oxide thickness (percent Fe as oxide in Fe (3p), percent aluminum as oxide in Al (2p)). As shown in Table II, there are no significant differences between steel samples processed by the new and old processes. Table III shows that the aqueous cleaning process produced aluminum surfaces with slightly higher carbon levels than the TCA process. The excess carbon was present in the form of a hydrocarbon. While the difference in carbon levels is statistically significant, the aqueous cleaned, gritblasted aluminum surfaces still have an extremely low surface carbon content, even by ESCA standards. There are no other differences in overall surface aluminum level, silicate levels, oxide thickness, or any other measure of surface contamination.

Table II. Comparison of Subscale Steel Aqueous Cleaning Process with Baseline Process

Process	Atom % C	Atom % Ca	Si/Zr Atom Ratio	Atom % Fe	% Fe as Oxide in Fe (3p)
TCA Vapor Degreasing	18.2 (2.7)	0.1 (0.1)	1.4 (0.2)	10.0 (0.4)	62.0 (1.3)
Brulin 1990 Aqueous Cleaning	19.4 (3.1)	0.1 (0.1)	1.3 (0.3)	11.1 (0.8)	60.6 (1.5)

Values in parentheses indicate one standard deviation.

Table III. Comparison of Subscale Aluminum Aqueous Cleaning Process with Baseline Process

Process	Atom % C	Atom % Ca	Si/Zr Atom Ratio	Atom % Al	% Al as Oxide in Al (2p)
TCA Vapor Degreasing	12.7 (1.6)	1.2 (0.2)	1.1 (0.2)	21.5 (0.6)	64.5 (1.9)
Brulin 1990 Aqueous Cleaning	17.0 (1.3)	1.0 (0.1)	1.2 (0.3)	22.4 (0.5)	64.1 (1.2)

Values in parentheses indicate one standard deviation.

It was therefore concluded that the aqueous cleaning process followed by a post-clean gritblast was capable of producing steel and aluminum surface chemistry identical to that of the baseline TCA process.

3.5 Initial Evaluation of Full-Scale Aqueous Cleaning Process

The next step in the implementation of aqueous cleaning was the construction of a full-scale spray-in-air aqueous cleaning facility at Thiokol production facilities in Utah. The equipment can process

steel and aluminum rocket motor parts as large as the 12-ft. diameter steel case segments used in construction of the Space Shuttle RSRM. The surface analysis instrumentation is located across the street from the production facility, which makes it especially convenient to support the production process.

In this evaluation, steel and aluminum "miniature witness panels" were processed alongside bonding specimens and full-scale hardware. Table IV shows the ESCA results for steel. Control specimens representative of the baseline process were also prepared and analyzed for purposes of comparison. Three separate specimens for each condition were run and results were averaged. Similar analyses on aluminum showed that the process was satisfactory, as did the results on steel to be discussed below.

During this initial evaluation of the full-scale process an upset to the rinsing process occurred. Ordinary tap water was inadvertently introduced into the deionized water process stream that is normally used for rinsing. For steel samples without a post-clean gritblast, this coincided with the appearance of pinpoint (100 μm or 0.1 mm) diameter corrosion (rust) spots. As shown in Table IV, ESCA detected Mg (present in hard water) and Ca (present in hard water, but possibly also from dissolved HD-2 grease in the Brulin bath) on the steel. Traces of Cl were detected on some samples, but it was difficult to see at low levels due to an interference from a zirconium loss peak.

Table IV. Summary of ESCA Results For D6AC Steel Coupons, Full Scale Aqueous Cleaning Facility Checkout

Processing	Atom % C	Atom % Ca	Atom % Fe	Si/Zr Atom Ratio	% Fe as Oxide in Fe (3p)	Additional Contaminants
Gritblast Only	14.9 (1.4)	0.9 (0.3)	10.8 (0.3)	1.5 (0.2)	68.4 (2.1)	--
Gritblast /TCA Vapor Degrease	16.6 (1.1)	0.9 (0.2)	11.7 (0.5)	1.3 (0.2)	70.1 (1.0)	--
HD-2 Grease, Aqueous Clean	21.3 (0.6)	2.3 (0.7)	7.3 (0.2)	2.6 (0.4)	75.6 (2.4)	Na, Mg, P
HD-2 Grease, Aqueous Clean, Gritblast	15.7 (0.7)	0.5 (0.2)	10.9 (0.1)	1.2 (0.1)	74.5 (0.2)	--
Mag Particle, Aqueous Clean	14.5 (1.7)	2.2 (0.1)	8.2 (0.4)	2.4 (0.2)	76.1 (0.8)	Na, Mg, P, Cl
Mag Particle, Aqueous Clean, Gritblast	14.5 (1.4)	0.6 (0.3)	9.8 (0.3)	1.4 (0.2)	74.3 (1.3)	--

Values in parentheses indicate one standard deviation.

AES was used to analyze several corrosion spots, and several noncorroded areas on samples that had been contaminated with magnetic particle solution residues and HD-2 grease and then aqueous cleaned. Figure 4 shows AES point spectra, on both a corroded and noncorroded area from a magnetic particle contaminated, aqueous cleaned surface. In the AES spectra chlorine was obviously present, and the level varied as a function of lateral position on the surface. While chlorine was detectable both on and off the corrosion spots, the levels seemed to be somewhat higher on the corrosion spots. The presence of chlorine strongly suggests that the corrosion was induced by chlorides in the rinse water. The post-clean gritblast step effectively removed this corrosion and gave good bond strengths.

Table IV shows that the aqueous cleaning process adequately removed HD-2 grease and magnetic particle solution residues as evidenced by the low levels of carbon left after aqueous cleaning. The steel oxidation levels, while higher than those of the freshly gritblasted surfaces described in Table II and Figures 1 - 3, are all within the range of normal experience for gritblasted steel surfaces that have been exposed to ambient environments. Table IV also indicates that the post-clean gritblast removed excess silicates and other Brulin residues. Bond strengths were in line with the baseline TCA process.

This study verified that the full-scale aqueous cleaning process with a post-clean gritblast was capable of producing an end result comparable to that given by the old TCA process. In addition, it demonstrated that the post-clean gritblast could overcome minor surface corrosion caused by process upsets such as impurities in the rinse water.

3.6 Extension of Bath Life in Full-Scale Aqueous Cleaning Process

Another milestone in the process development was to characterize and extend the life of Brulin 1990 cleaning bath. A discussion of the aspects of the bath solution chemistry, depletion mechanisms, and bath life extension study is being presented at this conference [2].

During implementation of the aqueous cleaning process the bath temperature had to be increased to 170°F (from 150°F) to compensate for cooling effects which caused unacceptably low temperatures at the spray-in-air nozzle. Even higher temperatures, in the vicinity of 200°F, can be attained locally next to the steam heating coils in the holding tank. It has been shown [2] that this excess heating causes accelerated hydrolysis of the sodium tripolyphosphate (STPP) builder which is a component of the aqueous cleaner. The hydrolysis of STPP produces free acid which lowers the pH of the bath. (The pH of the bath can also be lowered by absorption of atmospheric carbon dioxide.) The lower pH in turn causes polymerization and precipitation of sodium metasilicate (SM). Experience indicates that if nothing is done to stabilize the pH, the SM concentration will fall below specification limits after about eight days.

Laboratory studies [2] indicated that periodic potassium hydroxide (KOH) add-back could stabilize the bath pH and prevent depletion of SM. To test this on a production scale, a series of bath chemistry, bonding (with EA-913NA epoxy adhesive), and ESCA surface analysis tests on miniature witness panels of steel and aluminum were performed over a period of 127 days [2]. KOH add-back was performed periodically to keep the pH above 9.3, which is the critical value for SM precipitation. In the present study, it was necessary to add KOH at approximately 8, 14, 20, 35, 43, 53, and 103 days. The STPP level declined to an undetectable level (less than 3.3 ppm) after about 76 days.

Figure 9 shows ESCA carbon levels for steel coupons that were contaminated with HD-2 grease and aqueous cleaned. Results are presented for samples with and without a post-clean gritblast. (No post-clean gritblast surface data were obtained for the first three cycles.) Bonding data (TDCB fracture energy) are also included. Despite the depletion of the builder STPP, the cleaning efficiency of the bath for HD-2 grease remained excellent throughout the entire 127 day bath life study. Bonding data show good bond strengths both before and after the post-clean gritblast.

A series of aluminum coupons, treated with a "tri-acid etch" solution (containing nitric, hydrofluoric, and chromic acids), was also cleaned at the same time as the steel coupons. Figure 10 is a plot of the levels of some inorganic Brulin components (sodium, potassium, and phosphorus) left after aqueous cleaning and before the post-clean gritblast. Superimposed are bond strength data before and after a post-clean gritblast.

In contrast with the steel results, which typically only showed sodium and no phosphorus or potassium, the aluminum samples showed evidences of variable amounts of these contaminants. There were also varying small amounts of chromium and fluorine from the tri-acid etch, but these did not seem to have any correlation with bond strength. The bond data, prior to gritblast, show declines with local minima at 11, 57, and 99 days. The shelf life of the original lot of EA-913 NA adhesive expired between 57 and 72 days and was replaced with a new lot for the 72 day data point. Seventy-two day bond data acquired on aqueous cleaned surfaces with the old, expired lot of adhesive had a considerably lower fracture energy than shown in Figure 10. This at least raises the possibility that age-out of the adhesive had something to do with the decline in bond strength in the vicinity of 57 days.

The surface analysis data do not provide a clear-cut reason for the declines in bond strength but do shed some light on possible causes. The 57 and 99 day minima correspond with maxima in the combined

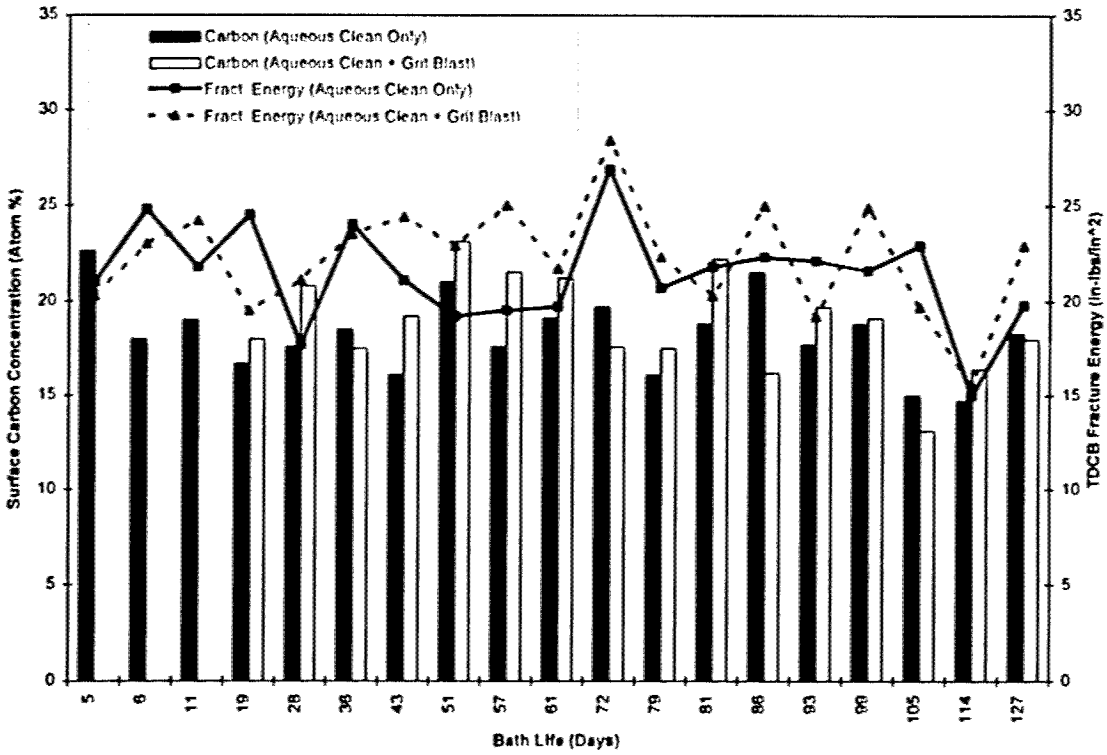


Figure 9. Comparison of Steel Surface Carbon Levels and Bond Strength Data, Full Scale Aqueous Cleaning Process Bath Life Study

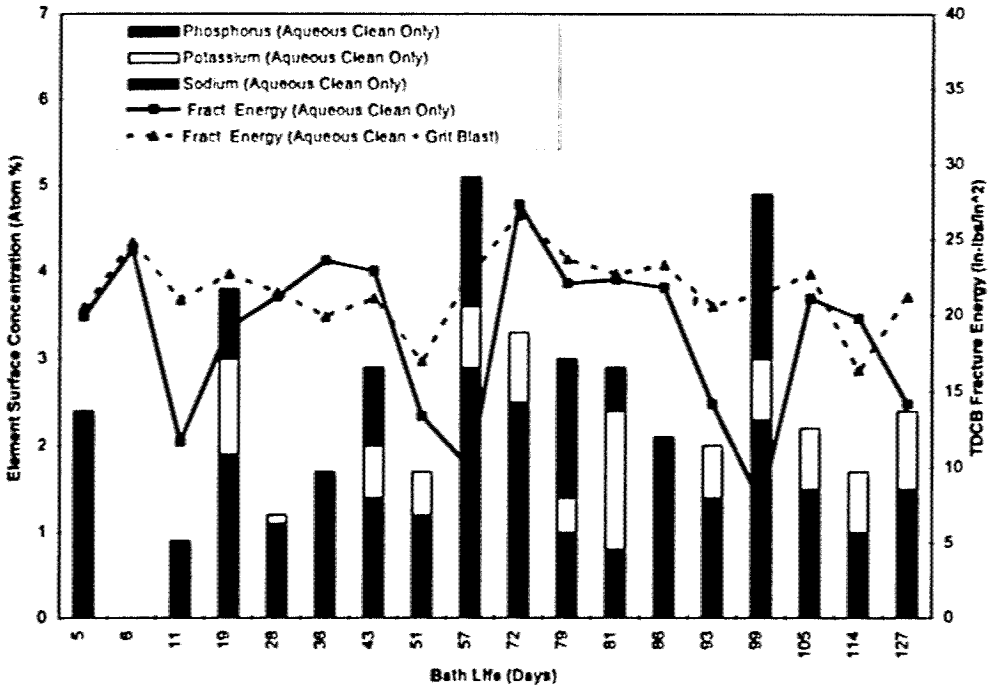


Figure 10. Comparison of ESCA Aluminum Cleaner Residue Results with Bond Strength Data, Full Scale Aqueous Cleaning Process Bath Life Study

amounts of sodium, potassium, and phosphorus. The samples at 57, 86 and 99 days also had larger amounts of the organic component of Brulin than the other samples. The rinse water conductivity was high at these times as well, suggesting impure rinse water was leaving contaminants behind on the surface. The decline at 11 days does not have an obvious explanation.

ESCA did indicate that this 11 day sample was excessively oxidized (no metallic Al detected in the Al(2p) scan) and was generally darker in color than the other coupons. The excess oxidation might have been a result of a longer than normal dry time for this sample set. In that case the extended contact with neutral or acidic water would have oxidized the aluminum.

It should be remembered that the ESCA tests were conducted on single specimens, while the TDCB tests were conducted on many specimens and averaged. The coefficients of variation for the TDCB tests were as high as 51 percent, suggesting the possibility of variations in surface chemistry on this order of magnitude. Perhaps, if it had been possible to run several replicates of the ESCA samples, a better correlation between contamination levels and bond strengths might have emerged.

Figure 10 also shows that a post-clean gritblast improves bond strengths of all specimens to acceptable levels. ESCA analyses on these samples showed that the post-clean gritblast effectively removed the sodium, potassium, phosphorus, organic Brulin components, tri-acid etch residues and excessive oxidation to produce surfaces that are similar to those of the baseline process.

These studies confirm the HD-2 grease cleaning efficiency of the bath over an extended period of time. ESCA results also support the notion that much of the variability in aluminum bond strength is due to Brulin components left behind from contaminated rinse water.

4.0 SUMMARY

This paper shows the utility of surface analysis techniques for complementing bonding tests and supporting cleaning process development for steel and aluminum. Surface analysis explained the mechanism of bond enhancement (formation of iron or aluminum silicate overlayers on the metal) by aqueous alkaline cleaners. It generally agreed with bonding tests as to the most important parameters (cleaner temperature and concentration) for aqueous cleaning, thus providing additional confirmation that the process was truly optimized. It verified that a post-clean gritblast restores an aqueous cleaned surface to a condition identical to that of a vapor degreased surface. It identified the cause (chorides in rinse water) of some corrosion that occurred during initial full-scale process check-out. Finally, it provided information to confirm the cleaning efficiency of the cleaning bath over a 127-day cycle.

5.0 REFERENCES

[1] M. W. Lesley, L. E. Davis, J. F. Moulder, and B. A. Carlson, "The Role Of Surface Chemical Analysis in a Study to Select Replacement Processes for TCA Vapor Degreasing," in: Proceedings of Aerospace Environmental Technology Conference, NASA Conference Publication 3298, 1995.

[2] C. Saunders, K. Evans, and N. Sagers, "Wash Solution Bath Life Extension for the Space Shuttle Rocket Motor Aqueous Cleaning System, " to be presented at third Aerospace Environmental Technology Conference, Huntsville, Alabama, 1998, and published in conference proceedings.

6.0 ACKNOWLEDGEMENTS

The author would like to acknowledge the contributions of John Moulder and Larry Davis of Physical Electronics for providing the early ESCA data, Thiokol colleagues Kurt Evans, Chad Saunders, and Neil Sagers for providing bond and processing data, and Thiokol colleague Andy Allen for design and interpretation of the subscale process development test matrix.

NEAR REAL-TIME ANALYSIS OF HYDROCARBON CONTAMINATION IN RSRM PRODUCTION

Michael Meltzer
Hugh Gregg
Carolyn Koester
Stephanie Ross
Lawrence Livermore National Laboratory
PO Box 808, L-621
Livermore CA 94551
(925) 424-6923
meltzer1@llnl.gov

Abstract

Lawrence Livermore National Laboratory (LLNL) is engaged in a study with Thiokol Aerospace and Industrial Technologies to examine the utility of a novel surface analysis system for determining contamination levels on Reusable Solid Rocket Motor (RSRM) parts. The analysis system, termed the "contamination analysis unit," or CAU, was developed and patented by LLNL to serve as a method of rapidly identifying the type and quantity of hydrocarbon contaminants on various substrates. The CAU uses vacuum and thermal desorption to remove sample contaminants from a surface, which are then analyzed in a Leybold Transpector mass spectrometer. The CAU is a portable instrument that can be used in the field. It has demonstrated detection limits of 1 $\mu g/cm^2$ or less for many hydrocarbon contaminants.

The Thiokol study seeks to evaluate the effectiveness of the CAU in detecting both solvent and soil residues on various RSRM substrates. Test coupons were supplied to LLNL by Thiokol that reproduced various RSRM critical soil/substrate combinations, and that were cleaned using either 1,1,1 trichloroethane (TCA), the control solvent, or one of the solvents recently implemented to replace TCA. The analysis was performed under both ambient and elevated temperature environments.

Project Objective

This project, which is at present only partially completed, involves the testing of a surface analysis system developed by Lawrence Livermore National Laboratory (LLNL) on Thiokol-manufactured parts. The system is termed the Contamination Analysis Unit, or "CAU, (Patent Number 5521381, issued on May 28, 1996). The CAU's capability for measuring trace amounts of surface contamination on RSRM and other parts is examined. Contamination can consist of either cleaning chemical residues or various soils.

Overview of CAU Design and Capabilities

The CAU analyzes a surface by removing trace amounts of contamination and passing them through a small but highly sensitive quadrapole mass spectrometer for analysis. Removal of the contaminants from the surface is accomplished through vacuum and thermal desorption. A vacuum of up to 10^{-7} atmospheres is applied to the section of surface being analyzed (typically a square inch in area). The CAU also bakes this area with infrared radiation and can raise its temperature to 200°C. The combination of heat and vacuum volatilizes contaminants on the surface, and allows them to pass through the mass spectrometer to be detected.

Major advantages of the CAU approach for surface analysis is that it is portable, provides quantitative data in near real time on the amount of hydrocarbon contaminant present, and also provides mass spectral data that can be used to identify the species of contaminants. If only a single contaminant (which might contain a mixture of compounds) is present, such as a machining coolant residue, identification is a straightforward task using the contaminant's unique mass spectrum. When *several* contaminants are present, unique mass peaks are used to identify the individual contaminants. Detection limits of the CAU are contaminant dependent, and are functions of both volatility and mass spectrometer response. Detection

limits under 1 $\mu g/cm^2$ have been demonstrated for many hydrocarbon contaminants, and for certain contaminants, under 0.5 $\mu g/cm^2$.

Figure 1 depicts the main CAU components. The instrument has a front end that interfaces with the surfaces under analysis, and that is mounted on a tripod for stability. This front end currently weighs about 17 pounds, although this may be reduced in the future to provide greater portability. The front end contains the instrument/part "interface chamber" and the residual gas analyzer mass spectrometer. **Figure 2** is a closeup photograph of the front of the interface chamber, inside which is the thermocouple for measuring the temperature of the surface, and the heating coil that raises the part's surface temperature to help desorb contaminants. Once the O-ring in the figure is pushed firmly against the part surface, the interface chamber is evacuated. The combination of vacuum and heat has proved efficient in removing many types of hydrocarbon residue from the part surface.

Experimental Approach

In the first phase of the study, the mass spectra of the cleaning compounds and hydrocarbon soils typically found on RSRM surfaces are collected, and the CAU's detection limits for these chemicals are determined.

The next phase involves the contamination of coupons representative of RSRM surfaces with RSRM critical soils, in a manner duplicating actual production conditions. The soils are then cleaned using either TCA (the control solvent), or one of the formulations recently implemented to replace TCA. Finally, the coupons are analyzed with the CAU in order to determine the level of cleanliness attained.

The CAU operates in two modes. *Full scan mode* collects data on all ions of the substance being analyzed, within a preset mass range. The maximum mass range of the CAU is 1 to 200 amu, although narrower mass ranges that capture the ions of interest are often used. Full scan mode identifies the detectable ions that can be used to characterize and monitor a given contaminant (see **Figure 3** for Ionox). It is difficult to get usable data for masses below 40, because of the large signals from trace amounts of atmospheric gases in the system. Also, ions with m/z above 150 are generally not seen from the analytes being examined. This might in part be due to volatility issues of heavier ions.

In *trending mode* (also referred to as "selected ion monitoring"), the CAU collects data on several preselected ions characteristic of a specific contaminant or set of contaminants. In trending mode, the CAU has the lowest detection limits, and thus it is the most useful mode for detecting very small amounts of surface contamination. **Figure 4** depicts a trending mode signal of m/z 101 for Ionox. While the higher masses such as m/z 101 typically have lower amplitude signals than lower masses (such as m/z 43, which is usually a large signal), there is a higher level of confidence that the high mass signals belong to only the contaminant. It is possible that the m/z 43 signal has contributions both from the contaminant and from the background (for instance, from oil from the roughing pump).

In using the CAU for surface analysis, it is vital to identify and eliminate background effects from the actual contaminant signatures, and to check that the instrument is calibrated correctly. To accomplish these ends, the following steps are taken before contaminant spectral data are collected and interpreted:

1) Check instrument background. Peaks at m/z 18 (water), 32 (O_2), and 28 (N_2) should be detected. These peaks are from trace amounts of air in the system and should be present at signal strengths of 10^{-8} to 10^{-9} amps. This procedure yields information regarding the CAU's sensitivity and mass accuracy.

2) Use perfluorotributylamine (PFTBA) to calibrate CAU. PFTBA has peaks at m/z 69, 131, and 169, and serves as a check to establish that the mass axis of the CAU is properly calibrated and that the peak shapes are correct.

3) Analyze background spectrum of a "blank" (clean) surface of the same type as the one that is contaminated. Blanks are analyzed between each sample analysis. Signals at m/z 44 originate from small CO_2 leaks from the atmosphere. Signals are also often seen at m/z 43, 55, and 57. These peaks are characteristic of many hydrocarbons, and may originate from trace amounts of oil that has entered the system from the roughing pump installed on one of our two CAU's. Our newer, portable CAU uses a diaphragm pump that is not a source of possible oil contamination.

Current cycle time to ramp a sample from ambient temperature to 200°C, and then to let the sample interface cool back to ambient is currently 15 to 20 minutes. Only 3 to 6 minutes of this time are currently used to ramp the temperature and collect data. The majority of the cycle time is required for the interface chamber of the instrument to cool back to ambient temperature. One of the main development goals of the CAU system is to significantly reduce this cycle time, possibly through introducing a cooling jacket around the interface chamber.

Analysis of Cleaning Compounds

Mass spectra have been obtained for the following cleaners:

PF Degreaser
PF d'Ink
PF Ionsol
PF 145 HP
Ionox BC
BioAct PCG
BioAct 113
BioAct 145
Reveille
Exosolve 5
OxSol 100

Spectra were not obtained for isopropanol and 1,1,1 trichloroethane. There are volatile solvents at ambient temperatures and were probably totally volatilized during evacuation of the CAU prior to mass spectrometric analysis.

The spectra have been used to develop calibration curves for the different cleaners. These curves correlate the amount present (in $\mu g/cm^2$) with an integrated signal area measured by the CAU. **Figure 5** depicts such curves for Ionox, for masses from 43 to 101. The x-axis of this plot lists the various concentrations of Ionox measured (0.5 to 10.3 $\mu g/cm^2$), and the y-axis gives the signal (measured by integrating the area under a trending curve (such as in Figure 4) for each mass).

Note from the table in Figure 5 that measurable signals are obtained for all masses for concentrations from 1.3 to 10.3 $\mu g/cm^2$. For 0.5 $\mu g/cm^2$, measurable signals are not obtained for m/z 72, 73 and 101. There are still significant signals from the other masses, however, indicating that the detection limit may be lower than 0.5 $\mu g/cm^2$.

The scatter in these measurements is directly related to the precision of the detection limits obtained. **Figure 6** depicts the mean values and standard deviation for Ionox signal amplitudes corresponding to masses ranging from 43 to 101, for Ionox concentrations 2 times the detection limit. **Figure 7** depicts the same thing, for Ionox concentrations 12 times the detection limit. It is not surprising that when the concentration of the compound is higher, the scatter in the data is considerably less.

Analysis of Soils

The effectiveness of the CAU system is currently being evaluated for detecting trace quantities of RSRM critical soils, after cleaning with either TCA (the control solvent) or one of the solvents recently implemented by Thiokol to replace TCA. The analyses include both cured and uncured soils.

To date, analysis of the following RSRM critical soils has been initiated:

HD-2Grease
Teflon Tape Adhesive Extract
RTV DC 90-006
Chemlok 205/233
Permacel Yellow Tape Adhesive Extract

Vacuum putty
Hycar
Celvacene

Mass spectra for most of these soils have been obtained. The mass spectra for Chemlok and vacuum putty are depicted in **Figures 8** and **9** respectively. Spectra for heat cured Hycar and Celvacene grease have proved more difficult to obtain. It is likely that the curing process removes the volatile components of the soils sufficiently that mass spectra are not obtainable on the CAU. These soils will be examined further during the remainder of the project.

After the soils are applied to the substrates and cured (if curing is typical for that soil), and mass spectral data is obtained, the substrates are wipe cleaned, using either TCA or one of its replacement cleaners, and employing the same procedures as used during production.

It is significant that after thorough cleaning, the CAU is still able to detect contamination on several of the coupons. **Figures 10** and **11** depicts signals obtained after cleaning various aluminum and steel (abbreviated "al" and "D6," respectively, in the graphs) with cleaners that included TCA, Ionox, and Reveille. In Figure 9, the m/z 91 Chemlok peak (see Chemlok's mass spectrum in Figure 7) is quite prominent on both of the D6 steel plates cleaned. In Figure 10, the m/z 57 and 69 peaks are visible on all four plates cleaned. Note the different Y-axis scales used for Figure 8 vs. 9.

The post-cleaning data shows that wipe cleaning parts until there is no contamination visible (the procedure currently used) still leaves detectable contamination on the surface. This appears to be the case not only with TCA, but with at least two of its replacement cleaners as well. It may be useful to develop a specification delineating a quantitative level of cleanliness that will not impair the functionality of the parts cleaned.

Conclusions

The CAU appears to be a tool that can detect trace amounts of a wide range of hydrocarbon contaminants on parts surfaces. Both RSRM critical cleaning chemicals and soils can be detected, as well as identified through their mass spectra. Volatility of the contaminant is critical for its detection. Contaminants which are highly volatile at ambient temperatures (such as TCA) are removed from the surface during pumpdown to vacuum, and are generally not able to be detected. Contaminants which are relatively nonvolatile at temperatures under 200°C (thermal-cured Celvacene and Hycar may fit into this category) also are difficult to detect. The CAU has demonstrated its ability to detect soil residues such as Chemlok or vacuum putty on steel and aluminum surfaces after they have been thoroughly cleaned according to RSRM protocols.

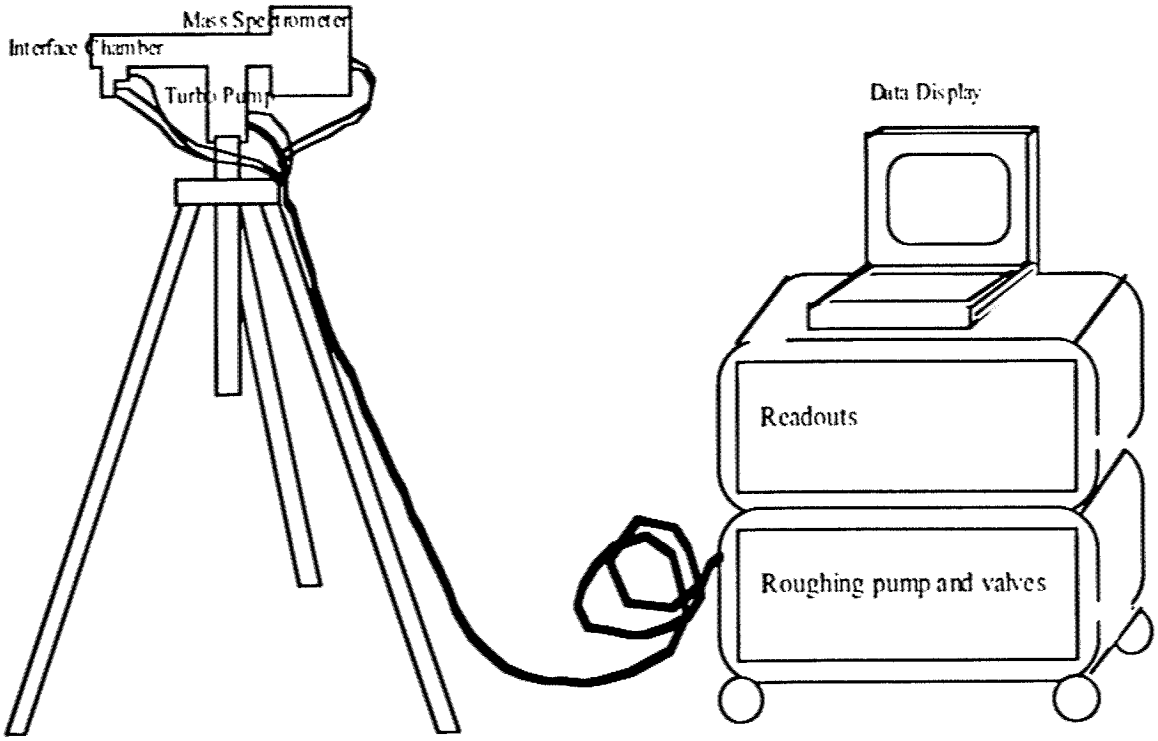


Figure 1
Main CAU Components

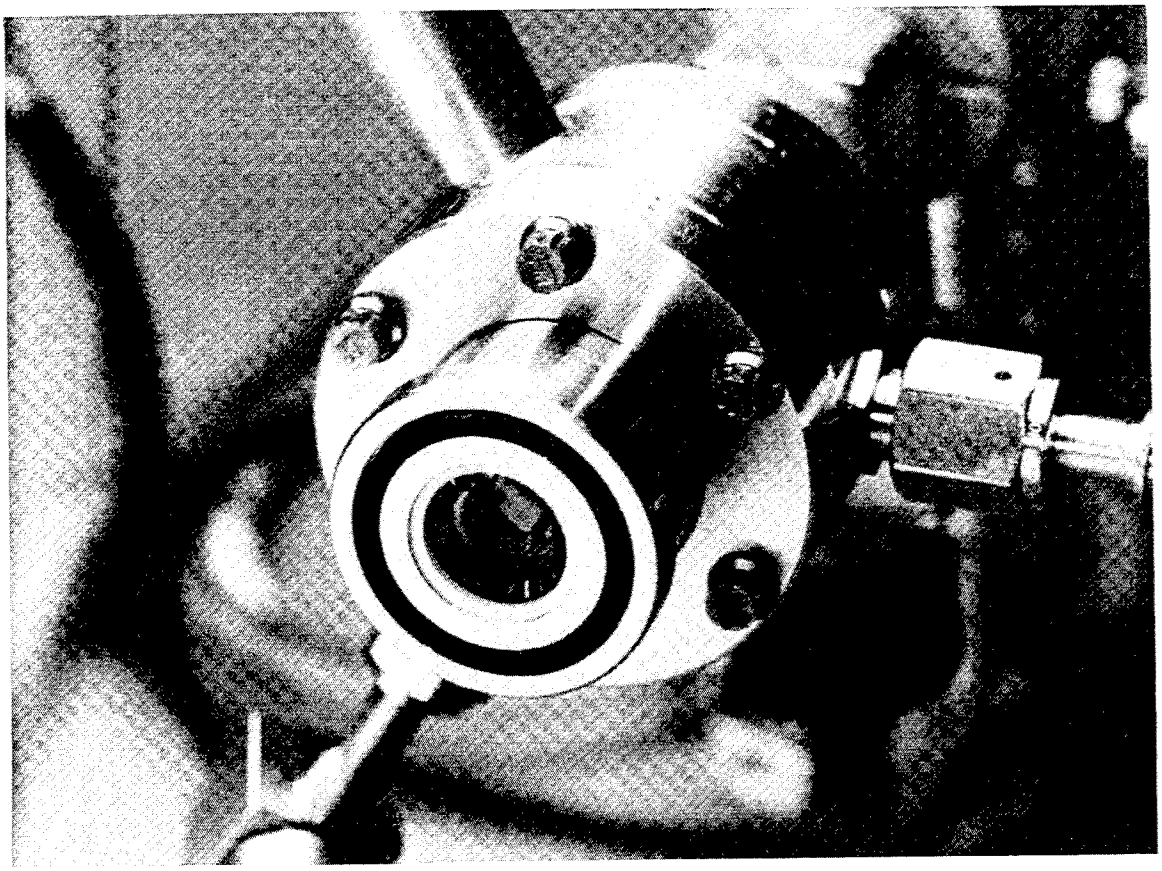


Figure 2
CAU Interface Chamber

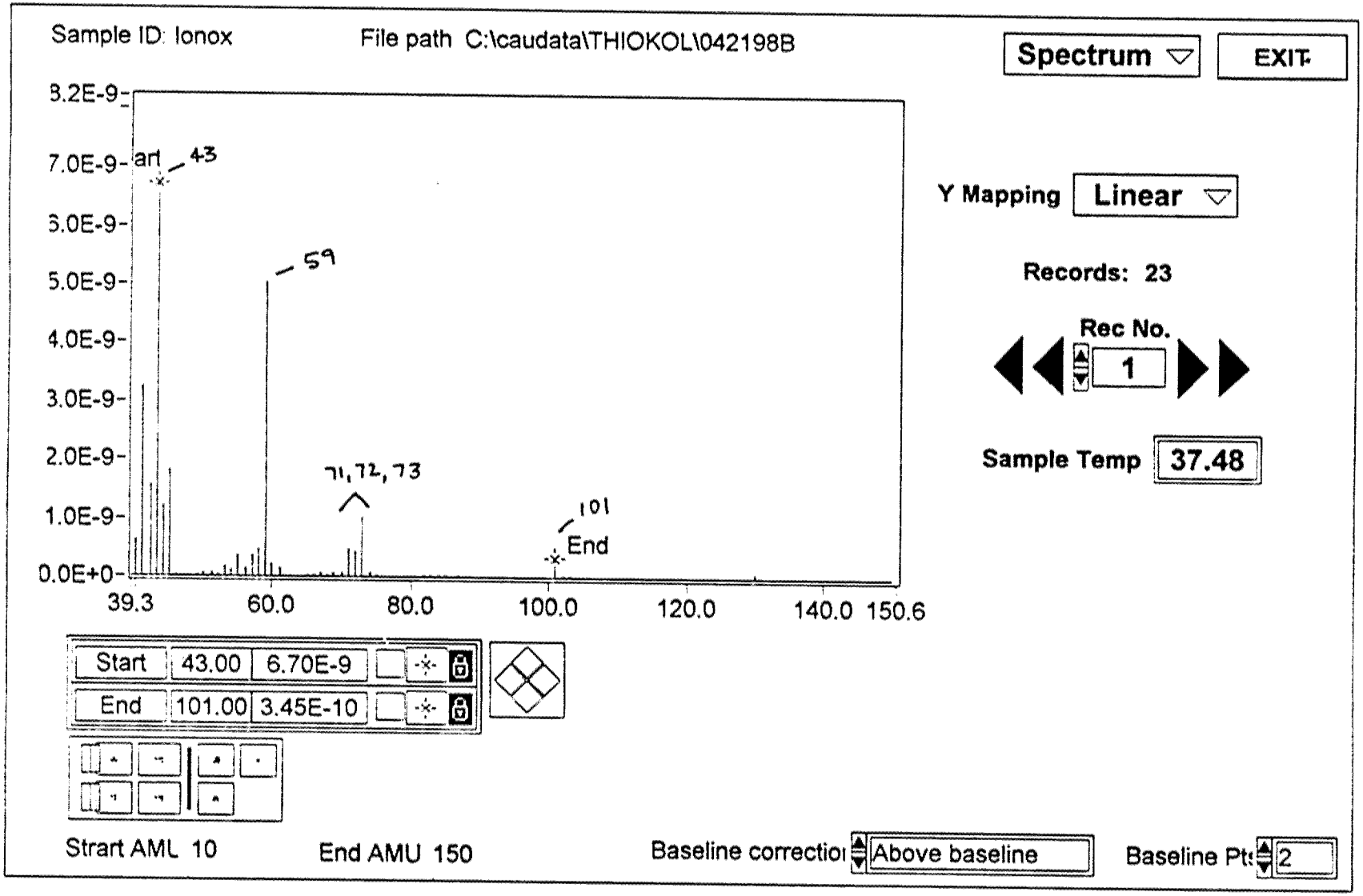


FIGURE 3
Mass Spectrum for Ionox (Current vs. m/z)

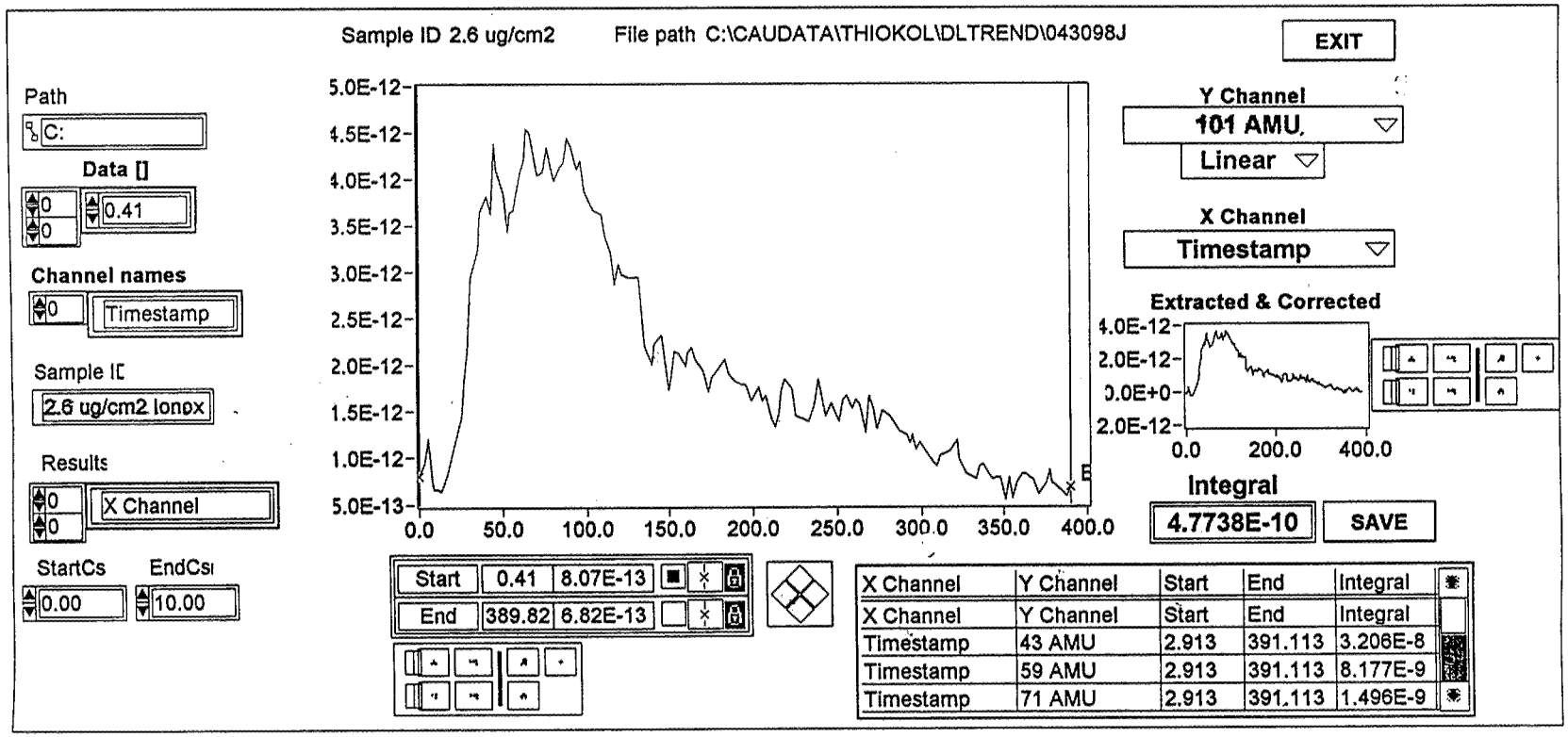


FIGURE 4
Trending Graph for Ionox (Current vs. Time)

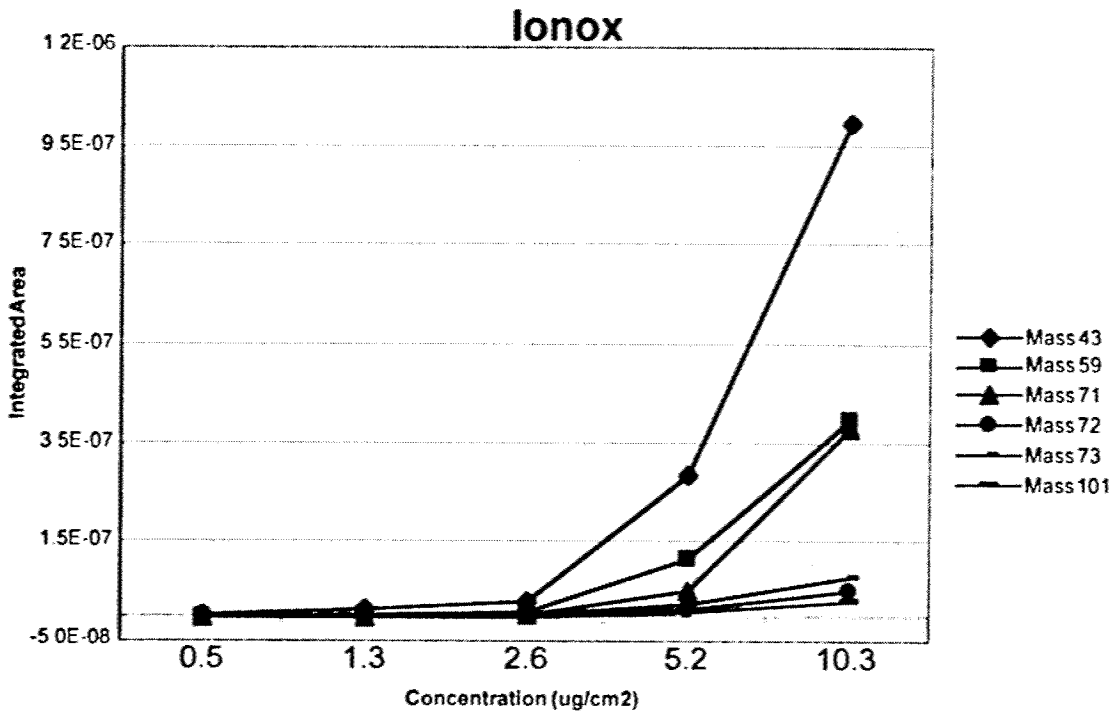


Figure 5
Ionox Calibration Curve

Figure 6

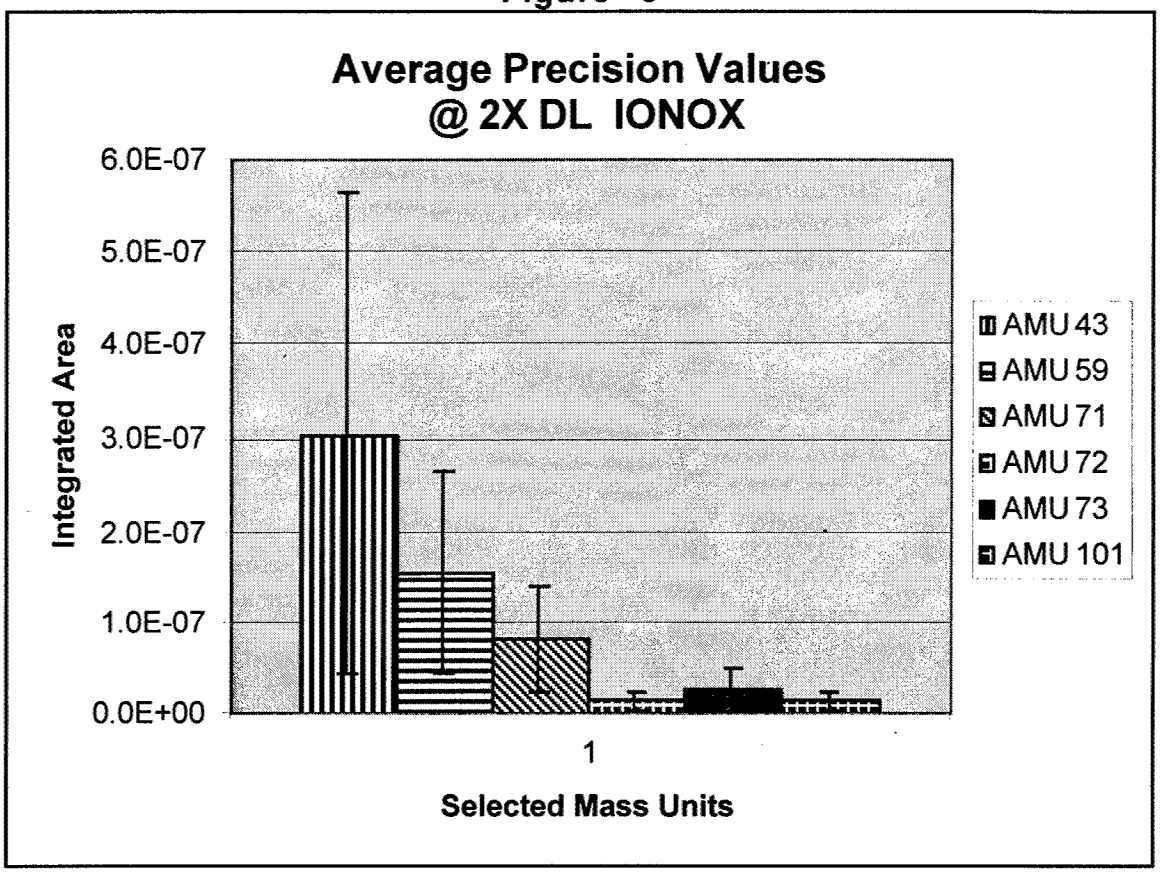
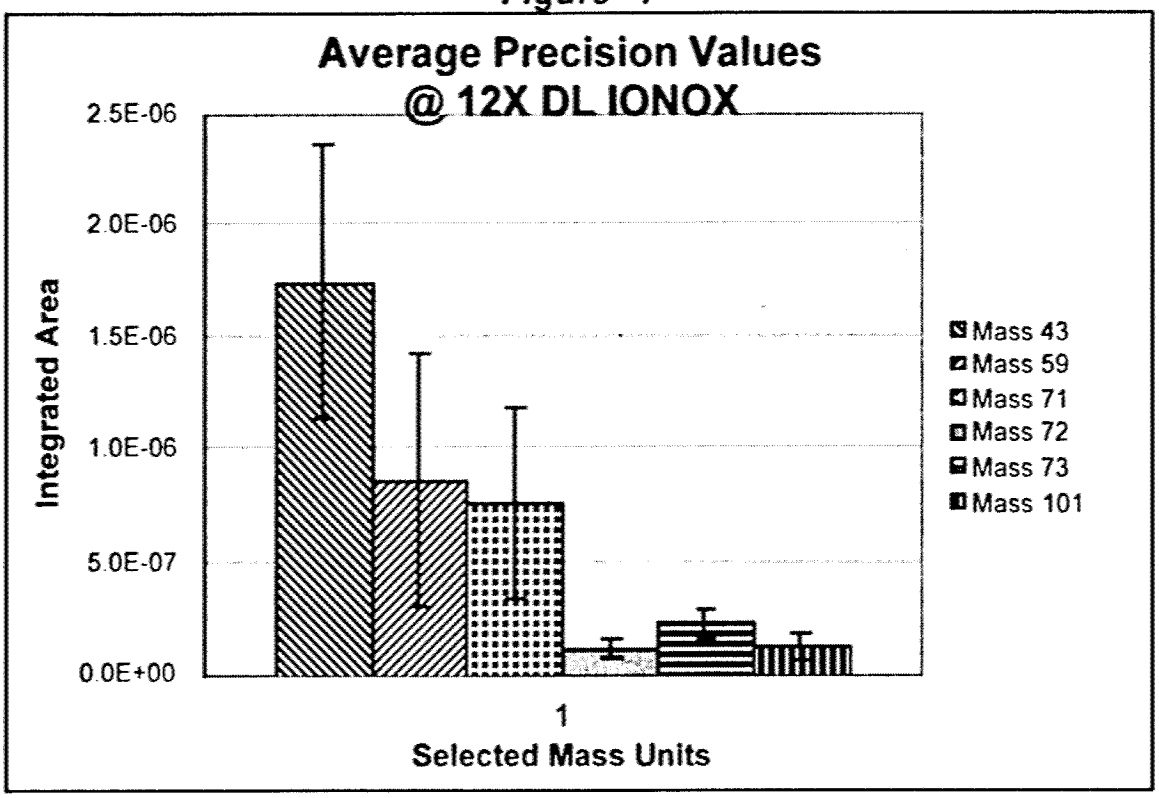

Average Precision Values
@ 2X DL IONOX
6.0E-07
5.0E-07
4.0E-07
3.0E-07
2.0E-07
1.0E-07
0.0E+00
Integrated Area
1
Selected Mass Units
AMU 43
AMU 59
AMU 71
AMU 72
AMU 73
AMU 101

Figure 7


Average Precision Values
@ 12X DL IONOX
2.5E-06
2.0E-06
1.5E-06
1.0E-06
5.0E-07
0.0E+00
Integrated Area
1
Selected Mass Units
Mass 43
Mass 59
Mass 71
Mass 72
Mass 73
Mass 101

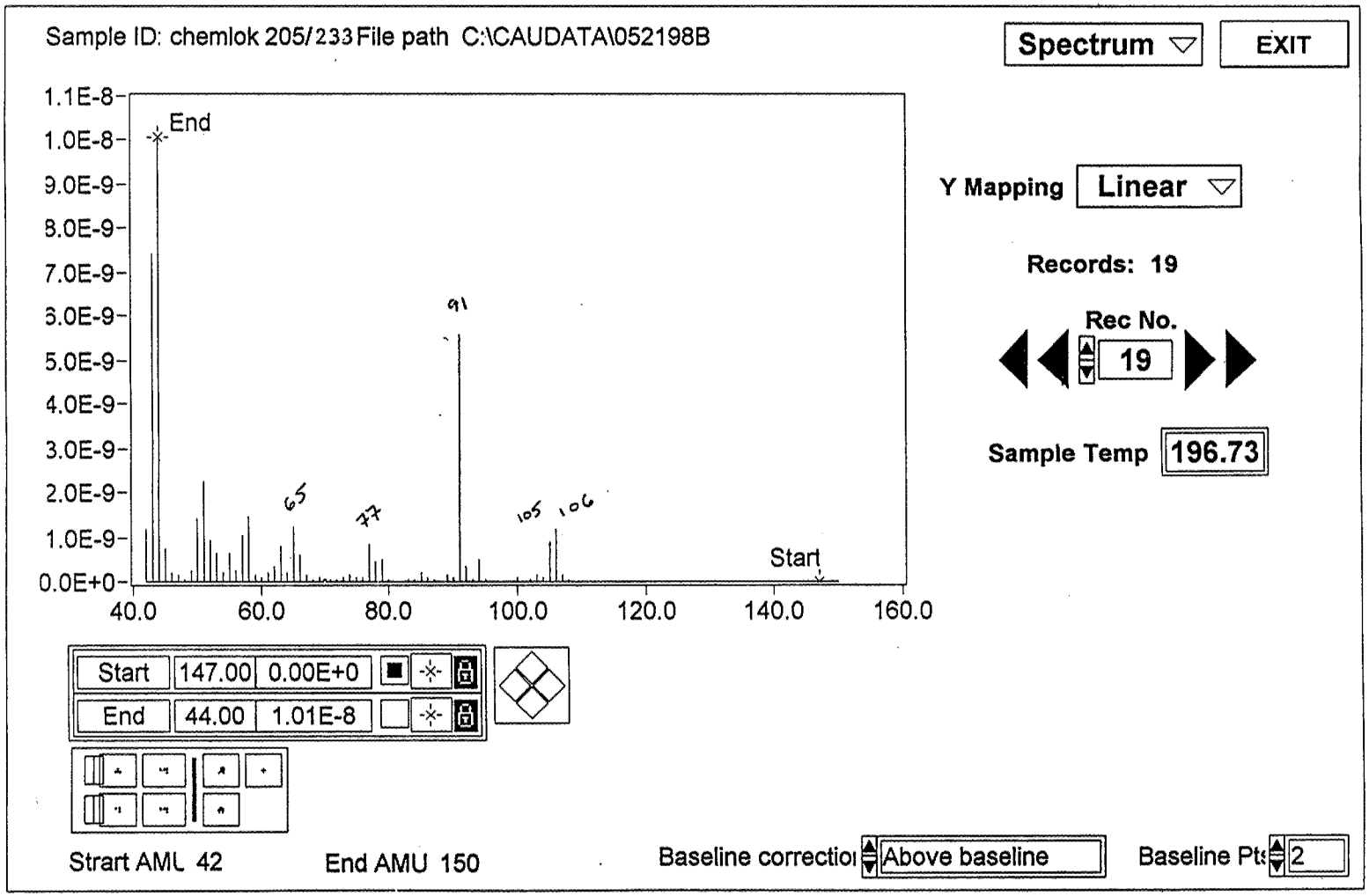


FIGURE 8
Mass Spectrum of Chemlok 205/233

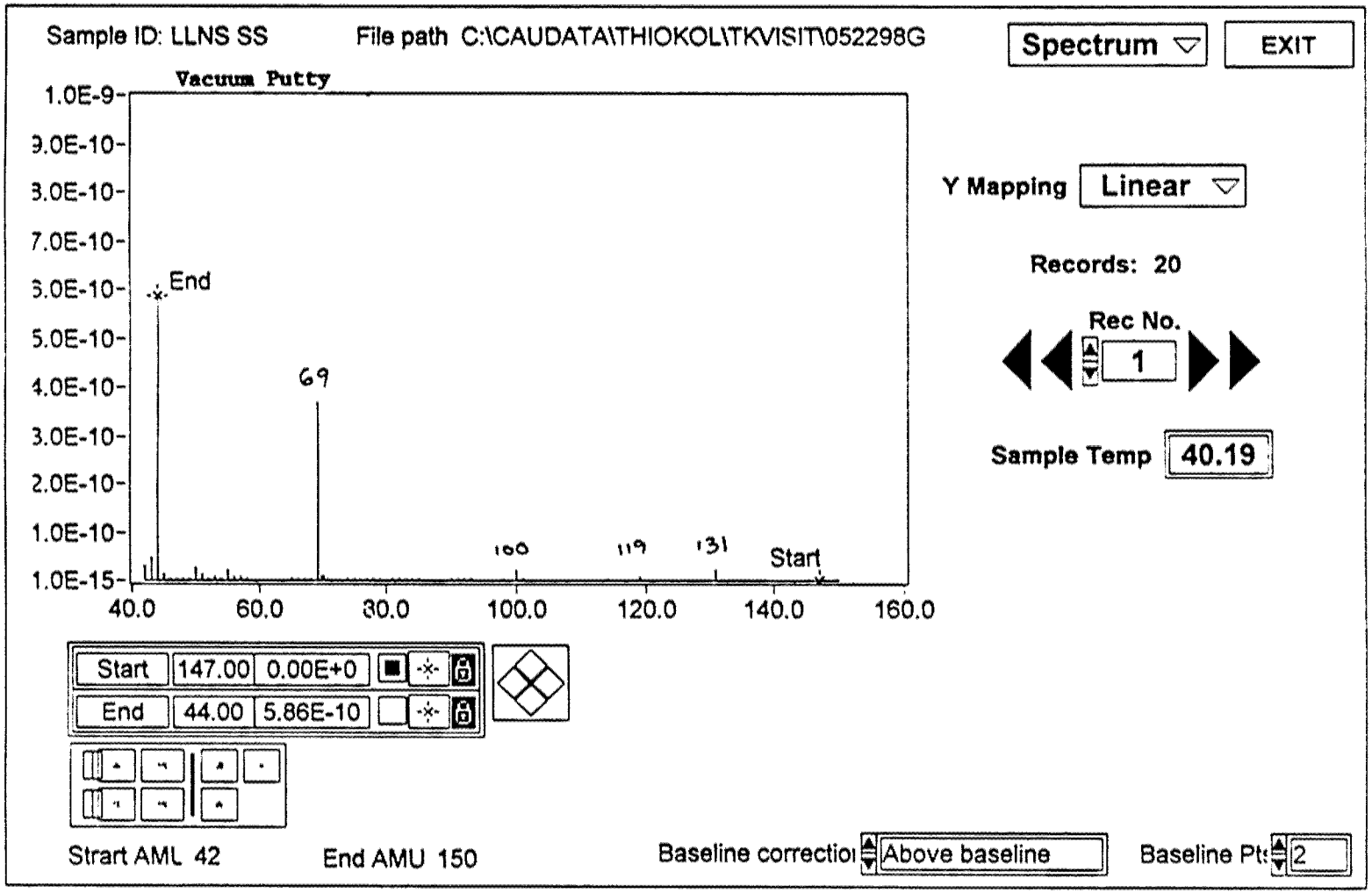


FIGURE 9
Mass Spectrum of Vacuum Putty

Figure 10

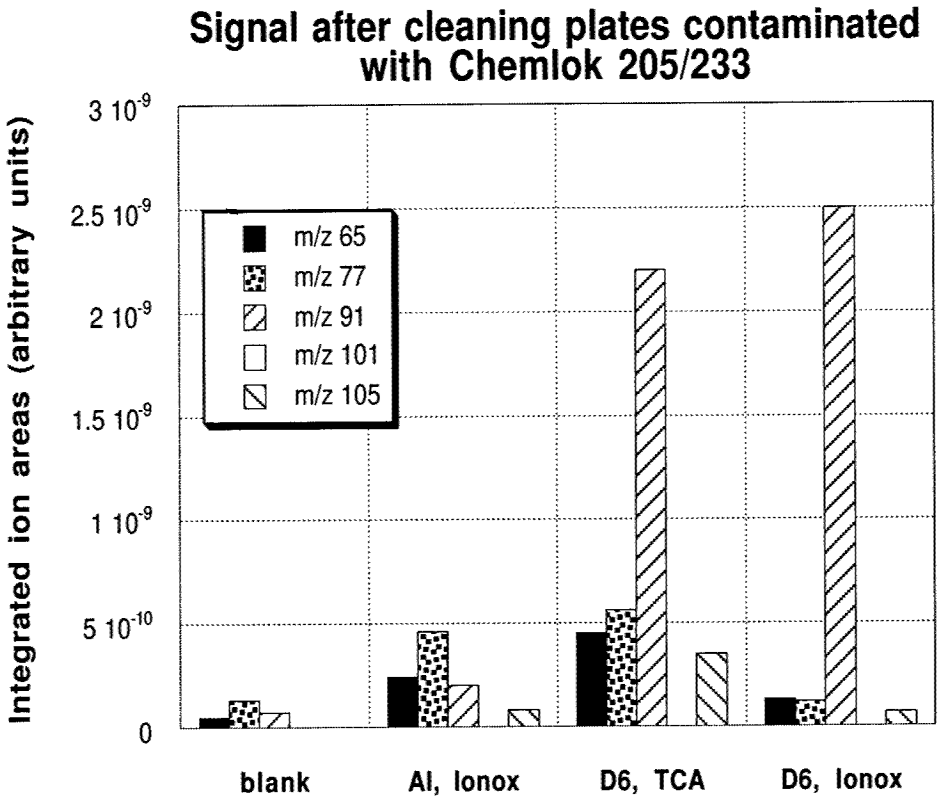
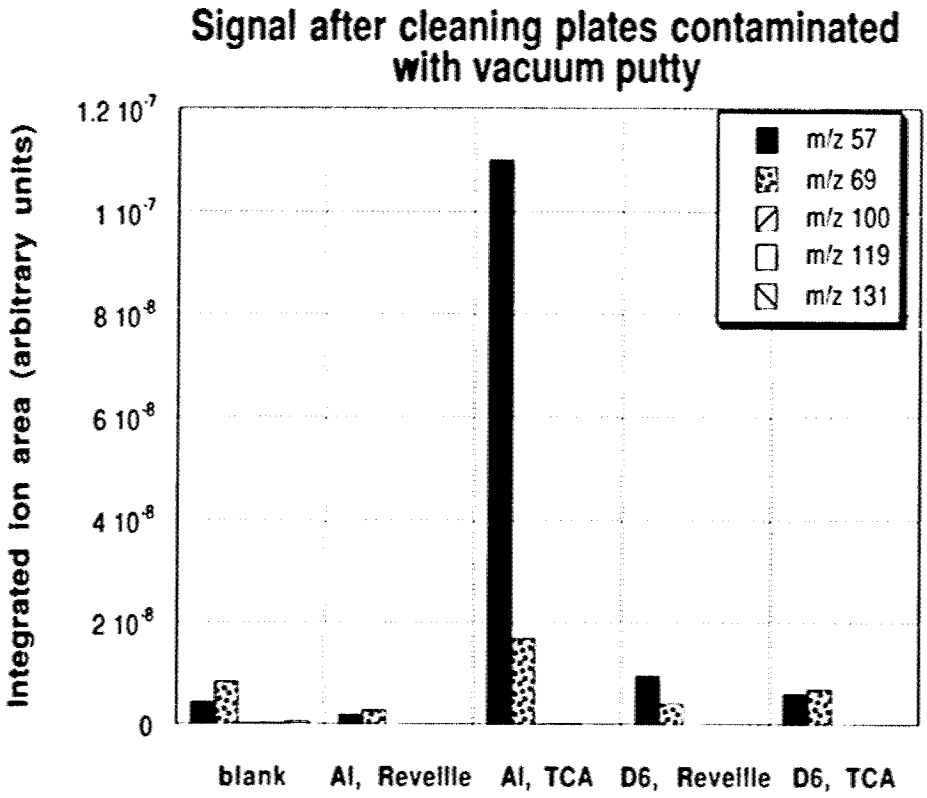

Signal after cleaning plates contaminated with Chemlok 205/233
Integrated ion areas (arbitrary units)
3 10-9
2.5 10-9
2 10-9
1.5 10-9
1 10-9
5 10-10
0
m/z 65
m/z 77
m/z 91
m/z 101
m/z 105
blank
Al, Ionox
D6, TCA
D6, Ionox

Figure 11


Signal after cleaning plates contaminated with vacuum putty
Integrated ion area (arbitrary units)
1.2 10^-7
1 10^-7
8 10^-8
6 10^-8
4 10^-8
2 10^-8
0
m/z 57
m/z 69
m/z 100
m/z 119
m/z 131
blank
Al, Reveille
Al, TCA
D6, Reveille
D6, TCA

REFINEMENT OF PORTABLE FTIR SPECTROSCOPY TO CHARACTERIZE METAL SURFACE CONTAMINATION

J. W. Blanks
Thiokol Corporation/Propulsion Group Huntsville Operations
Huntsville, AL 35812

ABSTRACT

Recent improvements were accomplished in using a portable FTIR infrared spectrometer to detect, identify, and quantify hydrocarbon grease and silicone contaminants on RSRM metal surfaces. Calibration techniques are discussed. Soundness of the method is built by validating calibration standards by a secondary method. Variation of contaminant concentration at multi-locations on a given specimen is examined. Effects of metal surface oxidation on low level contamination detection limits are discussed. Applications of the developed method to real world problems are presented.

INTRODUCTION

A quality control aspect of manufacturing solid rocket motors is a requirement of consistent bond integrity at all mating or bonding interfaces. In order to insure this control, surfaces are cleaned by such methods as solvent degreasing and grit blasting. In addition the surfaces are examined by instrumental methods to detect any contaminant after cleaning. In the past tested methods have included black light (UV), OSEE/Conscan, and more recently, flash UV fluorescence and near and mid infrared spectroscopy. At the present time, OSEE/Conscan is the only method used in manufacturing to identify the presence of certain types of contaminants. This method, along with black light, identifies only the presence of contamination, not the type or quantity of it. These methods also cannot discriminate between a foreign contaminant and surface oxidation. It would be desirable to have an instrument that could quantify the contamination, and is portable, easy to use, and accurate. The ability to identify the type and quantity of contamination can save the cost of re-cleaning hardware that has a type and/or level of contamination that does not affect critical bondlines.

One of the instruments presently being evaluated to detect contamination on metal surfaces is a compact portable Fourier transform infrared spectrophotometer (FTIR), the SOC400, Figure 1, manufactured by Surface Optics Corporation. This unit measures diffuse reflectance spectra of surfaces relative to a selected reference surface. The measurement head containing all the optical components can be hand held, manipulated on a robotics arm, or mounted on a stationary support. All the data in this study was collected with the unit mounted on a stationary support. The spectrometer is connected by way of a control cable to a computer for data storage and manipulation. The control cable also includes a gas purge line to keep CO_2 and water out of the spectrometer. A barrel ellipse detector receives focused diffused radiation from the sample surface. This detector is best suited for examining rough surfaces such as the normal grit blasted steel and aluminum hardware associated with RSRM motors.

The surface contaminants of major interest include silicone and hydrocarbon oils and greases. Dow 200 silicone oil, Conoco HD-2 grease, and hydraulic oil were used as contaminants for instrument calibration purposes. Tape adhesive residues are also of concern.

After calibration was complete, the SOC400 unit was applied to several problems that required verifying a certain level of contaminant had been applied to specimens or verifying that contaminated panels had been successfully cleaned of a contaminant.

Copyright 1998 Thiokol Corporation, All rights reserved.
Approved for public release; distribution is unlimited.

RESULTS AND DISCUSSION

STANDARDS

Calibration standards were prepared using an ultrasonic sprayer made by Sono-Tek Corporation. Solutions of a given contaminant dissolved in methyl chloroform were sprayed onto 8 x 12 inch steel and aluminum panels. The quantity of contaminant was determined by simultaneously spraying a tarred foil specimen, weighing the foil after drying and assuming the concentration of contaminant on the panel and foil were identical.

SOC400 INFRARED SPECTROMETER (FTIR) PARAMETERS

Spectra were collected on the SOC400 Fourier transform infrared spectrophotometer, 100 scans, 16 cm^{-1} resolution, 4000-500 cm^{-1} spectral width, at a non-contact head distance of 0.04-0.06 inches. The 8 x 12 inch panels were examined at 9 equally spaced locations to obtain an average contaminant value. Some spectra collected on specimens with low levels of contaminant included 500 scans. Reference spectra were acquired on clean grit blasted panels of the same metal as the samples.

EXAMINATION OF CALIBRATION STANDARDS

The Sono-Tek ultrasonic machine was shown to produce satisfactory calibration standards over the range selected. The average value of contaminant on the panel and reference foil was verified to be identical within experimental error. This analysis was accomplished by first preparing calibration curves for silicone oil and HD-2 grease in chloroform solution in a 0.1 millimeter sealed cell collecting data on a Nicolet 750 infrared spectrometer. Several of the calibration panels and corresponding reference foils were extracted with chloroform, diluted to a specific volume, the spectra collected in the sealed cell and the contaminant quantified. Figures 2 and 3 show the Nicolet calibration curves for silicone and HD-2 grease. Table I exhibits typical analysis data on extracted foils and panels, demonstrating validity of assumption that weight of contaminant on foil and panel are close. Although the average contaminant deposited on the calibration panels was close to theoretical, the uniformity on a given panel was not always ideal. Figures 4 and 5 display examples of the range of distribution obtained. The panel in Figure 4 shows moderately good uniformity while the contaminant distribution on the panel in Figure 5 is considered excessive. The averages of the absorbances versus contaminant concentrations at the nine locations on the numerous steel and aluminum calibration standards for silicone oil, HD-2 grease, and hydraulic oil are presented in Figures 6, 7, 8, 9, 10 and 11. An acceptable linear relationship is observed with each contaminant on both steel and aluminum.

LIMITS OF DETECTION

Based on past data, the detection of silicone contamination down to a lower detection level is considered more critical because a given silicone concentration has a greater effect on bond integrity than does HD2 grease or hydraulic oil. Recent data shows a silicone level of 5 milligrams per square foot (mg/sqft) on steel can cause a major reduction in bond strength with EA913 epoxy adhesive. Table II displays the measured values on panels with a target of 5 mg/sqft silicone. Although the measured values agree moderately close with the target level, the standard deviation for some of the panels is excessive. Even at 0.5 mg/sqft silicone some affect can be seen on the bond integrity with this adhesive. Table III shows the measured values on panels with a target of 0.5 mg/sqft silicone. The data indicates silicone concentrations at or below 0.5 mg/sqft can be detected and quantified.

Other factors come into play at very low contaminant levels. The metal oxide layer on the metal substrate is rough and porous. The oxide layer, especially on aluminum, can become thicker than the contaminant itself. Part of the incident infrared radiation is blocked by the oxide and does not reach the contaminant that permeates into the oxide layer. If the contaminant is present when the surface is cleaned, solvent or grit blasted, the contaminant may reduce the rate of metal oxidation. These types of

physical and chemical interactions can alter the contaminant value calculated by this method, using the SOC400, but not to the extent that the method is not useful. In a real world situation, whether the value of silicone detected and calculated is 1 or 2 or 3 mg/sqft, those levels of contamination would be considered too high and the surface would require re-cleaning.

APPLICATION OF SOC400 METHOD TO REAL PROBLEMS

DIGESIL™ EVALUATION

The developed calibration of the SOC400 spectrometer was successfully applied to several in-house problems. A commercial product, Digesil™, was evaluated for its effectiveness to remove Dow 200 silicone oil from contaminated steel panels. Examination by SOC400 of the two panels before cleaning revealed the average silicone concentrations of 21.9 and 22.7 mg/sqft. The panels were then cleaned following the Digesil™ instructions which included a water rinse and trichloroethane wipe. Reexamination of the panels after cleaning indicated a silicone concentration of less than 1 mg/sqft. The data indicates this product successfully cleaned the steel panels of silicone contamination. A disadvantage of the Digesil™ is its very acidic nature which may effect metal surface characteristics.

RTV REMOVAL

Eight steel plates (2x2in) were delivered for examination of any residual RTV (90-006, silicone) rubber after cleaning with eight different solvents. One other delivered steel plate contained a film of the RTV rubber on the surface for obtaining a reference spectrum of the rubber. A spectrum of the reference RTV rubber, Figure 10, was obtained using the SOC400 infrared spectrometer and was indicative of a typical silicone rubber or oil including the sharp peak near 1259 cm^{-1} used in the past to calibrate and quantify silicone oil on metal surfaces. The 1259 cm^{-1} portion of the expanded spectra of the eight subject plates are presented in Figure 11. No peak above the noise level is detected in any of the eight spectra. Each of the spectra is a composite of 500 scans in order to provide optimum signal to noise ratios and a low detection limit.

The infrared spectral data from the surfaces of the eight test plates define the level of silicone on each of the plates to be below the detection limit of the method estimated at 1 milligram per square foot.

BOND SPECIMEN PANELS

As stated earlier in this report, two sets of five steel panels were contaminated with Dow 200 silicone oil for preparation of bond specimens with the epoxy adhesive EA913. The target silicone concentrations were 0.5 and 5 mg/sqft. Tables II and III summarizes the average measured silicone concentrations using the SOC400 spectrometer. Several of the values are close to target , but variation at different locations on a given panel is high. The bond strengths of the final specimens were reduced by both these levels of silicone contamination.

TAPE RESIDUE DETECTION

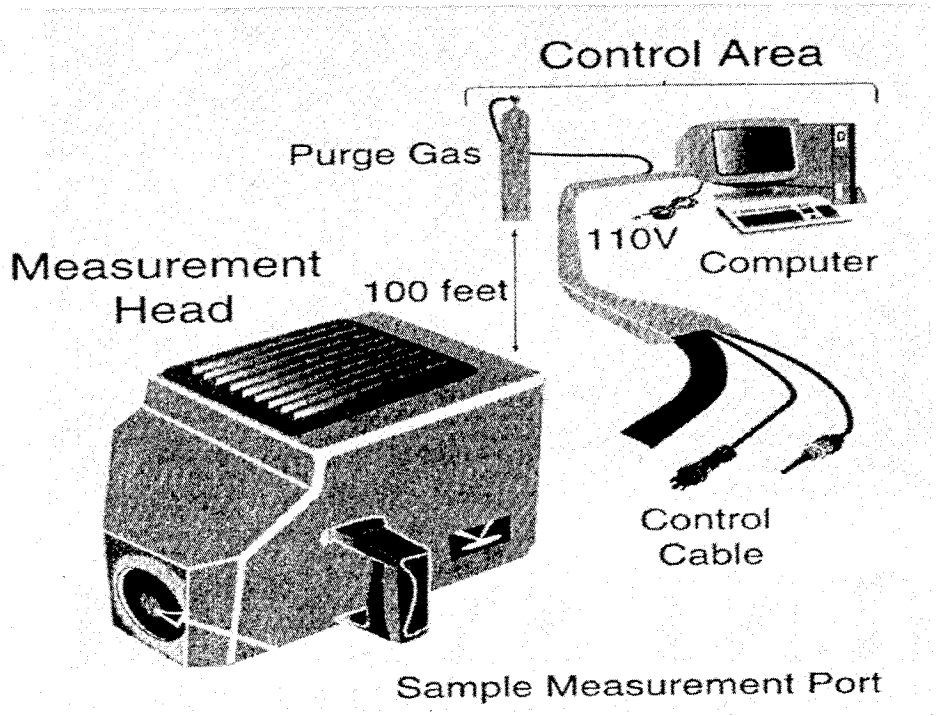
The SOC400 spectrometer was applied to tape residue from all the common tapes used in the RSRM manufacturing process. The tapes were applied to steel panels, removed , and the residual tape adhesive remaining on the surface examined. The spectral features of the residue easily allowed identification of the type of tape as to whether a silicone or hydrocarbon. In most cases the infrared spectral features of the adhesive residues were so unique that the specific tape could be identified. Based upon the calibration standards for silicone, HD2 grease, and hydraulic oil, the amount of each type of tape residue was calculated depending on its structure with the results shown in Table IV. The concentration of residue is in the range of 2 to 5 milligrams per square foot. These levels, especially the 4.6 mg/sqft of silicone residue from the brown Teflon tape is sufficient to cause bond problems.

SUMMARY

The SOC400 spectrometer was demonstrated as a successful tool to detect and quantify contaminants of interest on RSRM type metal hardware. The data supports further development of this type instrument as part of quality control for monitoring bond test panel preparation, identification and quantification of possible contaminant anomalies, and application to motor hardware components at specific areas where contamination is suspected.

CONCLUSIONS

- Concentrations of silicone oil, HD2 grease, and hydraulic oil on steel and aluminum panels show good correlation with spectral absorbance intensities obtained by the SOC400 spectrometer.
- Moderate variations were observed in contaminant concentrations at different locations on the calibration test panels.
- The average values on calibration standards were verified by extraction and quantification by a separate infrared instrument as being correct.
- Detection of contaminants at very low levels, less than 0.5 mg/sqft, were obtained on silicone and hydraulic oil.
- Collection of a large number of infrared scans are required for low detection limits.
- The method is able to detect and estimate the level of tape adhesive residues.
- The method developed was successfully applied to several in-house contamination problems.



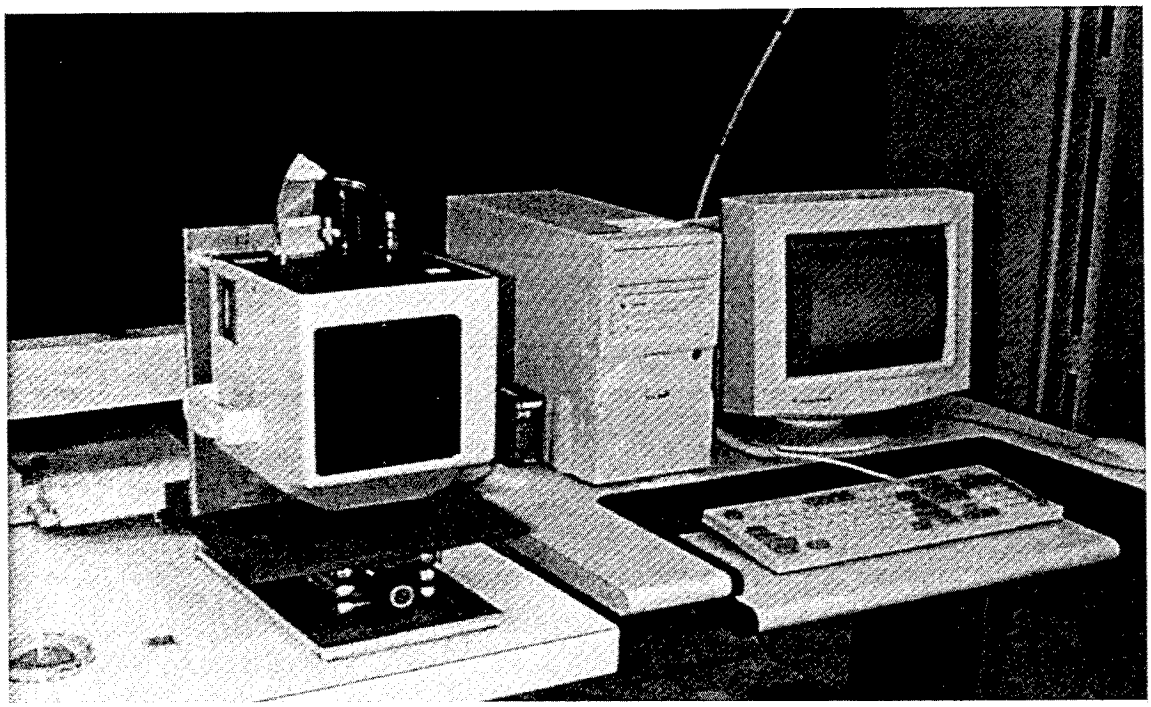


Figure 1. The SOC400 is a Portable FTIR Spectrometer that can be Hand Held, Manipulated with a Robotic Arm, or Mounted on a Stationary Support.

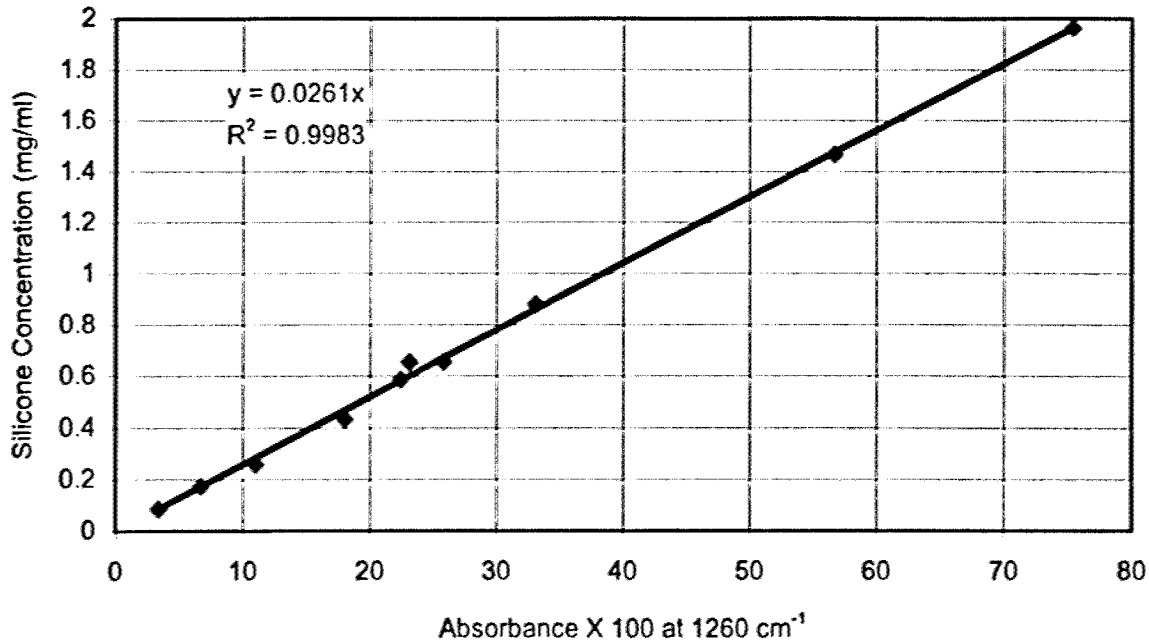


Figure 2. Standard Curve for DOW 200 Silicone Oil in Chloroform using Nicolet FTIR.

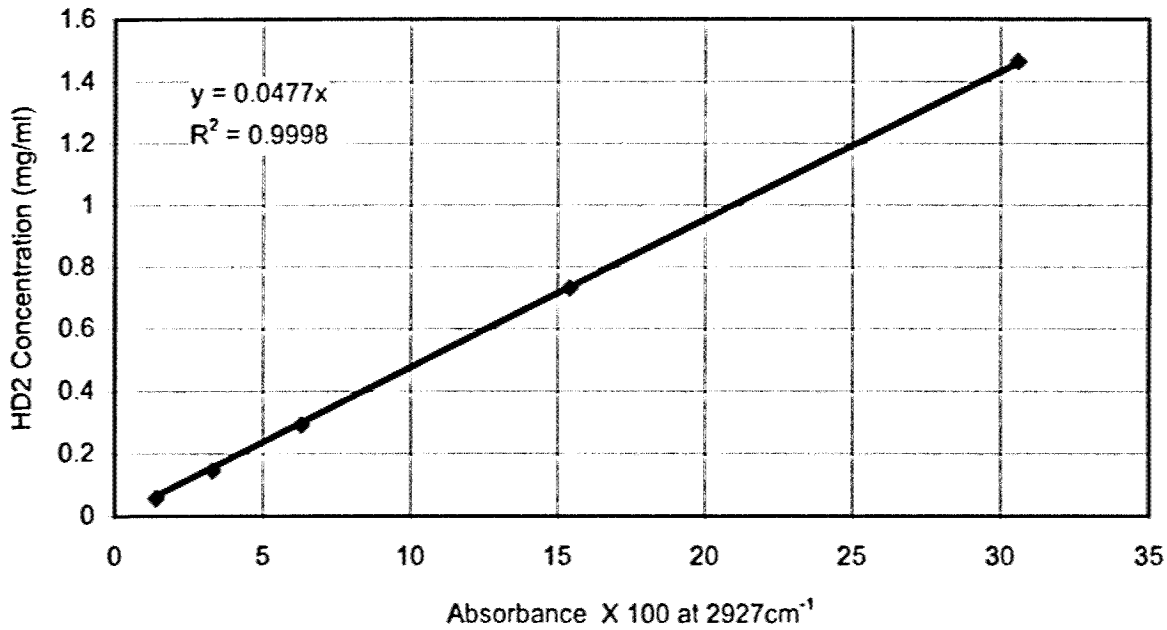


Figure 3. Standard Curve for HD-2 Grease in Chloroform using Nicolet FTIR.

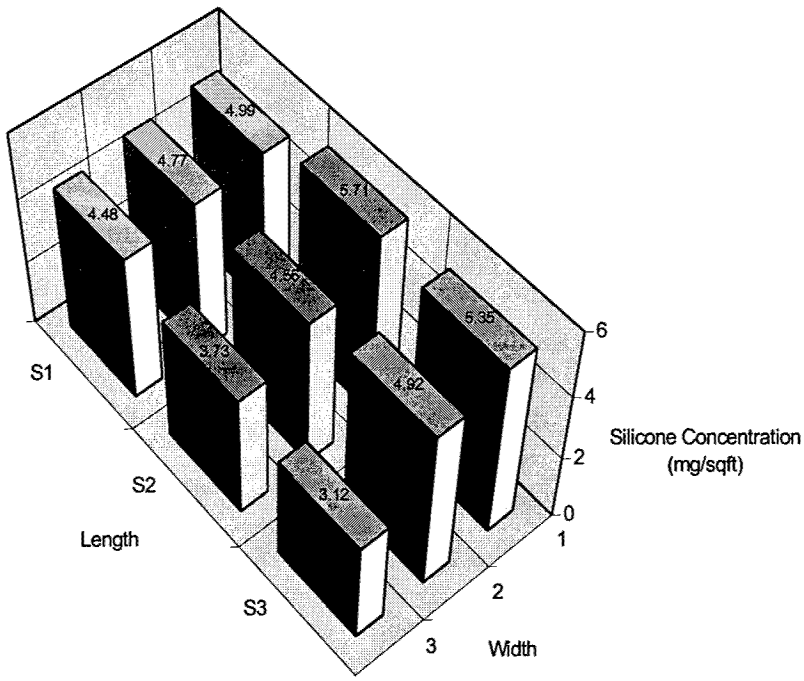


Figure 4. Steel Panel with Moderately Good Silicone Distribution Sampled at Nine Locations.

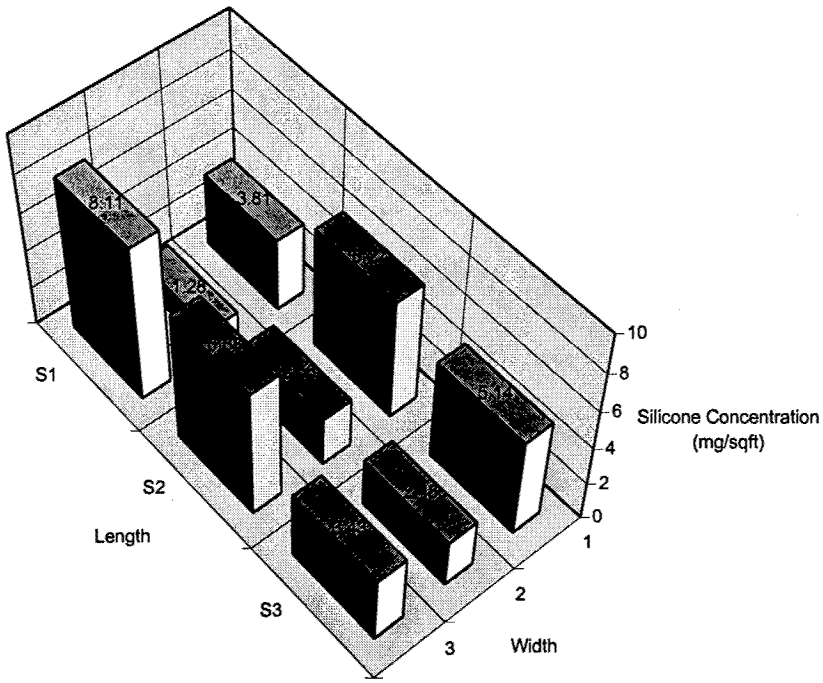


Figure 5. Steel Panel Having More Scatter in Silicone Distribution.

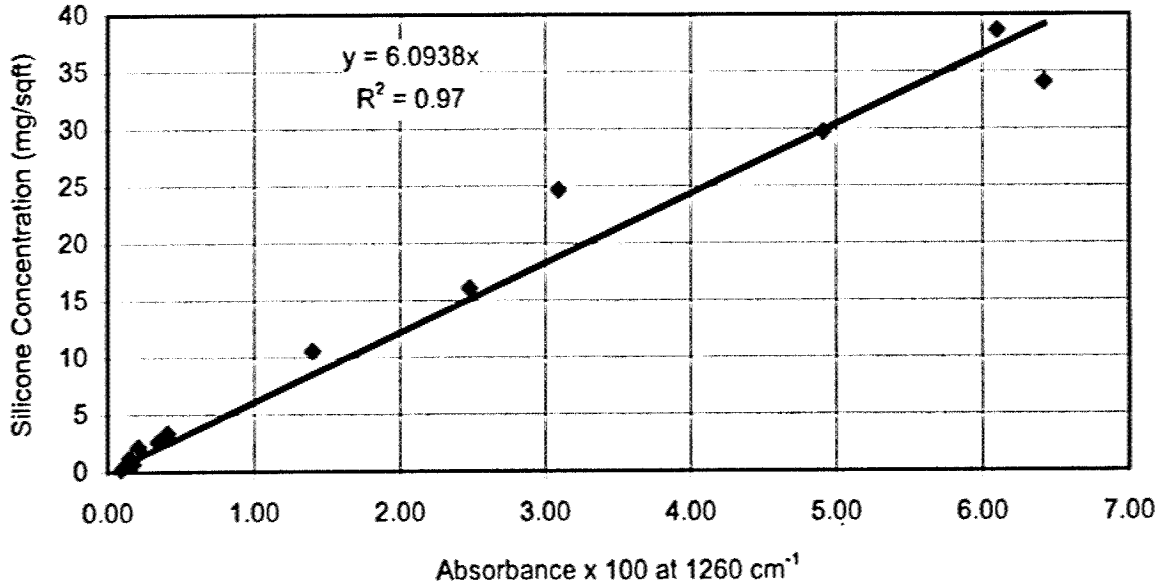


Figure 6. Standard Curve for Dow 200 Silicone Oil on Steel using SOC400 Spectrometer.

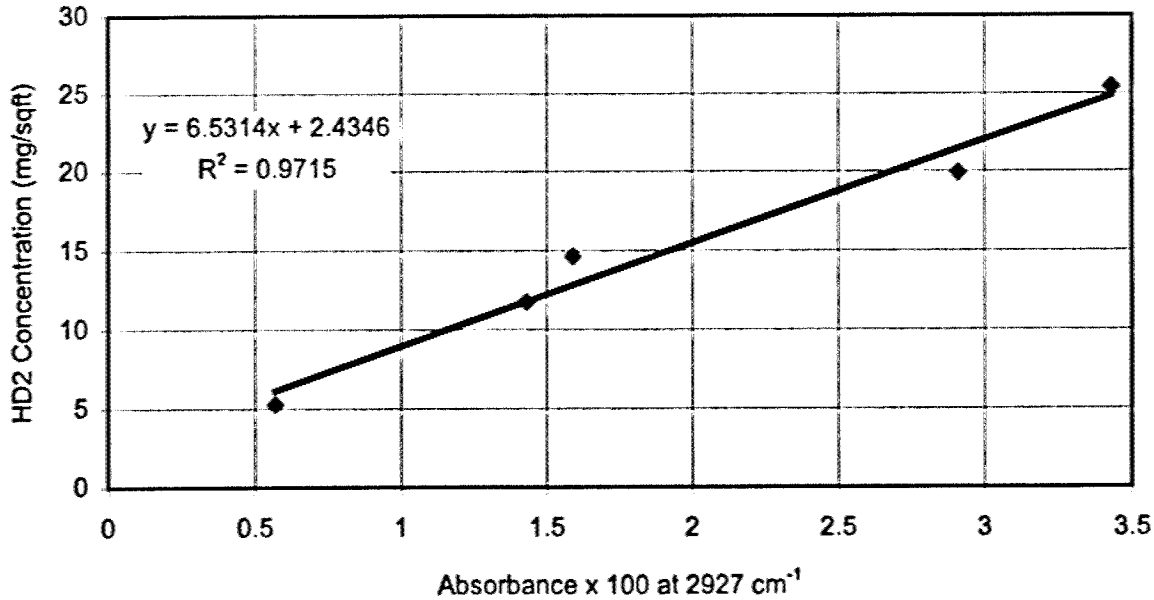


Figure 7. Standard Curve for HD2 Grease on Steel using SOC400 Spectrometer.

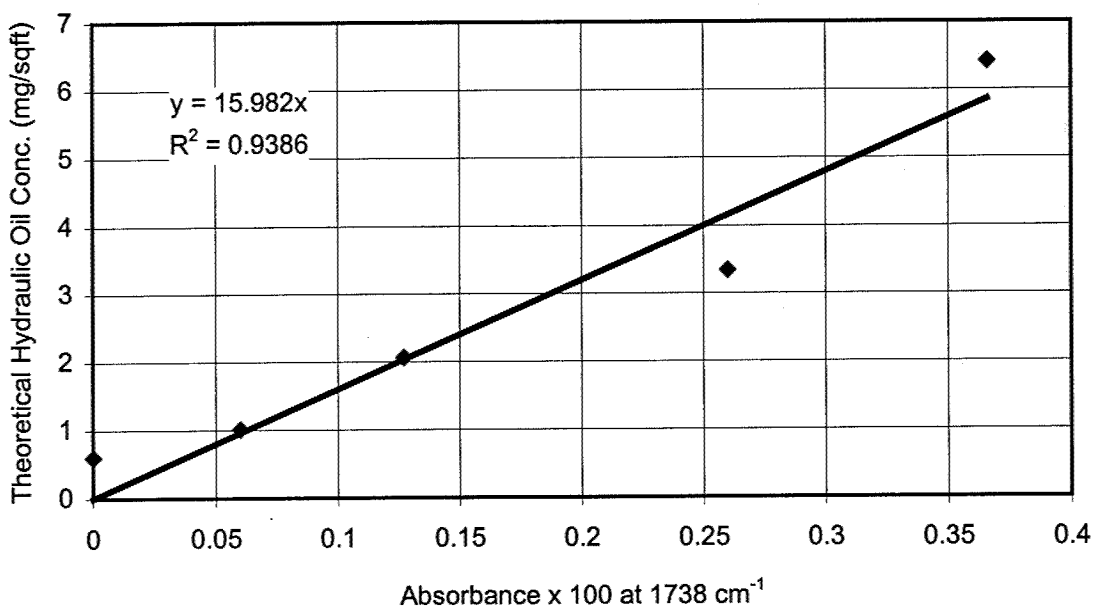


Figure 8. Standard Curve for Hydraulic Oil on Steel using SOC400 Spectrometer.

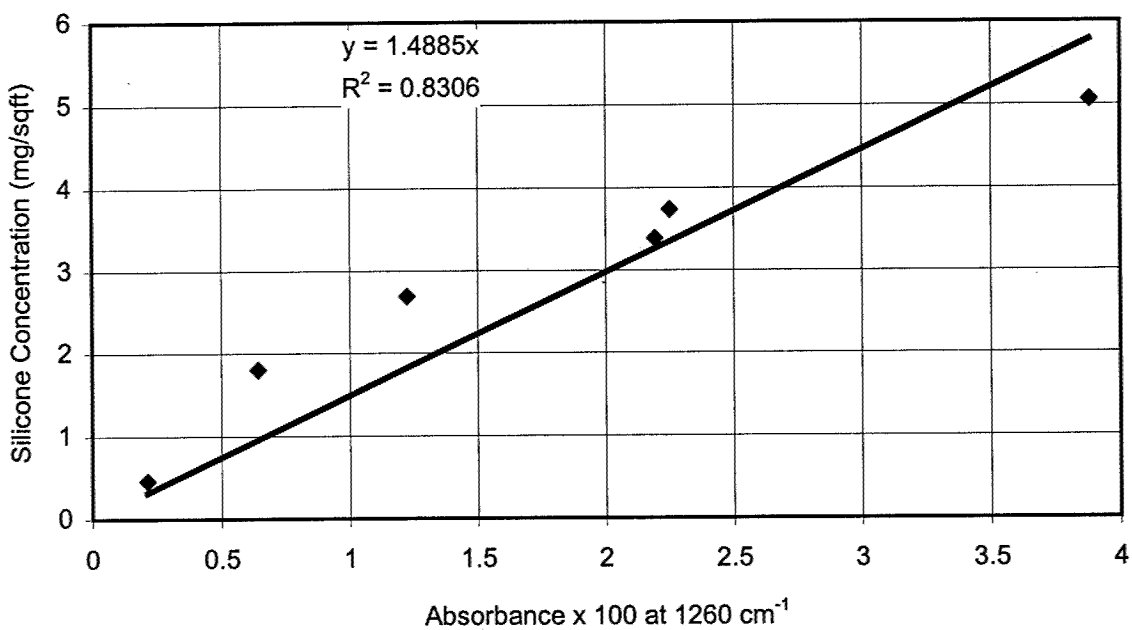


Figure 9. Standard Curve for Dow 200 Silicone Oil on Aluminum using SOC400 Spectrometer.

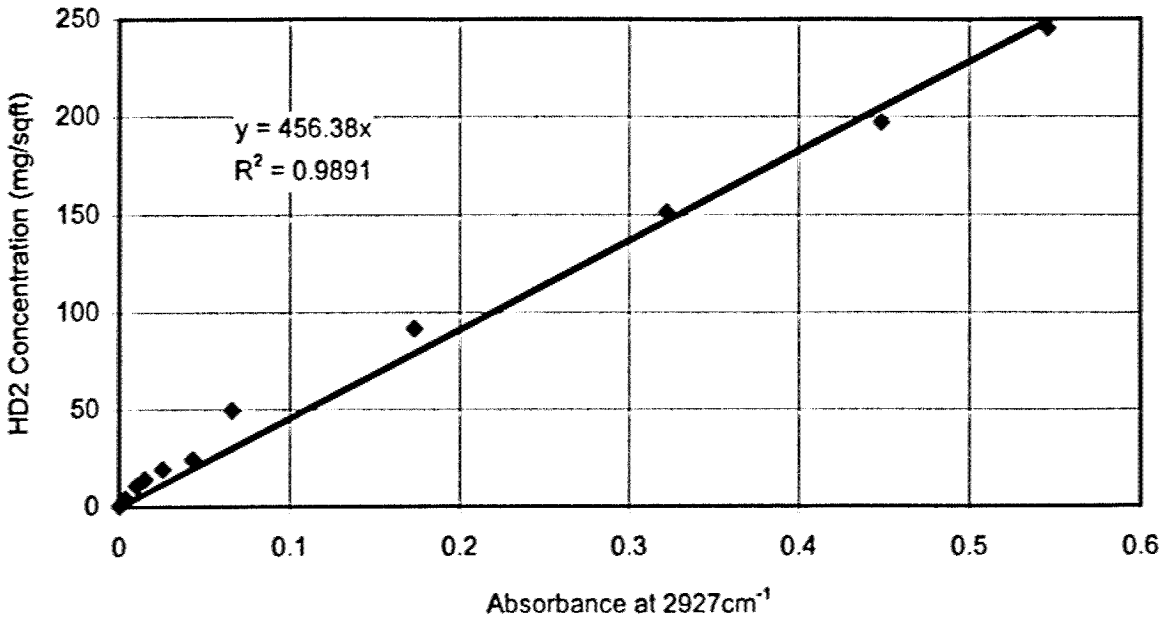


Figure 10. Standard Curve for HD2 Grease on Aluminum Using SOC400 Spectrometer.

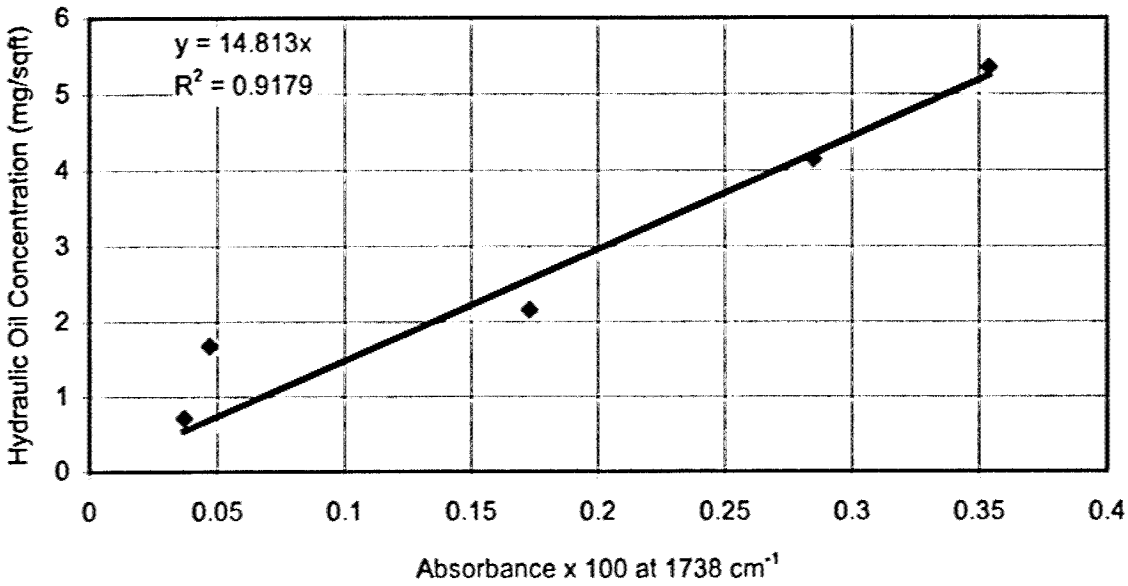


Figure 11. Standard Curve for Hydraulic Oil on Aluminum using SOC400 Spectrometer.

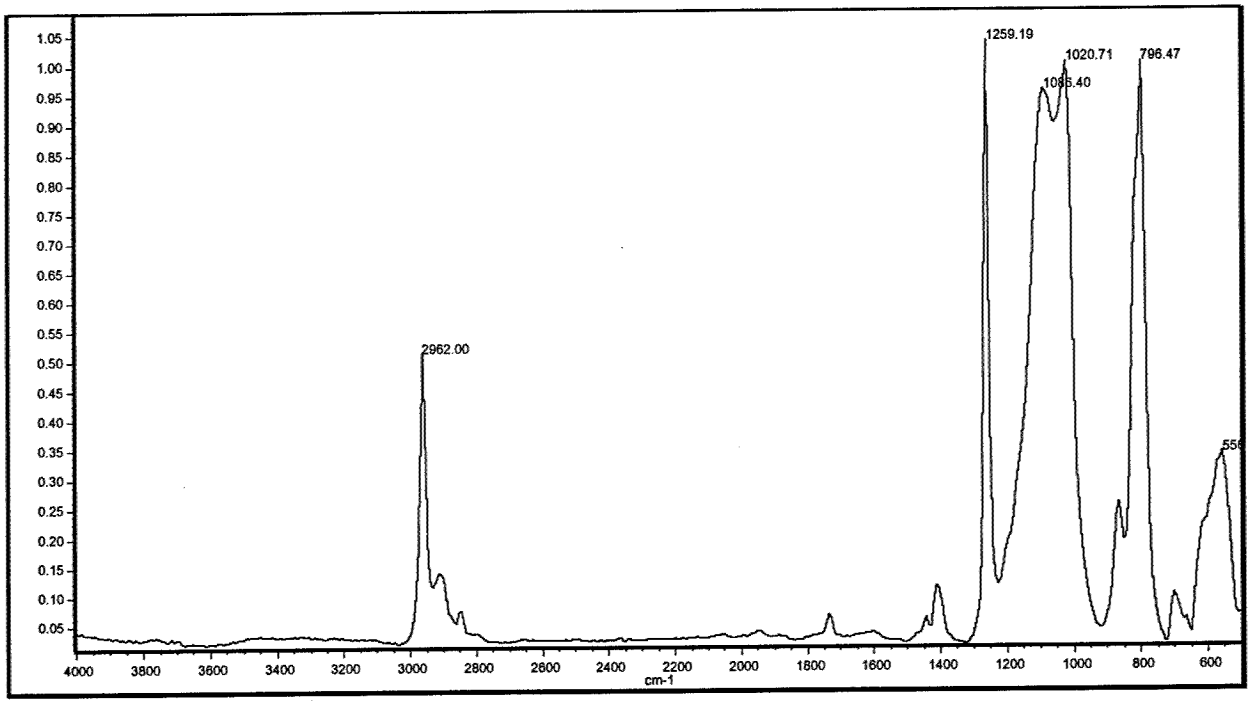


Figure 12. Infrared Spectrum of RTV Rubber on Steel Plate Acquired by SOC400 Spectrometer Showing Typical Silicone Peaks.

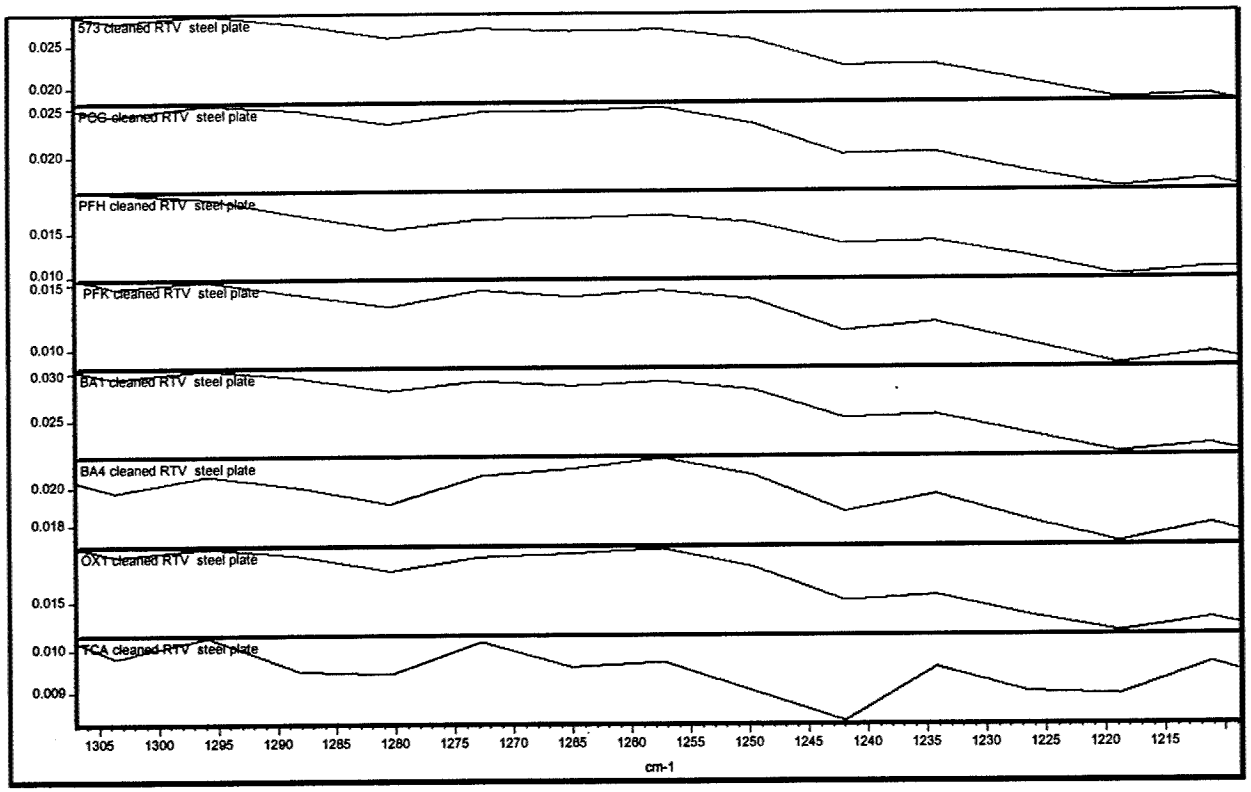


Figure 13. Infrared Spectra of the Eight Test Plates Including the 1260 cm^{-1} Region After Solvent Cleaning. No Silicone Peak is Detected at 1260 cm^{-1} in Any of the Spectra.

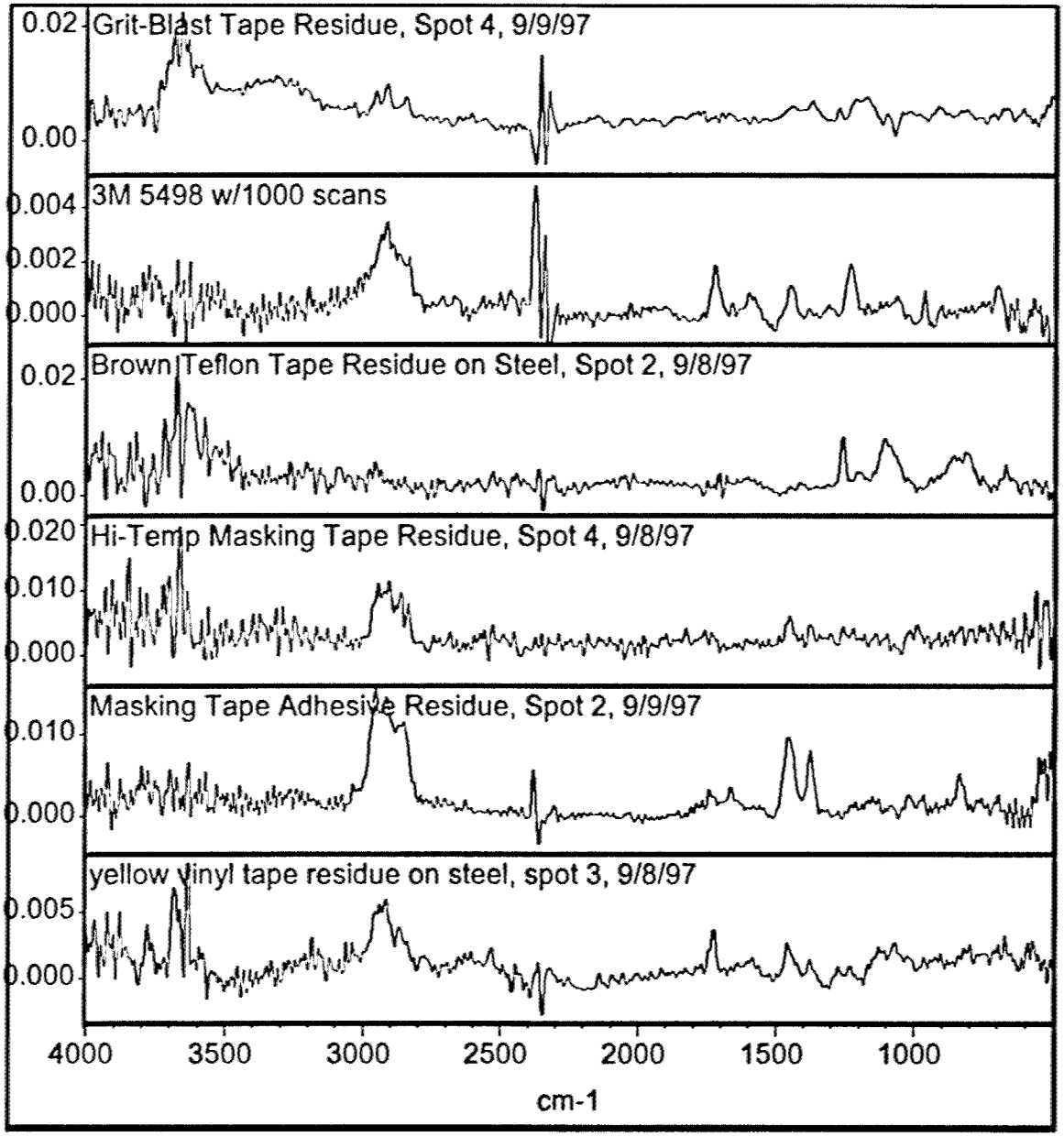


Figure 14. Examples of Infrared Spectra of Adhesive Residues from Six Manufacturing Tapes.

Table I. Silicone and HD2 Grease Analysis on Chloroform Wash of Panels and Foils Verifying Effectiveness of Sono-Tek Calibration Standard Process.

Silicone on Aluminum Foil (mg/sqft)		
Panel ID	Theoretical Silicone	Measured by Chloroform Wash
N3	105.8	103.4
TC3A	110.8	101.6
#16	102.7	99.9
Silicone on Steel Panels (mg/sqft)		
Panel ID	Theoretical Silicone	Measured by Chloroform Wash
N3	105.8	108.9
TC3A	110.8	122.0
#16	102.7	108.2
HD2 Grease on Aluminum Foil (mg/sqft)		
Foil No.	Theoretical HD2 Grease	Measured by Chloroform Wash
1	24.2	24.6
2	1.40	1.03
3	0.47	0.76

Table II. SOC400 Data on Five Steel Panels with Target of 5 Milligrams Silicone Per Square Foot.

Panel ID	Average Silicone Concentration (mg/sqft) by SOC400	Standard Deviation
D7	4.4	2.3
E8	3.6	2.1
K10	2.7	1.5
N1	2.5	1.8
T13	4.6	0.8

Table III. SOC400 Data on Five Steel Panels with Target of 0.5 Milligrams Silicone Per Square Foot.

Panel ID	Calculated Silicone Concentration (mg/sqft)
H3	0.35
H7	0.88
K9	0.33
TC13A	0.67
K2	0.34

Table IV. Manufacturing Tapes Whose Adhesives were Transferred to Steel and Aluminum Panels for Examination by Various Analytical Methods.

Tape Identification	Estimated Concentration on Steel (mg/sqft)
Yellow Vinyl Tape	3.2
3M 5498 Tape	2.6
Grit Blast Tape	2.0
Brown Teflon Tape	4.6
Masking Tape	2.6
Hi-Temp Masking Tape	3.1

Enhancing Infrared Reflectance Methods for Detection of Thin Organic Contaminant Films on Bonding Surfaces

L. H. Pearson
Thiokol Corporation
Propulsion Group
P.O. Box 707, M/S 245
Brigham City, Utah 84302

INTRODUCTION

With the elimination of solvents, such as methylchloroform, used in industry for cleaning of bonding surfaces, and their replacement with non-ozone depleting chemicals, the issue of surface cleanliness must be re-addressed. Contamination on bonding surfaces has been determined to be a primary cause for degraded bond strength with foreign hydrocarbon and silicone-based materials that are airborne or directly introduced to a surface being the most common sources of contamination. Specular and diffuse infrared (IR) reflectance methods have been extensively used for detection of foreign organic compounds on surfaces of various compositions and textures. This paper deals with methods for enhancing the sensitivity of IR reflectance methods for detection and characterization of thin absorbing films. Both diffuse and specular reflection methods are addressed for rough and smooth metal surfaces, respectively. Methods for detection of contaminant films on non-metal surfaces are also discussed. Experimental and data analysis methods having a basis in fundamental principles of light scattering and reflection are presented.

BACKGROUND

Optical spectroscopy methods which have historically been used for thin film, surface chemistry, and surface topography characterization [1,3,4,10-12], offer a class of viable nondestructive techniques for bond surface characterization. Of particular interest is the use of infrared (IR) reflection spectroscopy in characterization of organic contaminants on bonding surfaces [6-8]. Since material surfaces can be very rough the strong scattering or diffuse reflection of light must be considered in the measurement process. Reference [8] for example, shows that detection of backscattered IR light provides increased sensitivity to thin contamination films.

Organic contaminants generally have characteristic infrared absorbance spectral signatures. If a contaminant has a spectral signature, it can be detected and identified using IR reflection spectroscopy (or absorption spectroscopy) methods. This is accomplished by directing a broad band infrared light source on the surface and then evaluating the spectral content of the reflected beam. By controlling incident and detection beam angles, polarization of the incident beam, and by analyzing polarization content of the scattered beam for rough surfaces, detection of thin contaminant films can be enhanced [4,5]. Improving signal to noise ratios of reflected IR signals becomes an important issue when dealing with films that are a fraction of a wavelength thick. Bond strengths in some rocket motor components have been shown to be degraded by silicone and hydrocarbon contaminant film thicknesses that are on the order of a few hundredths of a micron. The following sections of this paper deal with methods for improving sensitivity to thin contaminant films on surfaces of various materials and textures.

SMOOTH SURFACES

Smooth in this context will be defined as smooth relative to a wavelength. More precisely, smooth is defined such that the root-mean-square average roughness (RA) value is much less than a wavelength. Rough, on the other hand, will be defined as a condition when the RA value is on the order of the wavelength or greater. For example, if the wavelength is about 3.4 microns (proximity of the carbon-hydrogen stretch absorption bands), an RA of 1.3 micro-inches (about 1/100th wavelength) would be considered smooth and a surface RA = 130 (about 1 wavelength) would be considered rough.

The approach to detection of thin organic films with IR spectroscopy is to measure a reflection (or absorption) spectrum by reflecting IR light from the surface and then determining if the characteristic signature of

the contaminant material is present in the spectrum. Figure 1, for example shows absorption spectra from reflection measurements of IR light off a metal surface with various thicknesses of a typical hydrocarbon-based grease. For very thin films, the absorption bands for the contaminant may be difficult to see and identify in the measured spectrum. The desire is to obtain a spectrum showing characteristic absorption bands for the contaminant above the background noise for contaminant films that are very thin, but can still effect bond strength. For some adhesive bonds and some contaminants, this may be quite thin (less than 0.05 microns).

A typical and effective approach to increasing sensitivity to thin absorbing films is to maximize absorption of the electric field portion of the IR wave by the film. The rate of conversion of electromagnetic energy into heat at any point in a medium is given by the Poynting theorem [4] which indicates that absorbed energy is proportional to the square of the electric field amplitude, $\langle E^2 \rangle$ (brackets imply time average). That is,

(1) $-\nabla \bullet S = \sigma \langle E^2 \rangle$

S is the Poynting vector, and $\sigma = nkf$, with n being the real part of the index of refraction, k being the imaginary part of the index of refraction, and f being the optical frequency. The implication from equation (1), then, is to increase sensitivity by maximizing $\langle E^2 \rangle$ at the material surface. This is accomplished through adjustment of the available experimental parameters such as incident angle and polarization of the incident wave. Figure 2 provides a conceptual diagram of the three electric field vector components for a field incident upon a surface. The x- and z-components (E_x and E_z) are combined as vector components to make what is conventionally called the parallel component of the electric field and the y-component (E_y) is conventionally referred to as the perpendicular component. Both are referenced with respect to the plane of incidence.

For a metal surface, the boundary conditions require that the tangential components, E_x and E_y, of the electric field vector approach zero at the surface, however, the normal component, E_z, remains large at the surface. Since the parallel component of the electric field contains E_z, it is expedient to set up the experiment to eliminate the perpendicular component which contributes very little to the ability to sense thin films at a metal surface. Also, by varying the incident angle, the strength of the electric field at the surface can be further maximized as illustrated in Figure 3 which contains a graph of $\langle E^2 \rangle$ evaluated at the metal surface versus incident angle for an air-metal interface. (These results along with other theoretical calculations presented in this paper are computed from theory found in reference 6.) Calculations are made assuming the wavelength is 3.4 microns and for an incident angle range of from 0 to 85 degrees. The wavelength, 3.4 microns, is chosen because it is near the center of the C-H stretch absorption bands for typical hydrocarbon contaminant films. At normal incidence the perpendicular and parallel components are equal since both are tangent to the surface, however, as the incident angle increases, the

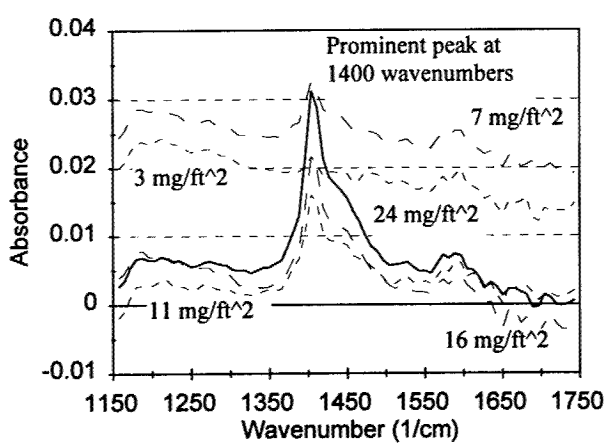


Figure 1. Infrared absorption spectra for thick and thin films of hydrocarbon films on grit blasted steel.

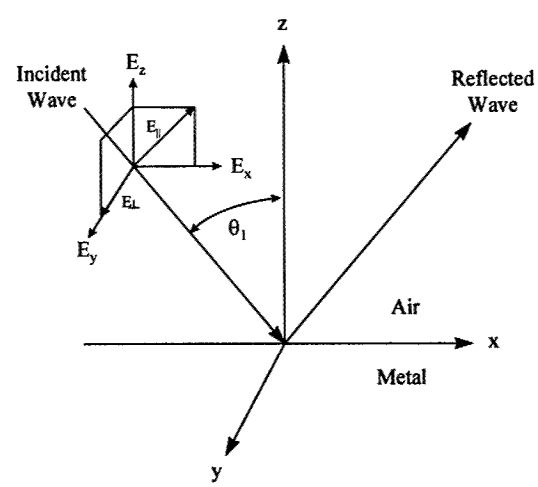


Figure 2. Schematic diagram of incident electric Field vector components.

parallel component of the electric field intensity increases substantially and reaches a maximum at a relatively wide angle. This angle can be shown to be given by:

(2) $\theta_B = \arctan(n_2/n_1)$

where θ_B is the Brewster angle, and n_1, n_2 are the indices of refraction for the two media, medium 1 being the incident medium (air). If the imaginary part of n_2 is not equal to zero as with metals and organic materials at IR frequencies, then the complex magnitude, $|n_2|$ is used in equation (2). The resultant angle, θ_B, is then referred to as the pseudo-Brewster angle. With an increase in the electric field strength at the surface, it is expected that, if a thin film is present, there will be a commensurate increase in absorbance by the film, and therefore a reduction in the reflected energy.

Figure 4 shows a graph of the relative reflectance from a smooth metal surface coated with a 0.05 micron thick film of a hydrocarbon grease. To obtain this curve, reflectance is computed for an air/contaminant/metal system, then for an air/metal system. The three layer system reflectance is then divided by the two layer system reflectance which is used as a "clean" reference. Calculations are made for a wavelength of 3.4 microns and for incident angles ranging from 0 to 85 degrees.

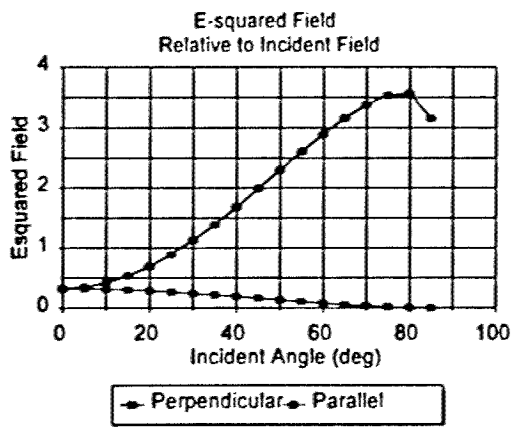


Figure 3. Time-averaged, normalized electric field intensities for perpendicular and parallel polarizations polarizations at air/metal interface for 3.4 microns.

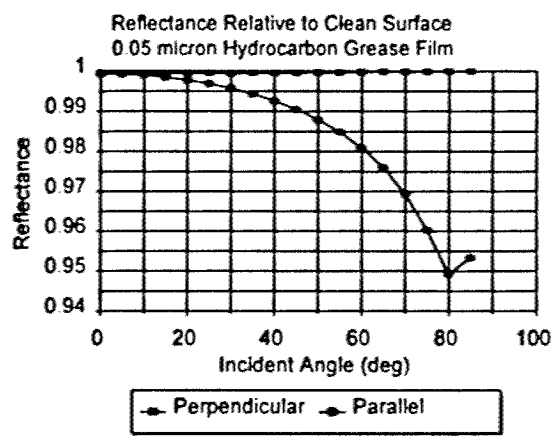


Figure 4. Reflectance from an air/hydrocarbon/ metal system (contaminated) referenced with respect to air/metal system (clean) at 3.4 microns.

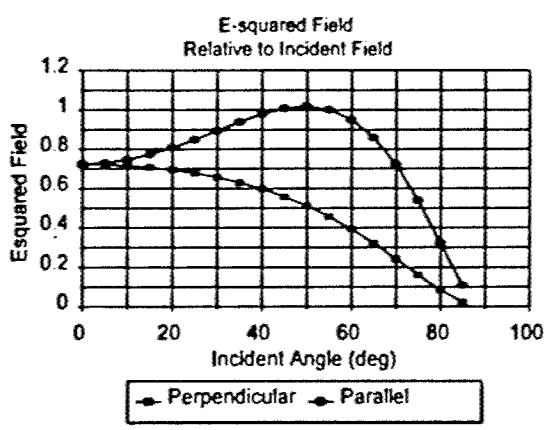


Figure 5. Time-averaged, normalized electric field intensities for perpendicular and parallel polarization at an air/dielectric interface for 3.4 microns.

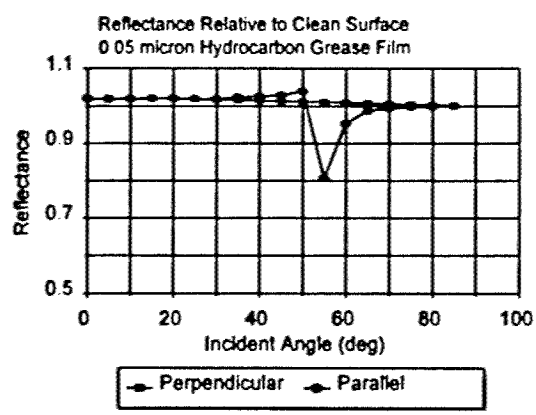


Figure 6. Reflectance from an air/hydrocarbon/ dielectric system (contaminated) referenced with respect to air/dielectric system (clean) at 3.4 microns.

It is noted from Figures 3 and 4 that lowest sensitivity to thin absorbing films is obtained at normal incidence and greatest sensitivity is achieved at the pseudo-Brewster angle which is large for metals. This is why grazing incidence methods are promoted for metal surfaces. I may not be practical, however, to make grazing incidence measurements and so a compromise may be necessary. Reference 4 suggests 45° incidence as a convenient choice.

Calculations of the electric field strength and relative reflectance curves for IR light incident upon a smooth dielectric (non-metal) surface are shown in Figures 5 and 6. These results are similar to the metal surface except that the pseudo-Brewster angle is at a smaller angle of incidence (about 55°) and the difference in the parallel and perpendicular electric field intensities is not as striking. An enhancement is noted in sensitivity to the hydrocarbon film near the pseudo-Brewster angle for parallel polarization as indicated in Figure 6. There is a tradeoff however, and that is the reflectance is very small at the pseudo-Brewster angle (see Figure 7) which will decrease the signal-to-noise ratio.

Figure 8 shows measurements of the absorption band height (signal) for the C-H stretch band at 3.4 microns for a hydrocarbon grease on an aluminum surface and Figure 9 shows the corresponding signal-to-noise ratios. (Note that absorbance is $-\log_{10}$[reflectance]). Measurements were made at a 45° incident angle and with perpendicular, parallel, and no polarization setups. These measurements corroborate theoretical predictions that parallel polarization provides the best sensitivity. Note that the absorbance measurements for no polarization and

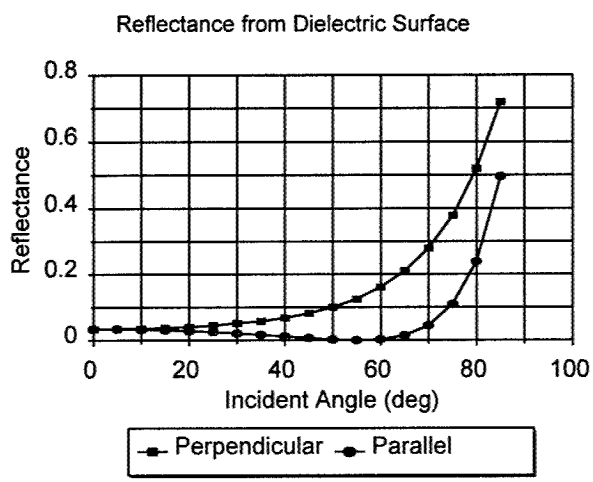


Figure 7. Reflectance of 3.4 micron IR light from an air/dielectric interface.

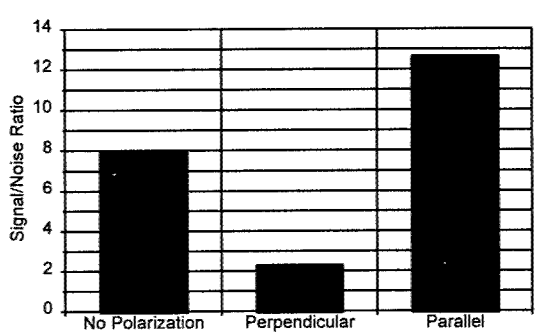


Figure 8. Measurements of the height of the C-H stretch absorption band (at 3.4 microns) for three polarization conditions: no polarization, perpendicular, and parallel.

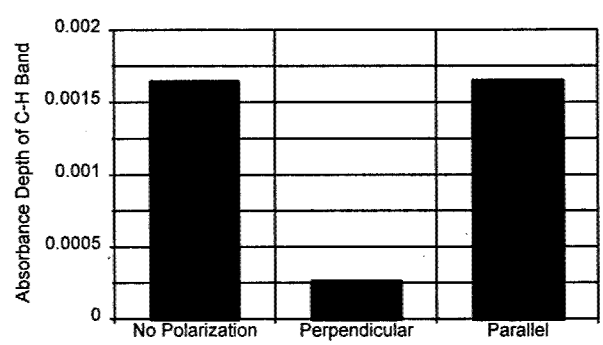


Figure 9. Measurements of the signal-to-noise ratio (absorbance/noise) for the same measurements as in Figure 8.

for parallel polarization are about the same, but the signal-to-noise ratio is nearly a factor of 2 greater for the parallel polarization measurement. This is because the perpendicular polarization component of the unpolarized beam does not contribute to the signal, but does contribute to noise in the signal.

ARBITRARY SURFACES WITH ORGANIC FILMS

The scattering properties of any object or surface can be described by a 4 x 4 scattering matrix referred to as the Mueller matrix [2,9]. An incident beam can be described by a four component vector called a Stokes vector. Mathematically, the Stokes vector for the source is multiplied by the material Mueller matrix to determine the properties of the scattered light, represented by another Stokes vector. The first element in the Stokes vector is the total intensity which, generally, is the only quantity that is or can be measured directly. By making use of polarizers in the incident beam and the detection beam optics trains, the measured intensity can be made to be mathematically dependent on different combinations of the Mueller matrix elements. All sixteen Mueller matrix elements can be determined from at least sixteen independent intensity measurements for given incident angle, detection angle, and wavelength. The independent intensity measurements are obtained from combinations of unpolarized (U), vertical (V), horizontal (H), +45° (P), -45° (M), right circular (R), and left circular (L) polarization in the source and detector optics trains. Mueller matrix elements are computed for given incident and detection angles, and wavelength. The mathematical process is illustrated in the Appendix. (For a detailed description of Stokes-Mueller mathematics, see references 2 and 9.)

Calculation of the Mueller matrix element values from a set of independent measurements, in practice, may not be necessary. However, the Mueller algebra can be used to determine the set of independent measurements that are needed to characterize a surface. After this set of measurements has been determined, all that may be necessary is to measure the independent intensities as a function of incident and detection angles and then use these values to determine the optimum optical setup for sensing thin films on a given material surface. The laboratory experimental setup shown in Figure 10 was constructed to perform measurements as described above.

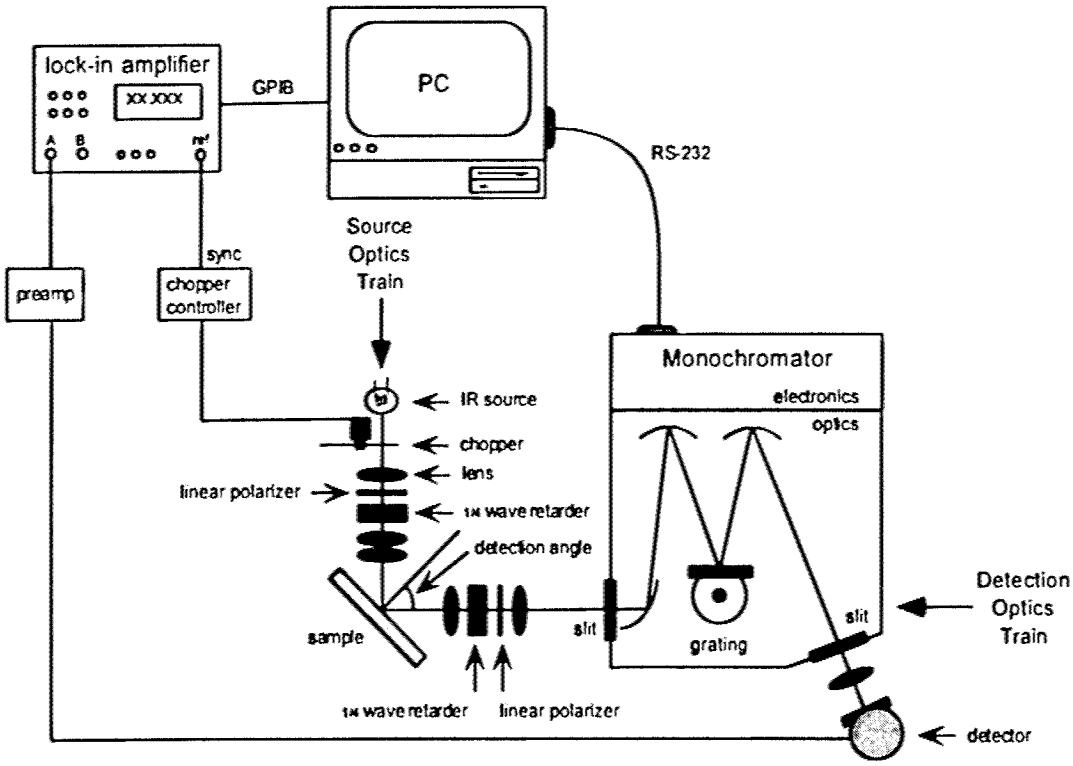
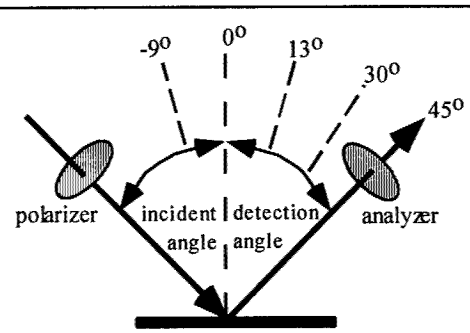


Figure 10. Experimental setup for making polarization and detection angle dependent measurements.

Figure 11 shows a test matrix that was designed for evaluating six surface types (grit blasted steel, grit blasted aluminum, machined carbon phenolic, machined glass phenolic, polished steel, and plastic coated steel) with one contamination type (hydrocarbon-based grease). Sixteen independent measurements are identified as determined by Mueller algebra[13], and four additional measurements are included for comparative information. The procedure used to make each measurement is described in Figure 12.

A summary of results for the metal and plastic coated steel samples is shown in Figures 13, 14, and 15. These figures show the signal and signal/noise ratio values for each material for the polarization combination measurements which gave the largest signals and the largest signal/noise ratios for the 0.3 μm thick grease film on each respective material surface. (The signal is defined as the depth of the C-H stretch absorption band in reflectance units.) It is noted in Figure 13 that the U-U polarization combination never provides the largest signal. Largest signals occur typically for detection angles at either 45 degrees (specular reflection) or at the largest backscatter angle (0 or -9 degrees). As the detection angle moves from the specular direction towards the backscatter direction, most polarization combinations show a reduction in the signal followed by a continual

Contaminant: Common hydrocarbon-basedgrease
Wavelength range: 3.1 - 3.8 mm (31 pts)
Incident angle: Fixed at 45 deg
Detection angles: -9, 0, +13, +30, +45 deg
Substrates:
grit blasted D6AC steel
grit blasted 7075 aluminum
machined carbon phenolic
machined glass phenolic
polished D6AC steel
Sermetel coated steel



Independent polarization combinations determined from Mueller algebra:
HH, HV, VH, VV, HP, VM, MV, MM, PP, VR, RV, PR, RP, ML, LR, RL, RR
where
H = horizontal, V = vertical, P = +45, M = -45, R = right circular, L = left circular
For comparison, some additional measurements were made:
UU, UV, VU, LL

Figure 11. Test matrix for polarization and detection angle dependent measurements.

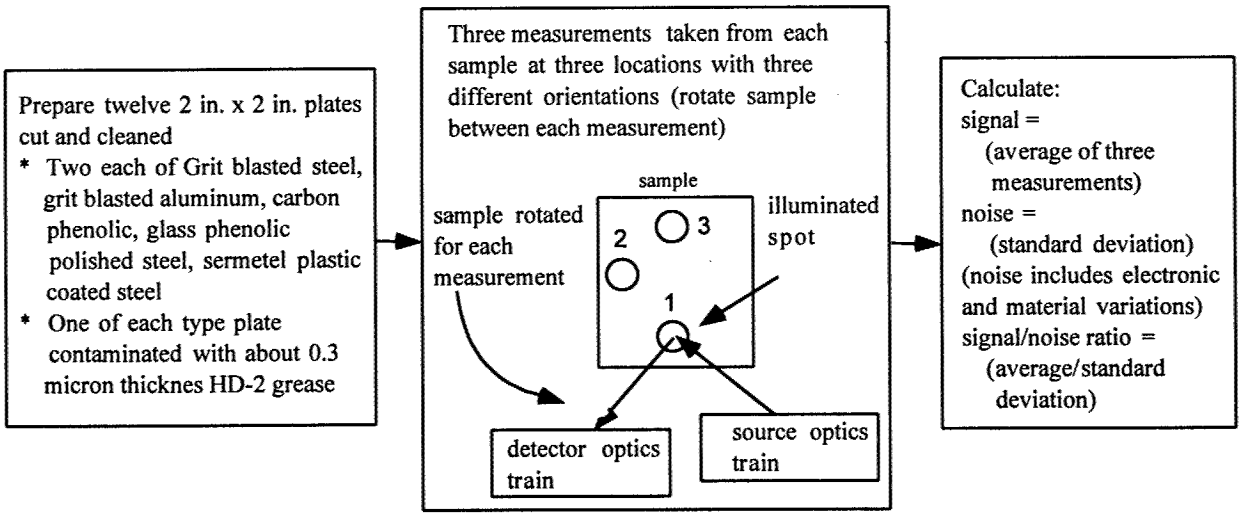


Figure 12. Procedure for Polarization and Detection Angle Dependent Measurements.

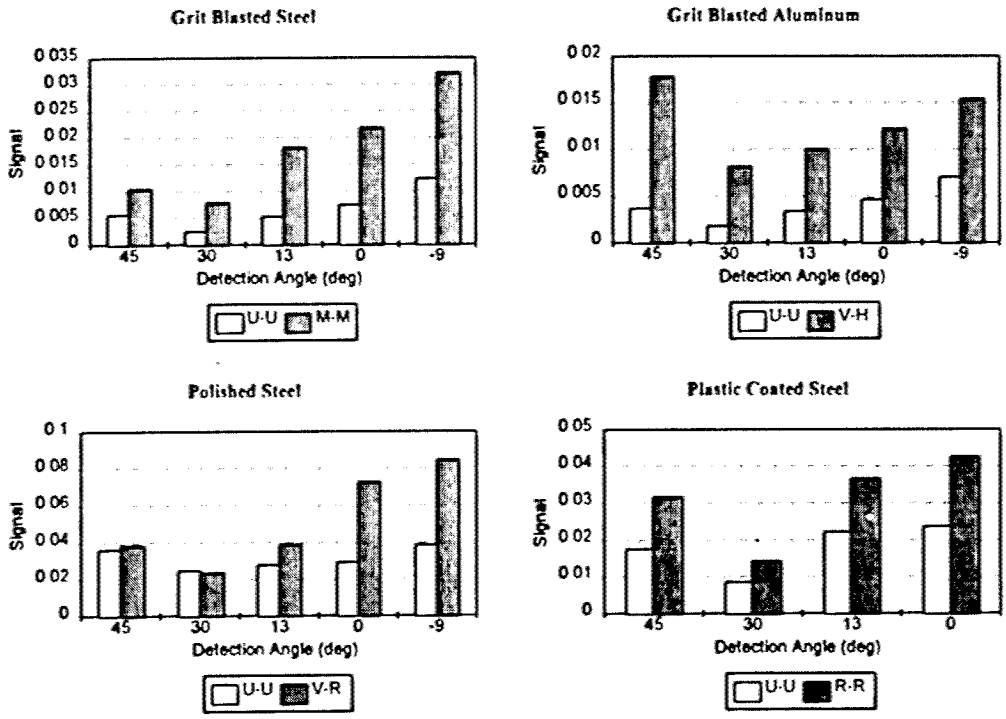


Figure 13. Graphical Summary of Results for Measurement with Greatest Signal Compared with Unpolarized (U-U) Measurement.

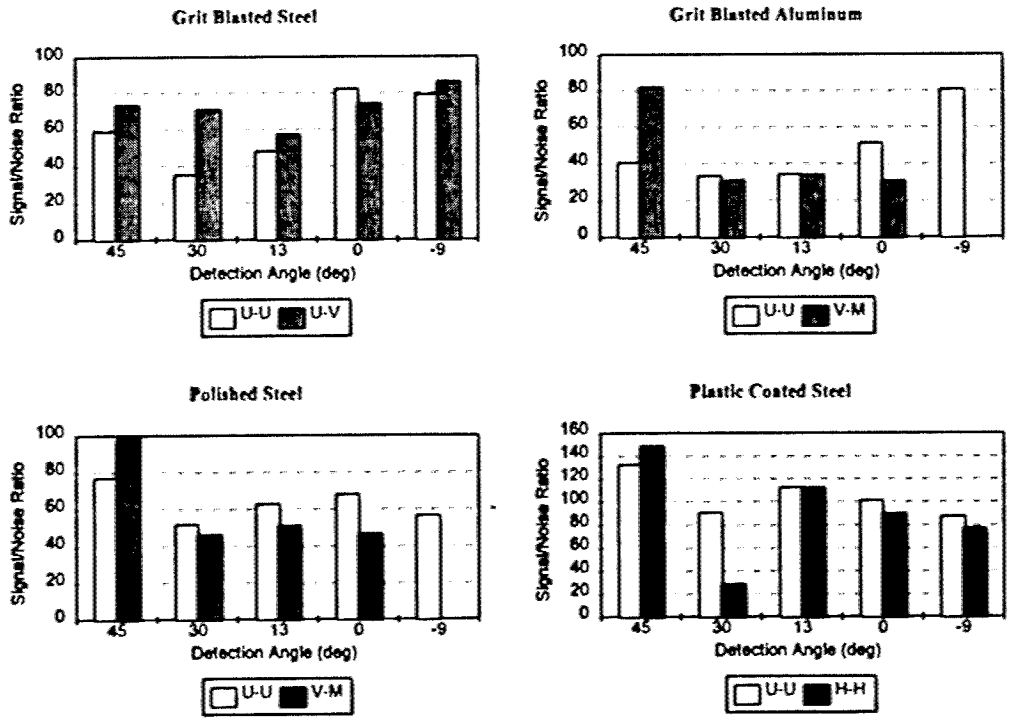


Figure 14. Graphical Summary of Results for Measurement with Greatest Signal-to-Noise Ratio Compared with Unpolarized (U-U) Measurement.

Material	Polarization Combination Largest Signal	Detection Angle	Polarization Combination Largest Signal/Noise	Detection Angle
Grit Blasted Steel	M-M	-9	U-V	-9
Grit Blasted Aluminum	V-H	45	V-M	45
Polished Steel	V-R	-9	V-M	45
Plastic Coated Steel	R-R	-9	H-H	45
Machined Carbon Phenolic	-	-	U-V	45
Machined Glass Phenolic	-	-	V-R	45

Figure 15. Summary of Results Showing Polarization Combinations and Respective Detection Angles for Obtaining Largest Signals and Signal/Noise Ratios

increase. The same apparent trend seems to show up in the signal/noise ratio measurements in Figure 14, although not as striking except with the grit blasted aluminum and polished steel. The unpolarized light measurements (U-U) show a significant enhancement in both signal and signal/noise ratio for the grit blasted metals in the backscatter directions. Figure 15 provides a tabular summary of most sensitive experimental settings for each material.

It is noted that vertical polarization (V) is found in either the incident polarizer or the detection analyzer position for the most sensitive measurements of almost all of the materials tested. This result is not surprising because it was shown above that sensitivity to thin films on smooth surfaces is proportional to the electric field strength at the surface and that the vertical (same as parallel in previous section) component of the electric field provides the greatest possible field strength at the surface particularly if the surface material is a metal.

CONCLUSIONS

Greatest sensitivity to absorbing films on smooth materials is obtained by making measurements at wide incident angles and near the pseudo-Brewster. Theory, corroborated by experimental results, indicates that parallel polarization is to be preferred over perpendicular or no polarization conditions. Normal incidence is the least sensitive setup for detecting thin absorbing films.

By introducing polarizers into both the source and detection optics trains, it is shown that increased sensitivity to thin hydrocarbon films on a variety of substrates can be achieved. Maximum sensitivity to contamination on the rough metal surfaces (grit blasted steel and aluminum) for 45° incidence and detection angles was achieved by using polarizers that are 90° rotated with respect to each other. For smooth materials (polished steel and sermetel plastic coated steel), circular polarization was important, and for the machined carbon and glass phenolics, the V-V combination was common to both materials.

REFERENCES

1. Anderson, W. J., and Hansen, W. N., "Reflection Spectroscopy Analysis of Surfaces and Thin films," SPIE Vol. 276, Optical Characterization Techniques for Semiconductor Technology, 1981, p. 214.
2. Bickel, W. S., and Bailey, W. M., "Stokes Vectors, Mueller Matrices, and Polarized Scattered Light," Am. J. Phys., Vol. 53, No. 5, pp. 468-478, May 1985.
3. Gunde, M. K., "Optical Effects in IR Spectroscopy: Thickness-Dependent Positions of Absorbance Lines in Spectra of Thin Films," Applied Spectroscopy, 46(2):365, 1992.
4. Hansen, W. N., "Reflection Spectroscopy of Optical coatings," J. Opt. Soc. Am., 69(2):264, 1979.
5. Haugland, S. M., Bahar, E., and Carrieri, A. H., "Identification of Contaminant Coatings Over Rough Surfaces Using Polarized Infrared Scattering," Applied Optics, 31(19):3847, 1992.
6. Pearson, L. H., "IR Spectroscopy for Bonding Surface Contamination Characterization," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 9, Edited by D. O. Thompson and D. E. Chimenti, Plenum Press, New York, 1990, p. 2017.

7. Pearson, L. H., "Diffuse Reflectance IR Spectroscopy for Bonding Surface Contamination Characterization," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 10, Edited by D. O. Thompson and D. E. Chimenti, Plenum Press, New York, 1991, p. 581.
8. Pearson, L. H., "Bond Surface Contamination Imaging Using an AOTF Spectrometer," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 12, Edited by D. O. Thompson and D. E. Chimenti, Plenum Press, New York, 1993, p. 1619.
9. Schiff, T. F., Stover, J. C., Swimley, B. D., and Bjork, D. R., "Mueller Matrix Measurements of Scattered Light," Proc. SPIE Vol. 1753-34, July 1992.
10. Stover, J. C., "Roughness Characterization of Smooth Machines Surfaces by Light Scattering," Applied Optics, 14(8):1796, 1975.
11. Stover, J. C., and Gillespie, C. H., "Calculation of Surface Statistics from Light Scatter," Optical Engineering, 23(4):406, 1984.
12. Wang, J. H., "A Versatile Analytical Method of Identifying Adhesive on Stamps by Specular-Reflectance Fourier Transform Infrared Spectroscopy," Applied Spectroscopy, 44(3):447, 1990.

APPENDIX. Stokes/Mueller Mathematics for Characterizing a Scatterer.

In General:

$S_s = M_s S_i$ Where $M_s = \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix}$ is the general scattering matrix and $S_s = \begin{bmatrix} |E_v|^2 + |E_h|^2 \\ |E_v|^2 - |E_h|^2 \\ 2\,|E_v|\,|E_h|\cos(\delta) \\ 2\,|E_v|\,|E_h|\sin(\delta) \end{bmatrix}$

is the general scattered Stokes vector. E_v is the vertical component of the electric field, E_h is the horizontal component of the electric field, δ is the phase difference between the two field components, and $M_{i,j}$ are the Mueller matrix elements. Mueller matrices for various polarizers which operate on incident and detected beams are:

Horizontal

$$M_H = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Vertical

$$M_V = \begin{bmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

+45 wrt Horizontal

$$M_P = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

-45 wrt Horizontal

$$M_M = \begin{bmatrix} 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Right Circular

$$M_R = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \end{bmatrix}$$

Left Circular

$$M_L = \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix}$$

Stokes Vectors for incident beams of various polarizations are:

Unpolarized

$$S_U = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Horizontal

$$S_H = \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$$

Vertical

$$S_V = \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix}$$

+45*

$$S_P = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix}$$

-45*

$$S_M = \begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix}$$

Right Circular

$$S_R = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Left Circular

$$S_L = \begin{bmatrix} 1 \\ 0 \\ 0 \\ -1 \end{bmatrix}$$

* Measured wrt horizontal

The following example shows how four of the Mueller matrix elements can be determined. The following measurements are needed:

Case 1. Incident beam horizontally polarized; detected beam horizontally analyzed

$$S_{HH} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} M_{11}+M_{21}+M_{12}+M_{22} \\ M_{11}+M_{21}+M_{12}+M_{22} \\ 0 \\ 0 \end{bmatrix}$$

Case 2. Incident beam horizontally polarized; detected beam vertically analyzed

$$S_{HV} = \begin{bmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} M_{11}-M_{21}+M_{12}-M_{22} \\ -M_{11}+M_{21}-M_{12}+M_{22} \\ 0 \\ 0 \end{bmatrix}$$

Case 3. Incident beam vertically polarized; detected beam horizontally analyzed

$$S_{VH} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} M_{11}+M_{21}-M_{12}-M_{22} \\ M_{11}+M_{21}-M_{12}-M_{22} \\ 0 \\ 0 \end{bmatrix}$$

Case 4. Incident beam vertically polarized; detected beam vertically analyzed

$$S_{VV} = \begin{bmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} M_{11}-M_{21}-M_{12}+M_{22} \\ -M_{11}+M_{21}+M_{12}-M_{22} \\ 0 \\ 0 \end{bmatrix}$$

Since intensity is the only quantity that is directly measured, only the first element in each S-vector is used to calculate the Mueller matrix elements.

Incident Horizontal

$I_{HH} = M_{11}+M_{21}+M_{12}+M_{22}$

$I_{HV} = M_{11}-M_{21}+M_{12}-M_{22}$

Incident Vertical

$I_{VH} = M_{11}+M_{21}-M_{12}-M_{22}$

$I_{VV} = M_{11}-M_{21}-M_{12}+M_{22}$

These four equations can be written in matrix form and then solved for the unknown Mueller matrix elements:

$$\begin{bmatrix} I_{HH} \\ I_{HV} \\ I_{VH} \\ I_{VV} \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix} \cdot \begin{bmatrix} M_{11} \\ M_{12} \\ M_{21} \\ M_{22} \end{bmatrix} \quad \text{or} \quad \begin{bmatrix} M_{11} \\ M_{12} \\ M_{21} \\ M_{22} \end{bmatrix} = \frac{1}{4} \cdot \begin{bmatrix} I_{HH}+I_{HV}+I_{VH}+I_{VV} \\ I_{HH}+I_{HV}-I_{VH}-I_{VV} \\ I_{HH}-I_{HV}+I_{VH}-I_{VV} \\ I_{HH}-I_{HV}-I_{VH}+I_{VV} \end{bmatrix}$$

For further detail on measurement methods for determining Mueller matrix elements, see reference 2.

Cleaning Solvents Based On *n*-Propyl Bromide Technology

Ronald L. Shubkin, Ph.D., and Suae-chen Chang, Ph.D.
Albemarle Corporation
8000 GSRI Avenue
Baton Rouge, LA 70820

Introduction

The cleaning of complex parts to exacting specifications has become a major consideration in the manufacture of a wide variety of machines, instruments, appliances and other equipment. The introduction of chlorinated solvents provided manufacturers and fabricators a convenient and economical way to clean a host of difficult soils from strategic parts. Efficient cleaning, rapid drying, low flammability, residue free parts and relatively low solvent costs all contributed to the popularity of chlorocarbon fluids. However, many chlorine containing solvents have now been banned or restricted because of environmental and/or health considerations. With the mandated elimination of the most popular cleaning solvents, many manufacturers switched to aqueous or semi-aqueous cleaning systems. While these proved to be viable solutions in many applications, they were not suitable for all situations. In the search to find more appropriate alternatives, a wide variety of new solvents were developed[1]. Many of the new solvent cleaners do excellent jobs, but still suffer from one or more deficiencies relative to the overall cost/performance of the chlorinated materials they replaced. Even some of the newer solvents, such as some hydrochloroflouorocarbons (HCFCs), have been shown to have environmental problems and have been banned from usage in cleaning applications or are scheduled for phase-out. In other cases, the newly introduced solvents meet the environmental and toxicological requirements, but do not meet the performance standards. The need in specialized applications for a high-performance cleaning agent that could be used in a safe and efficient manner led to the development of cleaning solvents based on *normal*-propyl bromide (nPB).

normal-Propyl Bromide -- An Attractive Alternative

A new solvent/cleaner based on *normal*-propyl bromide (nPB) was developed to meet the needs of those who require the cleaning efficiency of the chlorinated solvents, but who must meet the strict environmental standards for a replacement solvent.[2] The new solvent/cleaner does not suffer from many of the short-comings of other alternative solvents that have been offered to the market. nPB is an effective cleaning agent. It is safe to use under the proper conditions, has a low ODP and a low GWP, and it is not regulated under most environmental and worker safety rules. It is compatible with metals, has a low tendency to cause corrosion and may be used in most current vapor degreasing equipment. It is easily recycled and is moderately priced.

Physical Properties

Table I compares the physical properties of nPB to two hydrochlorocarbons and two

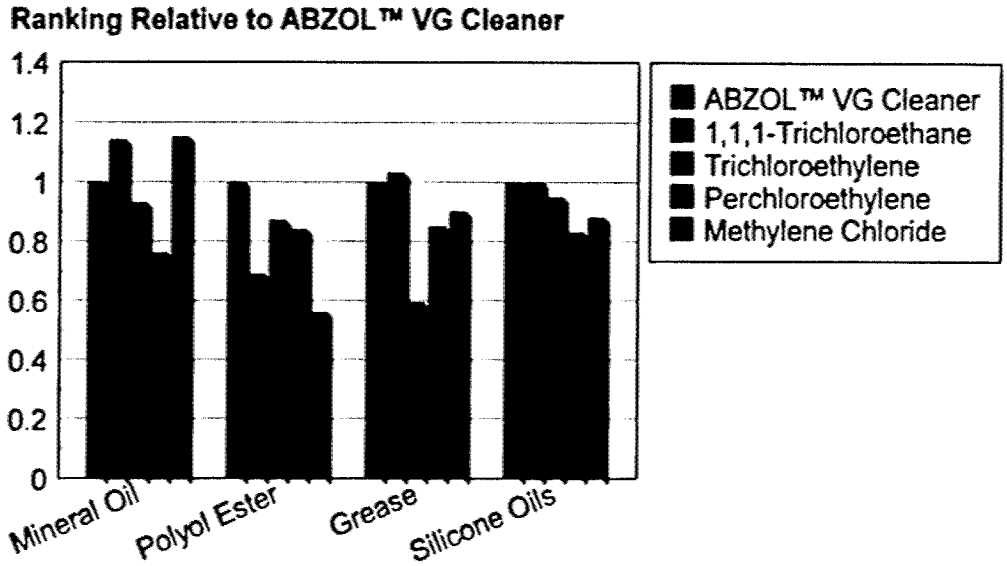
hydrochlorofluorocarbons. HCFC-141b is CH3-CCl_2F, and HCFC-225 is a mixture of the two isomers CF_3-CF_2-$CHCl_2$ and CF_2Cl-CF_2-CHClF. The physical properties of the nPB are similar to all four of these solvents, but particularly so to TCA.

TABLE I
Physical Property Comparisons

	n-Propyl Bromide	1,1,1-TCA	Trichloro-ethylene	HCFC-141-b	HCFC-225
Boiling Pt, °C	71	74	87	32	54
Sp. Grav., 25°C	1.35	1.32	1.46	1.24	1.55
Visc., 25°C, cP	0.49	0.79	0.54	0.43	0.59
Vapor Pressure, 20° C, torr	110.8	100	57.8	593	285
Specific Heat, 25°C	0.27	0.25	0.22	--	0.25
Latent Heat of Vap., cal/gm	58.8	57.5	57.2	52.3	33
Sol. in Water, gm/100 gms water	0.24	0.07	0.11	0.18	0.033
Sol. of Water, gms/100 gms solv.	0.05	0.05	0.03	0.042	0.03
Surface Tension, 25°C, dynes/cm	25.9	25.6	26.4	19.3	16.2
Flash Point, TCC, °C	None	None	None	None	None
Flammability Limits, volume %	4-7.8	7-13	8-10.5	7.6-17.7	None

Cleaning Efficiency

The cleaning efficiency of the chlorinated solvents is well known and well documented. The cleaning efficiency is related to the solubility of various soils in the solvent. Graph illustrates the comparability of the solvency characteristics of a nPB cleaning agent (ABZOL® VG Cleaner) with that of various popular chlorocarbon and hydrochlorocarbon cleaners.



Graph 1. Relative cleaning performance of a fully formulated cleaning solvent based on nPB and some of the common chlorinated solvents. Test was conducted at ambient temperature.

The cleaning power of nPB based cleaners is clearly equivalent to the popular chlorinated solvents that have been banned or restricted. Comparisons to the new alternative solvents that have been introduced to replace the chlorinated materials are even more dramatic. It is instructive to first compare the relative solvency power of nPB to some of the new solvents that are being offered in the cleaning market.

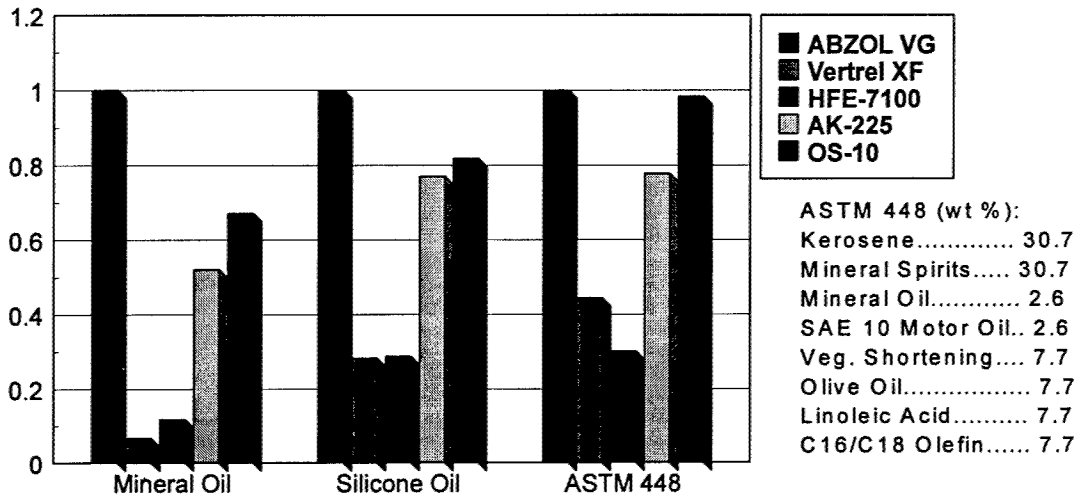
Table III compares the Kauri Butanol Number of nPB to decafluoropentane (DuPont Vertrel™ XF), methyl perfluorobutyl ether (3M HFE 7100), dichloropentafluoropropane (Asahi Glass AK-225) and hexamethyldisiloxane (Dow Corning OS-10). By this one measure, superior performance is expected from the cleaning formulations based on nPB.

TABLE III
Comparisons of Solvency Characteristics

Solvent	Kauri Butanol Number
normal-Propyl Bromide	125
Decafluoropentane	9
Methyl perfluorobutyl ether	10
Dichloropentafluoropropane	31
Hexamethyldisiloxane	17

Of course, the Kauri Butanol Number is only an indication of cleaning performance. Graph 2 shows the results of experiments that were conducted in the same manner as those carried out to compare nPB with the chlorinated solvents. For these experiments, performance was compared for the removal of mineral oil, silicone oil and a complex mixture of common soils that simulates the ASTM 448 Standard Soil (some minor substitutions were made). These experimental results indicate clearly superior cleaning performance for nPB.

Ranking relative to ABZOL™ VG Cleaner

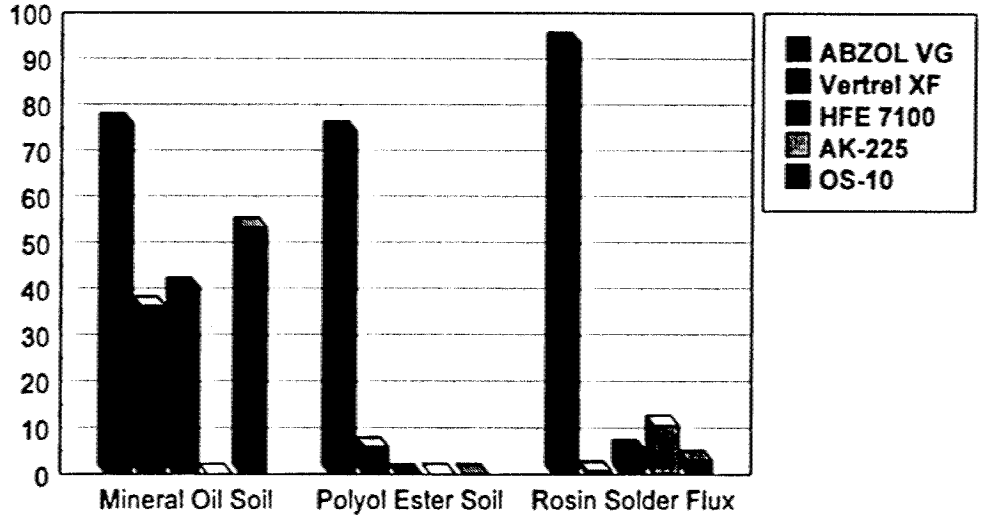


Graph 2. Relative cleaning performance of a fully formulated cleaning solvent based on nPB and a selection of other new alternative solvents. Tests were conducted at ambient temperature.

Cold cleaning is suitable for a variety of cleaning needs, but the very difficult soils usually require more severe conditions. For this reason, difficult soils are often removed using vapor degreasing equipment. In this equipment, the parts may be cleaned in the hot vapors of the solvent. For the most difficult soils, especially those that have been "baked on", the part to be cleaned is often immersed in the boiling solvent. Because cold cleaning performance does not always reflect performance at higher temperatures, and new cleaning test was designed.

Steel coupons (C1010) were weighed and coated with the selected soil (ca. 0.1 gms). The coupons were placed in an oven at 250°C for one hour, cooled and reweighed. The coupons were then immersed in boiling solvent for five minutes, dried and reweighed. Each trial was conducted in triplicate. The weight percent of soil removed for each coupon was recorded and averaged for the three trials. For this test, five formulated solvents were evaluated. The solvents were ABZOL VG Cleaner, Vertrel XF, HFE-7100, AK-225 and OS-10. The soils chosen were mineral oil, a polyol ester and a rosin based solder flux. The results show that the ABZOL VG Cleaner removes the baked-on mineral oil much more efficiently than the others. The baked-on polyol ester and the rosin-based solder flux remain nearly untouched by the other solvents, but is mostly removed after five minutes in boiling ABZOL® VG Cleaner. The results are shown in Graph 3.

Weight Percent of Soil Removed



Graph 3. Cleaning performance of a fully formulated solvent based on nPB versus three hydrofluorocarbon and one siloxane solvents. The soils were baked on metal coupons that were then cleaned in boiling solvent.

Cleaning of Electronics Components

The electronics industry faces some cleaning challenges not found in other types of cleaning applications. In particular, it is of utmost importance that ionic residues remaining on integrated circuit boards after soldering operations be removed to very low levels. Cleaners based on nPB and formulated for vapor degreasing have proven to be surprisingly good at the removal of ionics. However, a new formulation designed specifically for the electronics industry has recently been introduced. ABZOL™ EG Cleaner is a narrow boiling range (azeotropic or near azeotropic) blend of nPB, a specifically selected alcohol, and the appropriate levels of stabilizers.

Two independent experiments have demonstrated the high efficiency of the ABZOL™ EG Cleaner formulation for the removal of ionic residues from circuit boards. In one experiment, circuit boards were prepared by a potential customer. They were cleaned and evaluated for cleanliness at Detrex Corporation using an Omega Meter. In the second, circuit boards were prepared by Contamination Studies Laboratories (CSL). These boards were cleaned at the Albemarle Technical Center and returned to CSL for evaluation by the Omega Meter and by Ion Chromatography.

The circuit boards prepared by the potential customer were made of polyimide and were 6"x7" with solder mask on both sides. Each board contained twelve 20-pin LCCs (Leadless Chip Carriers) and two 68-pin LCCs. The LCCs had 50 mil pitch centers (distance between leads). The boards prepared by CSL were IPC-B-36 boards. First they were pre-cleaned to less than 0.1 microgram/sq.in. of NaCl residues. Alpha Metals RA321 RA solder paste was hand applied to

the test pads. The paste was reflowed in an oven in the usual fashion. After cooling, the boards were sprayed with Kester 1585-Mil RA flux and again reflowed.

The cleaning process at Detrex emulated an in-line process at the customer which included immersion in the boiling solvent for 100 seconds and the use of spray wands. The cleaning process at Albemarle employed a batch vapor degreaser with three minutes immersion in the boil sump. Three circuit boards were cleaned by each combination of cleaning process and evaluation. The levels of ionic contamination found on the boards were:

Board No.	Detrex Omega Meter	CSL Omega Meter	CSL Ion Chromatography
1	4.4 μgms/in^2	2.30 μgms/in^2	2.87 μgms/in^2
2	3.9	3.10	2.18
3	6.4	2.70	2.55
Ave.	4.9 μgms/in^2	2.70 μgms/in^2	2.55 μgms/in^2

Standard Requirements

Mil-C-28809	<14.0 μgms/in^2
Mil-STD-2000	<14.0
NASA NHB 5300.4 (3A-7)	<10.0

Contamination Studies Laboratory noted in their report that the maximum historically acceptable level for ionic contaminants is 14.0 μgms/in^2 (see Mil specs above). The report judges ABZOL™ EG Cleaner to perform better than the Freon TMS benchmark.

Compatibility With Plastics and Elastomers

Plastics and elastomers that pass short term compatibility tests (immersion in boiling solvent for fifteen minutes) include the following:

Plastics	**Elastomers**
Acculam™ epoxy glass	Adiprene™ polyurethane
Alathon™ HDPE	Aflas™ PTFE
Delrin™ acetal*	Buna-N™ rubber
Kynar™ polyvinyl fluoride*	Kalrez™ fluorelastomer*
Nylon™ (6 and 6.6)	Neoprene™ polychloroprene
Phenolics*	Viton-A™ fluoroelastomer**
Polyester (filled & unfilled)	Viton-B™ fluoroelastomer**
Polypropylene	
Teflon™ PTFE*	
Tefzel™ ethylene/PTFE*	
XLPE™ crosslinked PE	

---

* These materials are also compatible for long term (2 months) immersion at elevated

temperature (65°C).
** The Viton™ fluorelastomers are marginal for long term (2 months) immersion at elevated temperature (65°C).

Plastics and elastomers that were found to be unsuitable (U) or marginal (M) for contact with nPB at elevated temperature for short periods (15 min.) include:

Plastics	Elastomers	
Low density polyethylene (M)	Butyl rubber (M)	EPDM-60 (U)
Ultem™ polyether imide (M)	NBR nitrile rubber (M)	Silicone (U)

Toxicology - Acute

n-Propyl bromide is toxic, but can be handled safely if reasonable precautions are taken. Below is a compilation of the current acute toxicology for nPB:

Mammalian Genetic Toxicity - nPB is negative for dominant lethal activity in rats at 400 mg/kg/day given for 5 days to male rats prior to breeding once weekly for 8 successive weeks. No difference in mating performance was noted in treated males. Their frequency of fertile matings, mean numbers of corpora lutea, number of implants per female, number of live embryos per female, and the dominate lethal index was comparable to the negative control group at weeks 1,2,3,4,5,6,7 and 8 after treatment. The frequency of dead implants was higher at week 8 of treatment compared to the control group, but no increase was observed in the dominate lethal index at that or any other time. The frequency of dead implants in the treated group was comparable to the control group at weeks 1,2,3,4,5,6 and 7.

Mammalian Metabolism - The half-life of nPB in the rat is very short (approximately 2 hours). The majority of the administered dose is eliminated rapidly in expired air as the unchanged parent compound. The remainder is metabolized and excreted in the urine (predominant route) or in the expired air as CO_2(minor route).

Following a single intraperitoneal dose (200 mg/kg), the initial rate of excretion of unchanged (14C)-labeled parent compound in the expired air of the rat was rapid. Two hours after administration, 56% of the administered dose was exhaled as the parent compound. After 4 hours, 60% had been exhaled: only trace amounts were detected in expired air after this time. An earlier study also reported the elimination of the unchanged parent compound in expired air. Oxidation to CO_2 occurred only to a minor extent. Only 1.4 % of the total dose (or 3.5% of the metabolized dose) was exhaled as CO_2 over 48 hours. Approximately 40% of the total IP-administered dose was available for metabolism in the rat and excretion in the urine.

Aquatic Acute Toxicology - The solubility of nPB in is approximately 0.25g/100ml water at 20 C. The 96 hour LC50 in flathead minnows is 67300 μg/L.

Toxicology - Chronic

Ninety day inhalation studies with rats were used to set the Albemarle Workplace Exposure Guideline (AWEG) for workers using nPB on an eight hour shift, five shifts per week. The AWEG has been set at 100 ppm. At this level, solvent/cleaners based on nPB can be used safely with modern vapor degreasers and in other applications with proper handling. By comparison, the exposure guideline (PEL) for trichloroethylene is only 50 ppm (25 ppm in California).

Environmental and Health Regulatory Status

Worker safety, public safety and environmental protection are paramount in the development of any new product. The current status of *n*-propyl bromide and solvent/cleaner systems based upon it is given in Table IV.

TABLE IV
Environmental and Health Regulatory Status

Regulation	ABZOL™ Cleaners	1,1,1-Trichloroethane	Trichloroethylene
SARA	No	Yes	Yes
HAP	No	Yes	Yes
NESHAP	No	Yes	Yes
RCRA	No	Yes	Yes
HGWP	0.0001	0.023	Almost Zero?
ODP	0.0019, 0.027[3]	0.1	Almost Zero?
Atmospheric Lifetime	15 days[3]	5.4 years	??
PEL	100 ppm*	350 ppm	50 ppm
VOC	Yes	No	Yes
SNAP	Rule to be published in Federal Register	Unacceptable	Acceptable

* Albemarle Workplace Exposure Guideline

Summary

Solvent/Cleaner systems based on n-propyl bromide have been introduced as replacements for chlorinated solvents in cleaning applications. nPB is an aggressive, fast drying solvent that is suitable for a variety of difficult cleaning and degreasing applications. The use of nPB based solvents is not regulated under SARA, HAP, NESHAP or RCRA, and they are

approved for sale under SNAP (further review by EPA possible). nPB has low potentials for ozone depletion and for global warming, but it is currently classified as a VOC. The Albemarle Workplace Exposure Guideline is 100 ppm, which makes it safe to use with the proper precautions for worker safety. In comparative performance testing, nPB based formulations have been demonstrated to be as effective as chlorinated solvents and more effective than hydrochlorofluorocarbons, hydrofluorocarbons, hydrofluorocarbon ethers and volatile methyl siloxanes.

Case Histories

1. Electronic Equipment

A company that produces electronic components for clinical equipment used in biomedical applications had used CFC 113 blends in both liquid and vapor phase defluxing[4]. Exacting performance standards, rate of throughput, space limitations, limited capital equipment budget and lack of an adequate industrial water system were major constraints on a changeover to a new cleaning system.

The company attempted to switch to a system based on d-limonene. Residue from the cleaning agent, buildup of rosin flux and reactivity to produce assorted oxidation products made the electronic components unsuitable for use. An unacceptable green residue remained on the assemblies and there was an increase in product failures.

After switching to a cleaning solvent made from n-propyl bromide (ABZOL™ VG Cleaner), the company found that the new cleaner did a better job of removing flux than the CFC-113 blend. There were no residue problems as there were with d-limonene. Some of the plastic components did show some discoloration, but this problem was solved by shortening the exposure time -- an added benefit by increasing throughput.

2. Electric Motor Stators and Refrigeration Coils

The Galley Products Division of B/E Aerospace had a need to clean burnt oils from used electrical motor stators. They sent two such stators for cleaning. One was clean and the other was covered in oil. Both were cleaned using ABZOL™ VG Cleaner. They were first lowered into the vapor zone of a vapor degreaser and held there until condensation of the vapor on the parts ceased. This required about 5 minutes. They were then lowered into the ultrasonic bath for ten minutes and back into the vapor zone for 5 minutes. The parts were returned to B/E for examination.

B/E Aerospace reported that the parts were "perfect". No residual oils or other contaminants were found, and there was no damage to the electrical wiring or casings. This finding led B/E Aerospace to examine other applications for ABZOL® VG Cleaner. They have since devised a flushing station for cleaning the long coils of copper tubing used in refrigeration units. B/E presented a paper at the CleanTech'98 conference outlining the extensive selection process that lead to them choosing ABZOL® VG Cleaner for their tough cleaning problems.[5]

References:

1. Kanegsberg, B., "Precision Cleaning Without Ozone Depleting Chemicals," **Chemistry and Industry,** #20: 787,21, Oct., 1996.

2. Shubkin, R. L., "A New and Effective Solvent/Cleaner with Low Ozone Depletion Potential," **1996 International Conference on Ozone Protection Technologies, Proceedings and Presentation**, Washington, D. C., October 21-23, 1996.

3.Nelson, Jr., D. D, Wormhoudt, J. C., Zahniser, M. S., Kolb, C. E., Ko, M. K. W., and Weisenstein, D. K., "OH Reaction Kinetics and Atmospheric Impact of 1-Bromopropane,", **J. of Physical Chemistry A, Vol. 101,** no. 27, pp 4987-4990.

4. Kanegsberg, B., "Cleaning High Value Components for Biomedical and Other Applications," **1996 International Conference on Ozone Protection Technologies, Proceedings and Presentation**, Washington, D.C., October 21-23, 1996.

5. Petrulio, R. And Kanegsberg, B., "Practical Solutions to Cleaning and Flushing Problems," **CleanTech'98**, Rosemount, IL, May 19-21, 1998.

Semi-Aqueous and Vapor Degreasing Processes For Removing Waxes, Pitches, and Fixturing Compounds from Precision Parts

Elizabeth A. Bivins, Steven B. Hayes, and Frank J. Last, III
Petroferm Inc. 5415 First Coast Hwy., Fernandina Beach, FL 32034

ABSTRACT

This paper details the proper configuration and operation of semi-aqueous and vapor degreasing processes for removing wax, pitch, or fixturing compound from precision parts. These cleaning tasks have historically been performed in vapor degreasers using chlorinated solvents. For a variety of environmental, health and safety reasons, chlorinated solvents have fallen out of favor with many companies. Most of the alternative processes and chemistries which have been implemented have produced results which were unsatisfactory in one way or another. By contrast, the processes described in this paper have been implemented in several manufacturing facilities in the aerospace, optics, electronics, and general metalworking industries with excellent results. Critical issues for semi-aqueous cleaning such as cleaning equipment design, operating parameters, ventilation, bath recycling, air emissions, and waste disposal are addressed. For vapor degreasing, selection of non-NESHAP regulated solvents, cleaning equipment configuration, and system operating parameters will be discussed.

INTRODUCTION

Vapor degreasing with chlorinated solvents has for many years been the process of choice for removing waxes, pitches, and fixturing compounds used in a range of manufacturing industries. More recently, increasing awareness of health, safety, and environmental issues has challenged industry to develop new cleaners and processes for these and other cleaning tasks. Federal NESHAP (National Emission Standards for Hazardous Air Pollutants) regulations presently require the modification of most existing vapor degreasing equipment to operate with chlorinated solvents. Rather than modify existing equipment for operation with solvents of health and environmental concern, many manufacturers are looking for environmentally sound alternatives to chlorinated solvent vapor degreasing. Several alternative cleaning chemistries and processes have been proposed for these cleaning applications, but they have usually produced results which were unsatisfactory in one way or another. Much of the time, the alternative process did not completely eliminate the need for chlorinated solvent vapor degreasing.

In the early 1990s, semi-aqueous processes began to see use in metalworking industries for removing wax, pitch, and fixturing compound. In 1994, a semi-aqueous process using an environmentally sound, semi-aqueous cleaning agent* was tested and approved by Pratt & Whitney Aircraft Engines for removing wax and fixturing compound from gas turbine engine parts during original manufacture, repair and overhaul processes. The process and cleaning agent were subsequently approved by both General Electric and Rolls Royce. Since the original approval by Pratt & Whitney, the use of the semi-aqueous process for removing waxes and fixturing compounds has proliferated, especially in aircraft-related industries. In 1996, semi-aqueous processes were implemented in the optics and silicon wafer industries for removing pitches which are commonly used for fixturing purposes.

Recently, vapor degreasing has become a viable option for these tasks as alternative non-chlorinated solvents have become available. Single-solvent and co-solvent vapor degreasing with these alternative solvents are both effective.

* BIOACT® 280 Precision Cleaner from Petroferm Inc., Fernandina Beach, Florida

SEMI-AQUEOUS CLEANING

Semi-aqueous cleaning was introduced several years ago as an alternative cleaning technology for those who require performance levels unattainable with CFCs and aqueous cleaning. With more than 1000 users, it is no longer just an alternative; for many applications it is the de facto standard, better in many ways than either vapor degreasing or aqueous cleaning. An ideal semi-aqueous cleaning agent will posses a range of desirable characteristics including good solvency for the soils to be removed, low toxicity, low VOC content, low odor, high flash point, and high soil loading capacity.

Semi-aqueous processes consist of three basic steps: a wash in a bath of semi-aqueous cleaning agent, a water rinse (or series of water rinses), and a drying step. Figure 1 depicts two common configurations for semi-aqueous systems designed for wax removal. More than 20 manufacturers are currently using semi-aqueous processes for this purpose. Some have converted vapor degreasers to serve as vessels for the semi-aqueous cleaning agent and rinse water, some have configured systems using tanks previously deployed in plating processes, some have manufactured their own tanks, and others have purchased new equipment purposefully constructed to accomplish this cleaning task. While individual systems may differ, all are capable of carrying out the fundamental operations depicted in Figure 1: a wash in the semi-aqueous cleaning agent and a rinse, or series of rinses, in water.

WAX REMOVAL PER PRATT & WHITNEY SPOP 37 - METHOD 2

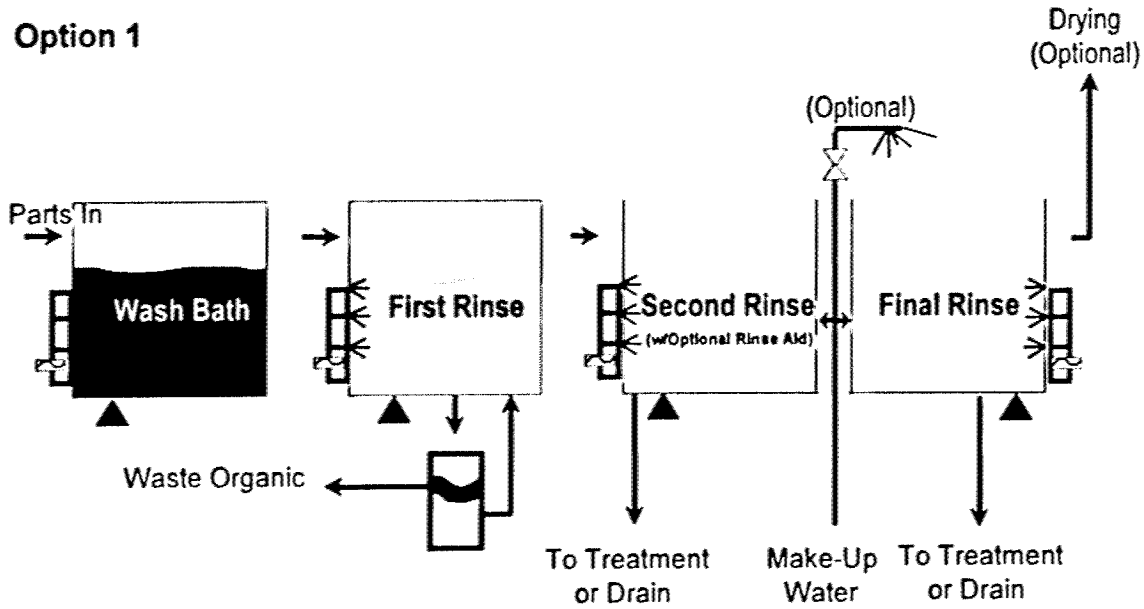
Many of the semi-aqueous wax removal processes in use today are governed by Pratt & Whitney specifications. As defined by SPOP 37 - Method 2 in the Pratt & Whitney Commercial Standard Practices Manual, the semi-aqueous wax removal process is as described below. The comments and suggestions in *italics* result from experiences with this process but are not to be construed as part of SPOP 37 - Method 2.

1. Remove bulk of wax by dipping in the wax tank to dissolve build-up.
This serves to reduce wax consumption and to prolong the service life of the cleaning agent bath. Some users of this process immerse the parts in a bath of hot (82°C; 180°F) water to remove the excess wax. Wax removed in the hot water bath can be recovered and reused.

2. Immerse the part in [the cleaning agent] at 93 - 110°C (200 - 230°F) for 5 - 20 minutes. Mechanical agitation is recommended.
Spray under immersion is the most common method of bath agitation. A revision of SPOP 37 - Method 2 released May, 1996 approves the use of 82 - 110°C (180 - 230°F) bath temperatures. Most customers operate the cleaning agent bath near 82°C (180°F).

3. Immerse the part in mechanically agitated hot water for 1 to 5 minutes as required. Water should be slightly overflowing to skim removed wax residues. The temperature of the water should be 60° - 100°C (140° - 212°F).
At least two rinses following the cleaning agent bath are recommended in order to keep the final rinse relatively uncontaminated by the cleaning agent/wax mixture. Operating the rinse baths at or near the melting point of the wax will improve rinsibility of the cleaning agent/wax mixture as the concentration of wax increases in the wash bath, and will maximize the service life of the cleaning agent bath. Spray-in-air final rinses have been also been used with excellent results.

4. If required, clean the part by SPOP 209.
SPOP 209 is an aqueous cleaning process. An aqueous cleaning agent which is approved for use in SPOP 209 is sometimes used as a rinse aid in the second rinse tank of the semi-aqueous process to reduce the amount of bath agitation required to effectively rinse the mixture of semi-aqueous cleaner and wax from the parts.



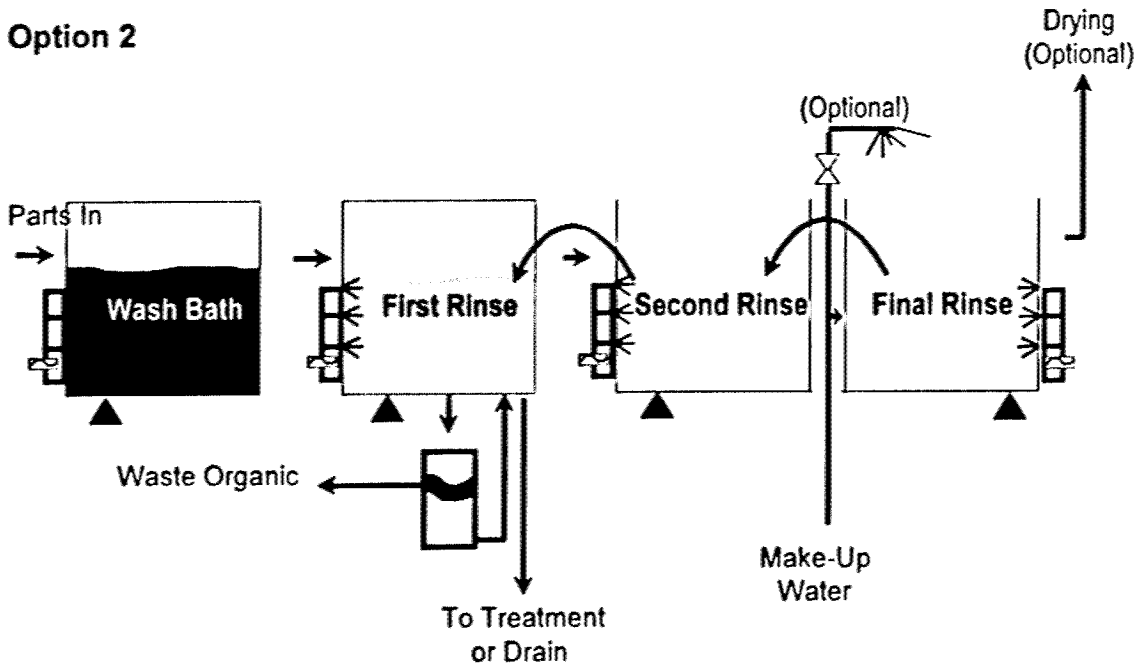


Figure 1
Semi-Aqueous Process for Wax Removal

GENERAL PROCESS GUIDELINES

Bath temperatures

For optimal cleaning performance, the temperature of the cleaning agent bath should be at or above the melting point of the wax being removed. Cleaning agents with closed cup flash points exceeding 120°C (248°F) allow for a comfortable margin of safety when operating at the typical melting points of popular waxes (< 82°C; <180°F).

Rinse bath temperature requirements are governed primarily by the concentration of wax in the cleaning agent bath. As the wax load increases to 15 wt. % or more, higher rinse temperatures may be required to effectively rinse the cleaning agent/wax solution from the parts. Rinse water temperatures at or above the melting point of the wax will yield maximum rinse effectiveness and allow the longest possible service life from the cleaning agent bath. When an alkaline cleaner is used as a rinse aid, the operating temperature of the bath should be determined from the use instructions for that particular cleaner.

Bath agitation

Aggressive agitation in the cleaning agent bath will speed the cleaning process and may be essential for optimal performance if the parts being cleaned contain particularly complex geometries or small passageways. Aggressive rinse bath agitation is necessary for optimal rinsing performance on parts of any configuration if no aqueous rinse aid is used.

The most common method of bath agitation is spray-under-immersion. Two different methods have been used to create agitation of this type. The easiest and simplest to use is a single-source agitator such as a propeller-type turbulator or a recirculating pump returning fluid to the bath through a single discharge tube. This method of agitation generally works well in the cleaning agent bath and in the rinse stage in systems where a rinse aid is used.

Another method of providing spray-under-immersion agitation is via a manifold system fed by a high-volume pump. If the system operates without an aqueous rinse aid, the high-volume pump and manifold system is required in the rinse stage. Properly designed pump-and-manifold systems have proven to provide effective agitation when the pump's gallons-per-minute capacity is equal to approximately one-half of the tank volume and induction type nozzles are used.

In addition to spray-under-immersion rinse bath agitation, some users have installed spray-in-air type final rinses. This method is effective and is an excellent option for systems without aggressive rinse bath agitation. Typically, a hand-held spray wand is fed either by fresh water or with water from the final rinse bath. With this type rinse process, care should be taken to direct the spray into any hard-to-reach areas of the parts. In applications utilizing a final spray-in-air rinse with fresh water, the final rinse bath can be operated with a relatively high contamination level. Operating in this manner, depending upon the number of parts being cleaned per unit of time, it may be possible to minimize or eliminate the routine discharge of rinse water from the system if the amount of fresh water introduced into the system through the final rinse matches the amount of water lost to evaporation and drag out.

Some semi-aqueous users have opted for spray-in-air throughout the rinse phase of the process. This method provides excellent results when the parts being cleaned are configured such that the rinse water spray can contact all surfaces.

Other methods of bath agitation have also been used with varying degrees of success including ultrasonic agitation, platform-lift type agitators, and air agitation.

Ultrasonic bath agitation is very effective but may be prohibitively expensive in applications where very large parts such as jet engine component assemblies necessitate large bath volumes. More importantly, ultrasonics may not be allowed with some parts.

Platform-lift agitators are usually capable of providing satisfactory agitation for the wash bath but they may not provide sufficiently vigorous agitation to yield effective rinsing in systems operating without an aqueous rinse aid.

Air agitation is not recommended in this application due to its lack of aggression and tendency to generate waxy bubbles in the initial rinse stage.

Drying of Parts

Parts cleaned in aqueous or semi-aqueous processes incorporating final rinses in hot water will usually flash dry as a result of heat retention in the part. In cases where drying assistance is needed, forced air is most often used, but the parts can be dried by a variety of other methods including oven, vacuum chamber, or centrifugal force. Appropriate drying methods are chosen based upon the particular parts in question and the specific needs of the application.

System plumbing precautions

As the cleaning agent becomes loaded with wax or pitch, the viscosity of the solution increases. (This characteristic is most noticeable at room temperature but of no real consequence at normal operating temperatures.) The higher the wax loading, the higher the freezing point of the solution. With most waxes, the solution is no longer pourable at 25°C (77°F) once the wax loading reaches approximately 20% by weight.

Properly designed cleaning systems allow the use of the cleaning agent bath until it is loaded with wax to approximately 40% by weight. In systems which incorporate a pump, spray-under-immersion manifold, and the associated plumbing network, the viscosity increase associated with increased wax loading must be addressed. If a loaded system is shut down and allowed to cool to a temperature below the freezing point of the solution, restarting the system may be difficult due to the presence of frozen cleaning agent/wax solution in the pump and plumbing network.

One way to address the potential for frozen plumbing is to install steam traces or heat tape around the plumbing network which is exterior to the cleaning agent bath. (The bath itself is not of concern as the heating elements, once activated, will liquefy the bath.) An alternative method is to install valves and drain cocks at the appropriate points in the plumbing network so that the network can be drained prior to cool-down whenever the system is shut down. This method should be suitable for systems which will operate continuously, but could become labor-intensive for systems which will be shut down frequently.

Ventilation

The vapor pressure of the most widely used semi-aqueous wax-cleaning agent is <0.001 mm Hg at 20°C, and the chemistry has essentially no odor. At normal operating temperatures, very little vapor or odor are produced and minimal (if any) ventilation is required for the cleaning agent bath. Many waxes produce an odor when heated, and a wax odor may be produced when such waxes are loaded into the cleaning agent bath. Adequate ventilation for controlling odor can be achieved with lip vents around the cleaning agent tank or by use of a hood above or behind the bath.

Steam from the water-rinse baths can be vented to the atmosphere in most jurisdictions. Users in areas with especially restrictive regulations may be required to install demisters in the air stream, depending upon local regulations.

Bath Life and Recycling

The service life of the cleaning agent bath is governed largely by the effectiveness of the rinse process. In a properly designed system, a bath of cleaning agent can normally be used until it is loaded with wax to approximately 40% by weight. Because the cleaning agent does not evaporate to any significant extent, it can be used until it is loaded, regardless of how long loading takes.

With certain waxes it may be possible to decant a portion of the cleaning agent from a loaded cleaning agent/wax solution after the solution has stood undisturbed at room temperature for a few hours or days. This method is marginally effective for most waxes and pitches, but works well for most thermoplastic fixturing compounds. Bench testing can confirm the feasibility of separation.

Service life of the rinse baths is determined primarily by the level of cleanliness required for the parts being cleaned. For example, if the wax removal process also serves as the final cleaning step for the parts, the water-quality requirement for final rinse may be higher than that for parts destined for subsequent cleaning. The final rinse bath will become progressively contaminated as parts are processed through the cleaning agent bath, through the initial rinse(s), and then into the final rinse. Rinse processes are usually configured so that water is metered into the final rinse bath at a rate sufficient to keep the bath adequately purged of contamination (see Figure 1).

In applications where waste water discharge must be kept to a minimum, water from the cleaning process can be recycled through distillation. Any cleaning agent/wax solution which has accumulated in the rinse water will be concentrated in the still bottoms.

AIR EMISSIONS

Due to its very low vapor pressure, <0.001 mm Hg at 20°C, volatile emissions of the semi-aqueous cleaning agent specified in SPOP 37 - Method 2 are exceptionally low.

WASTE DISPOSAL

Cleaning agent/wax solution

The most common method of disposal of the cleaning agent/wax solution is fuel blending. The cleaning agent referred to in this paper is not considered hazardous waste in the United States according to 40CFR261, and it has a fuel value >15,000 Btu per pound. Waste handlers in the United States typically charge $50 to $100 per 55-gallon drum for disposal of the cleaning agent/wax mixture.

Water

Waste water from the process can be handled in a variety of ways. The cleaning agent described in this paper is readily biodegradable, so in many jurisdictions, rinse water containing low concentrations of cleaning agent may be put directly to the sewer. Sewerability of any industrial waste is, of course, controlled by the local governing authority. Other options include in-plant waste treatment, and evaporation. Evaporation is an especially good method of reducing the volume of waste water from this cleaning process as the cleaning agent/wax solution in the water will remain in the evaporator and can be disposed of through fuel blending or incineration.

VAPOR DEGREASING

Single-Solvent Vapor Degreasing

Within the last couple of years, solvents and blends have become available that will allow manufacturers to continue using vapor degreasing without the safety and environmental concerns associated with chlorinated solvents. N-propyl bromide and its azeotropes are excellent solvents for waxes, pitch, and fixturing compounds. Some of the properties of an azeotrope containing n-propyl bromide that make it a good choice as a chlorinated solvent replacement are listed in Table 1.

TABLE 1

	npb Azeotrope	Perchloroethylene	Trichloroethylene	1,1,1-TCA
Composition	n-propyl bromide IPA	—	—	—
Boiling Pt (°F)	145	250	189	165
Specific Gravity (25°C)	1.25	1.6	1.46	1.56
Surface Tension, dynes/cm	TBD	32	26.4	26
Heat of Vaporization (cal/g)	58.8	50	57.2	35
Flash Point (TCC)	None	None	None	None
Flammability Limits (vol %)	4 – 7.8	None	8 – 10.5	Yes
Kauri Butanol Value	>125	90	129	124
Atmospheric Lifetime	2–3 weeks	<1 year	<1 year	6.1 years
ODP	Approx. 0.02	0	0	0.1
TLV (ppm)	npb 100[1] IPA 400[2]	25[2]	50[2]	350[2]

1 Manufacturer's recommended exposure limit
2 ACGIH TWA

A recent study by a major relay manufacturer compared the characteristics, performance, and economics of the major non-NESHAP regulated vapor degreasing compounds.[1] The solvents evaluated are shown in Tables 2 and 3 along with safety and environmental considerations and many of their physical properties: HCFC-141b is included for comparison. The data presented in these tables are for the base solvent, or the molecule indicated in the heading. The solvents tested were actually azeotropes of these base solvents and the properties of the azeotropes vary slightly. Chart 1 shows the total annual costs determined for the various compounds. While this particular study was not on wax removal, the economics should be applicable. It should be pointed out that the manufacturer of HCFC-123 has since withdrawn this solvent from the market. Of the five solvents evaluated, the nPB azeotrope was chosen as the best replacement for the HCFC-141b. It provided the best combination of cleaning cost, environmental and safety properties.

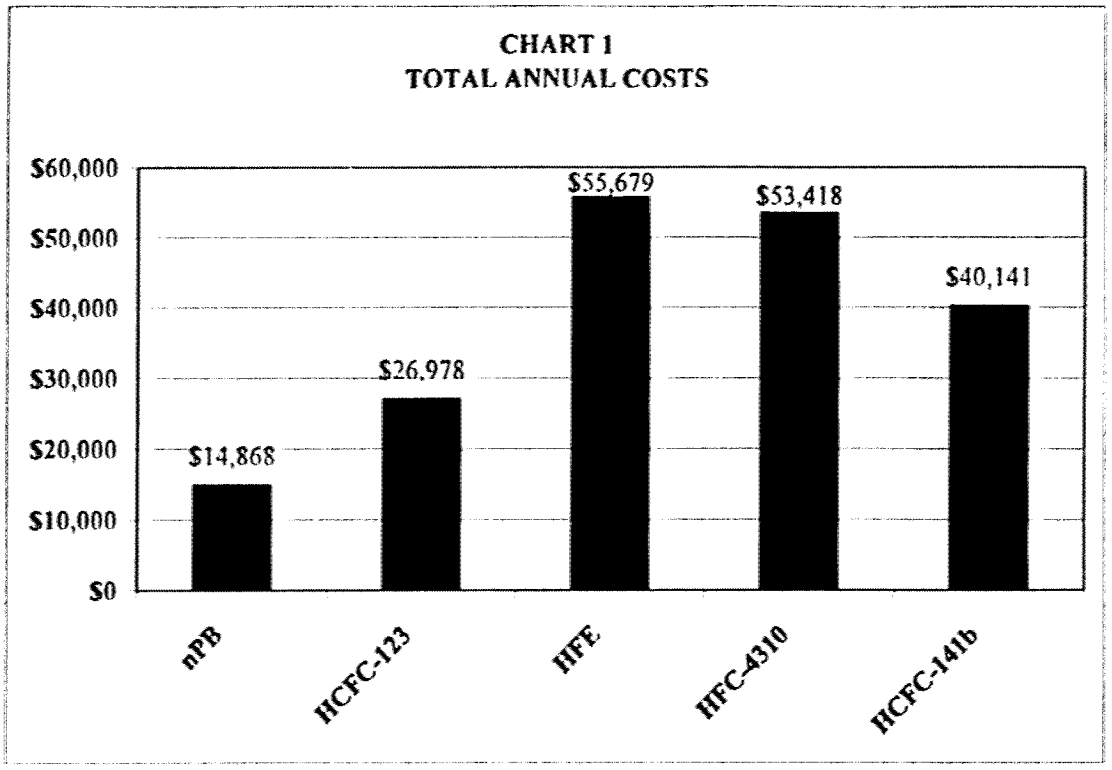
TABLE 2 SAFETY AND ENVIRONMENTAL PROPERTIES

	HCFC-123	HCFC-225	HFC-4310	Hydro-fluoroether	nPB	HCFC-141b
Cleaning Electronics	Alcohol azeotrope very good	Alcohol azeotrope very good	Alcohol azeotrope very good	Alcohol/dce* azeotrope very good	Alcohol azeotrope very good	Alcohol azeotrope very good
EPA/SNAP	No longer available	SNAP restrictions	SNAP	SNAP	SNAP pending	Aerosol only
ODP (Ozone Depletion Potential)	0.02	0.03	0.0	0.0	0.006	0.10
GWP (Global Warming Potential)	93	170/530 (2 isomers)	1600	500	(11 day atmospheric lifetime)	630
VOC	No	No	No	No	Yes	No
Toxicity of base solvent AEL/TLV (ppm)**	50	50	200	600	100	500

TABLE 3 PHYSICAL PROPERTIES OF BASE SOLVENTS

	HCFC-123	HCFC-225	HFC-4310	Hydro-fluoroether	nPB	HCFC-141b
Boiling Pt (°C)	27	54	55	60	71	32
Specific Gravity (25°C)	1.46	1.55	1.58	1.5	1.35	1.24
Viscosity (25°C), cp	0.45	0.59	0.67	0.61	0.49	0.43
Surface Tension, dynes/cm	16	16.2	14.1	13.6	25.9	19.3
Vapor Pressure (mm Hg @ 20°C)	~349	283	226	170	110.8	593
Evaporation Rate (TCA = 1)	<1	>1	>1	<1	0.96	>1
Specific Heat (25°C)	.28	0.25	0.27	0.28	0.27	
Heat of Vaporization (cal/g)	~38	33	31.0	30	58.8	52.3
Solubility in Water (ppm)	3900	330	140	<20	240	180
Solubility of Water (ppm)	Not available	300	490	95	500	420
Flash Point (TCC)	None	None	None	None	None	None

* dce is trans-1,2-dichloroethylene.
** The toxicities of the components of the azeotropes other than the base solvent are not listed here.



Equipment Recommendations

Products based on n-propyl bromide can be operated safely and efficiently in most modern vapor degreasing equipment. Minimum recommended freeboard is 100%, and should be 150% to minimize emissive losses and worker exposure. Freeboard refrigeration is also recommended.

Operating Parameters

For removal of wax, pitch and fixturing compounds using an n-propyl bromide azeotrope, the following process provides optimum cleaning:

a. Immersion in the boiling sump for 5–10 minutes;
b. Immersion in the clean sump for 5–10 minutes;
c. Dwell in vapor for time sufficient for condensation of solvent on part to stop.

Ultrasonics in the clean sump will enhance soil removal and shorten cleaning times.

Many vapor degreasing processes with chlorinated solvents employ cleaning in the vapor only (no immersion in the solvent). Immersion in the solvent not only enhances soil removal—it also reduces solvent losses, and hence consumption and operating cost.

CO-SOLVENT VAPOR DEGREASING

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 and water is used for rinsing. In the co-solvent cleaning process described in this article, 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, and the solvents are low in toxicity.

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 solvents such as trichloroethylene 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 in the boil sump does not change the way the process is run.

The only practical difference between vapor degreasing with a single solvent process and a co-solvent process 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.

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, such as 3M™ HFE-7100. 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 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.

SUMMARY

The processes described in this paper are proven alternatives to 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene for removing waxes, pitches, and fixturing compounds commonly used across a range of industries. Combining excellent cleaning performance, low environmental impact, and good process economics, these are viable alternatives to vapor degreasing with chlorinated solvents.

Reference

1. Zintel, Rebecca, Magnecraft and Struthers-Drum, Darlington, SC, "Successful Replacement of HCFC-141b for High Reliablity, Aerospace and Nuclear Industry Relay Cleaning with n-Propyl Bromide," Reprints available from Petroferm Inc. (904-261-8286).

ENVIRONMENTALLY ACCEPTABLE HYDRAULIC OIL FLUSH SOLVENT CLEANING PROGRAM FOR THE REPLACEMENT OF FREON, AN OZONE DEPLETING CHEMICAL

PREPARED BY

John Weir, P.E.
Lead Engineer
Northrop Grumman D08-001
Bethpage, NY 11714

Richard Doria, P.E.
Manager, Environmental, Health, & Safety
Northrop Grumman
5000 U.S. 1 North
P.O. Drawer 3447
St. Augustine, FL 32085-3447

Allen Sinowitz
Lead Test Engineer
CDI-Northrop Grumman D08-001
Bethpage, NY 11714

Abstract

Laboratory testing indicated that 3M's HFE 7100 and Petroferm's PFC 265-141 solvents can be used to replace Freon TF (CFC113) for cleaning off hydraulic oil, MIL-H-83282 from the interior of E2C and F-14 aircraft surfaces. Hydraulic oil removal rates, as well as, material compatibility testing resulted in selecting PFC 265-141 solvent for oil removal followed by a final flush of HFE 7100 to assure the complete removal of the oil contaminated PFC 265-141 solvent. Testing indicated that 3M's HFE 71DE and Dupont's Vertrel SMT and Vertrel MCA were not compatible with MIL-L-81352 acrylic coatings used on the aforementioned production aircraft.

The presentation reports the data generated during the test program and describes the methodology used to qualify the materials for this application. The methodology considered functional testing which included hydraulic oil removal rates, evaporation rate, and flash point considerations. Additionally, extensive material compatibility testing was accomplished on aircraft materials to assure the selected solvents would not damage aircraft coatings, sealant, part markings, wiring, electrical connectors, tube markings as well as high strength steel.

Introduction

During the aircraft manufacturing and rework processes, hydraulic fittings, tubing and components are pressure tested at various stages of assembly. Pressure testing of the hydraulic subsystems continues as the hydraulic system is built up along with the aircraft.

From time to time the systems do not initially pass hydraulic pressure testing and as a result hydraulic leaks do occur. This some times results in a messy affair with hydraulic oil spraying all over the interior portions of the built up structural subassemblies or the interior of the finished aircraft. Freon TF (CFC113) was the preferred solvent used for many years to clean up hydraulic oil and spills that have occurred inside aircraft fuselages and structures. The primary reasons Freon was selected for this type of application is the fact that Freon is non-flammable and will not harm most aircraft materials. Unfortunately, Freon TF is an ozone depleting chemical and has been phased out of production under the Clean Air Act and the Montreal Protocol.

Background

Northrop Grumman operations at St. Augustine, FL needed a replacement for Freon TF to clean hydraulic oil out from the inside of E2C and F-14 aircraft fuselages and subassemblies. This required that a test program be accomplished to assure the replacement solvent would be capable of cleaning off hydraulic oil in a similar fashion to Freon TF. The program also required that the replacement solvent not harm any of the aircraft materials that could come into contact with the solvent, during the flushing operation. Flammability was also an issue and hence it was required that the new environmentally acceptable solvent be non-flammable or be capable of being adequately controlled through proper ventilation to make sure the lower explosive limit (LEL) is never achieved.

Functional Test Protocol and Results

The following is a summary of each of the functional test methods used during the test program and the respective data generated from the testing.

Hydraulic Oil Flushing Test Protocol and Results

The test protocol consisted of solvent flushing off a light film of hydraulic oil from a primed 4"x6" aluminum test panel. Each of the primed test panels were weighed prior to and after a coating of hydraulic oil was applied to the primed surface. The panels were then held at a 45 degree angle and flushed with approximately one once of the test solvent. The panels were the weighed again to determine how much hydraulic oil was removed during the flushing operation. This procedure was repeated until the hydraulic oil was removed or upon reaching ten flushes. The efficiency of removal was recorded by determining the number of flushes required to bring the test panel weight back to the original panel weight prior to the application of the hydraulic oil coating. See Table 1 for a cleaning efficiency comparison between Freon TF, HFE-7100, Vertrel SMT and Vertrel MCA.

TABLE 1

PRIMER	HIGH SOLIDS	WATER BORNE	HIGH SOLIDS	WATER BORNE	HIGH SOLIDS	WATER BORNE	HIGH SOLIDS	WATER BORNE	HIGH SOLIDS	WATER BORNE
TEST SOLVENT	HFE-7100	HFE-7100	FREON TF	FREON TF	SMT	SMT	MCA	MCA	HFE-71DE	HFE-71DE
ORIGINAL WEIGHT, GMS	80.5	78.1	80.8	78.1	80.5	77.5	80.5	77.5	80.5	77.5
WEIGHT with HYDRAULIC OIL,GMS	80.9	78.5	80.9	78.5	80.9	77.8	80.8	77.8	81.0	77.9
WEIGHT after 1 FLUSHING, GMS	---	---	80.9	78.3	80.6	77.6	80.5	77.5	80.5	77.5
WEIGHT after 2 FLUSHING, GMS	---	---	80.9	78.1	80.5	77.5	80.5	77.5	80.5	77.5
WEIGHT after 3 FLUSHING, GMS	80.7	78.3	80.8	---						
WEIGHT after 6 FLUSHING, GMS	80.6	78.2								
WEIGHT after 10 FLUSHING, GMS	80.7	78.3								
NOTES	(1)(5)	(1)(6)	(2)(5)	(3)(6)	(3)(5)	(3)(6)	(4)(5)	(4)(6)	(4)(5)	(4)(6)

1) The MIL-H-83282 hydraulic oil remained on the test panels after ten solvents flushes.

2) The MIL-H-83282 hydraulic oil was removed from the test panels after three solvents flushes.

3) The MIL-H-83282 hydraulic oil was removed from the test panels after two solvents flushes.

4) The MIL-H-83282 hydraulic oil was removed from the test panels after one solvent flush.

5) Spraylat MIL-P-23377G TY1 CL C High Solids Epoxy Primer.

6) Spraylat MIL-P-85582B TY1 CL C2 Water Borne Epoxy Primer.

See Table 2 for the cleaning efficiency of the Petroferm PFC 265-141 and PFC 265-173 solvents. Note both the Petroferm solvents cleaned the test panels after two flushes similar to the control Freon TF and the other candidate test solvents with the exception of HFE-7100 which failed to clean the test panel after ten flushes.

Table 2

TEST SOLVENT	PFC 265-141	PFC 265-141	PFC 265-173	PFC 265-173
	First Run	Second Run	First Run	Second Run
ORIGINAL WEIGHT, GMS	80.5	77.5	80.8	78.3
WEIGHT with HYDRAULIC OIL,GMS	80.7	77.7	81.0	78.4
WEIGHT after 1 FLUSHING, GMS	80.6	77.5	80.8	78.3
WEIGHT after 2 FLUSHING, GMS	80.5	77.5	80.8	78.3
NOTES	(1)(2)	(1)(3)	(1)(2)	(1)(3)

1) The MIL-H-83282 hydraulic oil was removed from the test panels after two solvents flushes.
2) Primer used was Spraylat MIL-P-23377G TY1 High Solids.
3) Primer used was Spraylat MIL-P-85582 TY1 Water Borne.

Evaporation Rate Test Protocol and Results

A 50 ml quantity of the test solvent was placed in a previously weighted individual Coors porcelain evaporating dish part number 60198. The dish was 80mm in diameter and had a capacity of 80 ml. The depth of the starting fluid for each of the solvents was 0.9 inches. The porcelain dishes were weighed in one hour intervals. The remaining solvent weights were then calculated and summarized in Table 3. Only the HFE-7100 and Petroferm PFC265-141 solvents were completely evaporated after a four hour period. Note: The addition of hydraulic oil the PFC 265-141 solvent did slow down the evaporation of the solvent by approximately one hour.

Table 3

TIME	TEST SOLVENTS,EVAPORATION (weight of solvent in dish, gms)					
HOURS	HFE-7100	HFE-7100/OS-20	PFC 265-141	PFC 265-173	IPA	PFC 265-141/ HYDRAULIC OIL(90%/10%)
0	71.7 (1)	66.5 (1)	49.5 (1)	50.3 (1)	35.8 (1)	47.6 (1)
1	35.6	35.0	22.5	35.6	31.1	21.5
2	10.9	16.3	7.6	31.1	26.6	4.6
3	0	9.1	0.8	27.5	22.7	1.7
4	---	5.3	0	24.6	19.5	1.5
5	---	3.4	---	21.4	not measured	1.4 (2)
6	---	2.7	---	18.8	not measured	---
21	---	0	---	not measured	0	---
23	---	---	---	1.1	---	---
24	---	---	---	0.5	---	---

(1) Original weight of solvent at time zero.
(2) Original weight of the hydraulic oil. Weight of solvent is zero as all solvent has evaporated.

Test Protocol and Results for the Evaluation of Solvent Compatibility with Polysulfide and RTV Silicone Sealant

Two formulations of polysulfides and three formulations of silicone RTV were immersed in the following solvents, 3M's HFE-7100, HFE-71DE, Petroferm's PFC 265-141, PFC 265-173, and Dupont's SMT. At periodic intervals the samples were removed from the solvents, weighted and Durometer hardness (A scale) readings were taken. The samples were then returned to the solvents. After 24 hours of immersion, the samples were allowed to recover in air and then had weight and hardness readings taken. See Tables 4, 4A, 4B, and 4C for the test results.

TABLE 4 HFE-7100 and Vertrel SMT Sealant Compatibility Test Results

	POLYSULFIDES				RTV					
	P/S880A-12		PR1436G		3140		102		60	
TIME HOURS	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A
IMMERSION	TEST SOLVENT HFE-7100									
0	25.5	45	21.6	45	18.6	37	7.1	28	22.2	60
0.25	25.5	48	21.7	49	19.2	31	7.2	24	22.2	61
0.5	25.4	48	21.7	45	20.1	28	7.4	27	22.9	61
1	25.5	45	21.7	48	20.8	34	7.6	28	23.2	57
2	25.5	48	21.7	49	21.4	30	7.7	28	23.3	60
4	25.5	48	21.7	51	22.0	28	7.9	28	23.7	62
8	25.5	48	21.7	51	23.1	31	8.3	31	24.4	63
24	25.4	51	21.6	51	23.8	31	8.7	31	25.5	62
% Original	99.6	113	100	113	128	83	123	111	115	103
RECOVERY										
After 24	25.4	51	21.6	52	18.4	33	7.1	26	22.4	64
% Original	99.6	113	100	115	98	89	100	92	101	106
IMMERSION	TEST SOLVENT SMT									
0	25.4	51	21.6	52	18.4	33	7.1	26	22.4	64
0.25	26.9	51	22.8	46	26.0	40	8.3	27	25.0	60
0.5	27.1	45	23.0	43	27.2	38	9.0	25	25.6	60
1	27.4	41	23.2	42	29.1	29	9.4	24	26.6	57
2	27.9	41	23.7	43	30.3	26	9.8	25	27.2	63
4	28.6	39	24.1	39	29.3	27	10.7	28	29.1	61
8	29.0	39	24.2	41	30.2	30	11.2	22	27.8	61
24	28.5	42	24.1	41	23.4	38	9.0	24	25.0	60
% Original	112	82	112	79	127	115	127	108	112	94
RECOVERY										
After 24	26.2	48	21.8	54	18.6	32	7.0	30	22.3	64
% Original	103	94	101	96	101	97	99	115	99.5	100

TABLE 4A
PFC 265-141 Sealant Compatibility Test Results

	POLYSULFIDES				RTV					
	P/S880A-12		PR1436G		3140		102		162	
TIME	WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS	
HOURS	grams	Durometer A	grams	Durometer A	grams	Durometer A	grams	Durometer A	grams	Durometer A
IMMERSION	**TEST SOLVENT PFC 265-141**									
0	27.9	49	17.2	58	4.0	32	3.9	29	4.1	38
0.25	27.9	49	17.2	60	5.2	31	4.6	25	4.6	34
0.5	27.9	49	17.2	60	5.6	31	4.7	30	4.7	31
1	27.9	51	17.2	57	6.0	37	5.2	27	5.2	31
2	27.9	51	17.2	59	8.5	41	6.3	24	6.3	29
4	27.9	51	17.2	62	9.0	31	6.9	25	7.1	29
6	27.8	47	17.1	59	9.4	36	7.3	30	7.4	41
24	27.9	50	17.2	59	10.6	35	8.9	24	9.9	29
RECOVERY										
After 24	27.8	48	17.2	61	3.9	36	3.8	27	4.0	39
% of Original	99.6	98.0	100	105.2	97.5	112.5	97.4	93.1	97.6	102.6

TABLE 4B
PFC 265-173 Sealant Compatibility Test Results

	P/S880A-12		PR1741		3140		102		162	
TIME	WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS		WEIGHT-HARDNESS	
HOURS	grams	Durometer A	grams	Durometer A	grams	Durometer A	grams	Durometer A	grams	Durometer A
IMMERSION	**TEST SOLVENT PFC 265-173**									
0	27.7	52	25.6	53	4.4	39	3.2	32	2.9	44
0.25	27.7	50	25.7	54	5.7	37	3.9	31	3.2	43
0.5	27.8	51	25.7	52	6.0	36	4.0	26	3.5	38
1	27.7	53	25.6	53	7.8	31	4.8	24	4.1	31
2	27.7	53	25.7	52	8.8	33	5.6	23	4.8	30
4	27.7	51	25.7	55	10.2	33	6.1	27	5.2	32
8	27.7	52	25.6	52	12.0	31	7.5	24	6.2	29
24	27.7	51	25.7	55	12.1	35	9.7	33	7.5	28
% of Original	100.0	98.1	100.4	104	275	90	303	103		
RECOVERY										
After 24	27.7	52	25.6	53	4.2	44	3.1	29	2.8	35
% of Original	100	100	100	100	95.5	113	97	91	97	80

TABLE 4C
HFE-71DE Sealant Compatibility Test Results

	POLYSULFIDES				RTV					
	P/S880A-12		PR1436G		3140		102		162	
TIME HOURS	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A	WEIGHT-HARDNESS grams	Durometer A
IMMERSION	TEST SOLVENT HFE-71DE									
0	25.7	49	21.4	56	18.6	40	7.0	32	22.2	65
0.25	27.0	48	22.3	51	29.7	35	8.8	28	25.8	61
0.5	27.3	46	22.6	53	33.1	37	9.9	29	26.9	60
1	27.9	46	23.1	48	39.3	24	12.5	27	29.5	58
2	28.8	40	23.9	47	50.3	24	15.6	21	33.1	61
4	30.1	42	25.0	44	61.2	24	19.3	27	37.1	64
8	31.8	36	26.0	41	62.6	27	20.4	20	37.7	60
24	35.4	38	29.1	36	66.9	29	24.3	24	41.8	56
% of Original	137.7	77.5	136.0	64.3	359.7	72.5	347.1	75.0	188.3	86.2
RECOVERY										
After 24	28.6	49	23.8	53	18.3	32	7.1	31	22.3	67
% of Original	111.3	100	111.2	94.6	98.4	80.0	101.4	96.9	100.5	103.1

Test Protocol for
Evaluation of Flush Solvents For Silicone Rubber Compatibility

Two samples of silicone rubber samples were immersed in 3M's HFE-7100. At periodic intervals the samples were removed from the solvent, weighed and had durometer (conforming to ASTM D 2240) hardness (A scale) readings taken. After 24 hours of immersion the samples were allowed to recover in air for 1 hour and then were weighed and hardness readings taken. See Table 5 for test data.

Rubber Specification: ZZ-R-765, CL.2B GR.40 CMPD-5610 3/Q/88

TABLE 5

TIME HOURS	SAMPLE 1		SAMPLE 2	
	WEIGHT, grams	HARDNESS*	WEIGHT, grams	HARDNESS*
0	1.9	54	2.1	54
24 IMMERSION	2.3	49	2.5	49
% ORIGINAL	121	90	119	90
1 RECOVERY	2.0	54	2.0	54
% ORIGINAL	105	100	95	100

* Durometer Hardness, A scale

Test Protocol and Results for the Evaluation of Flush Solvents for the Compatibility with Acrylic Topcoats

SUBSTRATE: Clad 0.032 gage 2024-T3, Alodined 600, primed with MIL-P- 23377G TY1 CL C (Spraylat High Solids) and top-coated with MIL-L-81352 Acrylic (Randolph)

The above substrates were placed in samples of HFE-7100 and Vertrel SMT for a period of 24 hours. Prior to immersion of the substrates, pencil hardness readings were taken below.

TABLE 6A

IMMERSION TIME HOURS	SOLVENT **Vertrel SMT** OBSERVATIONS Pencil Hardness	SOLVENT **HFE-7100** OBSERVATIONS Pencil Hardness
0	4H	4H
24	N/A (1)	4H (2)

Pencil Hardness was taken in accordance with ASTM D 3363

NOTES

1) The Acrylic topcoat started to dissolve immediately, test stopped.

2) The Acrylic topcoat was slightly etched with no reduction in hardness.

Test Protocol and Results for Evaluation of Flush Solvents For Compatibility with Acrylic MIL-L-81352 Topcoats.

SUBSTRATE: Clad 0.032 gage 2024-T3, Alodined 600, primed with MIL-P- 23377G TY1 CL C (Spraylat High Solids) and top-coated with MIL-L-81352 Acrylic (Randolph)

TEST SOLVENTS: 3M's HFE-71DE, Petroferm's PFC 265-141 and PFC 265-173.

The above substrates were coated with a light film of MIL-H-83282 hydraulic oil and placed in a fixture holding the specimens at a angle of 45 degrees. The panels were then flushed cleaned with the test solvent. Pencil hardness readings were immediately taken at the specified intervals to check recovery. See Tables 6A and 6B for results.

TABLE 6B

TIME HOURS	SOLVENT **HFE -71DE** Pencil Hardness	SOLVENT **PFC 265-141** Pencil Hardness	SOLVENT **PFC 265-173** Pencil Hardness
BASELINE	4H	4H	4H
AFTER FLUSHING			
0+	B	4H	4H
.25	H	4H	4H
.50	3H	---	---
1	3H	---	---
2	3H	---	---
4	3H	---	---
24	3H	---	---

After one flush, the PFC 265-141and the PFC 265-173 test solvents did not degrade the pencil hardness of the acrylic coating MIL-L-81352.

After one flush, the HFE-71DE test solvent significantly reduced pencil hardness of the acrylic coating for a short period of time. Coating recovery started after flushing and recovered to a 3H hardness which was within one point of original coating hardness for the HFE-71DE flushed panel.

Test Protocol and Results for the Evaluation of Flush Solvent Compatibility with Selected Primed and Topcoated Surfaces

The purpose of this test was to evaluate Petroferm's PFC 265-141 and PFC 265-173 flush solvents and its compatibility with selected primed and top-coated surfaces. The substrates were immersed in Petroferm's PFC 265-141 and PFC 265-173 solvents. At periodic intervals the samples were removed from the solvents, pencil hardness readings were taken. The samples were then returned to the solvent. After 24 hours of immersion, the samples were allowed to recover in air and then had hardness readings taken. See Table 7 for results.

TABLE 7
PFC 265-141 and PFC 265-173 Coating Compatibility Test Results

TIME DURATION HOURS	COATING					
	MIL-P-23377		MIL-P-85582		MIL-C-85285	
	PENCIL HARDNESS		PENCIL HARDNESS		PENCIL HARDNESS	
IMMERSION	PFC265-141	PFC265-173	PFC265-141	PFC265-173	PFC265-141	PFC265-173
0	4H	4H	3H	3H	4H	4H
0.25	4H	4H	3H	3H	4H	4H
0.50	4H	4H	3H	3H	4H	4H
1	4H	4H	3H	3H	4H	3H
2	4H	4H	3H	3H	4H	3H
4	4H	4H	3H	3H	4H	3H
6	4H	4H	3H	3H	4H	3H
24	4H	4H	4H	4H	3H	3H
RECOVERY						
24	4H	4H	3H	3H	3H	3H

Test Protocol and Results for the Evaluation of Flush Solvents for Selected Electrical Connector Compatibility.

The purpose of this test was to evaluate various flush solvents and their compatibility with selected electrical fittings. Two samples of electrical fittings were immersed in the following solvents Petroferm's PFC 265-141 and 3M's HFE-7100. At periodic intervals the samples were removed from the solvents, weighted and Durometer hardness (A scale) readings were taken. The samples were then returned to the solvents. After 24 hours of immersion, the samples were allowed to recover in air and then had weight and hardness readings taken. See Tables 8A and 8B for test results.

TABLE 8A

SOLVENT HFE - 7100

IMMERSION TIME HOURS	CONNECTOR (1)		CONNECTOR (2)
	WEIGHT	HARDNESS	WEIGHT
	Grams	DUROMETER A	Grams
0	105.1	60	123.1
.25	106.0	60	124.8
.50	106.2	60	125.2
1	106.4	60	125.8
2	106.7	60	126.8
4	106.8	60	126.9
8	106.4	60	127.0
24	106.4	60	128.5
RECOVERY			
24	105.3	60	123.2
% of Original (3)	100.2	100	100.1

TABLE 8B

SOLVENT PFC 265-141

IMMERSION TIME HOURS	CONNECTOR (1)		CONNECTOR (2)
	WEIGHT	HARDNESS	WEIGHT
	Grams	DUROMETER A	Grams
0	104.8	62	123.0
.25	105.7	62	124.9
.50	105.9	60	126.1
1	106.4	62	126.7
2	106.3	62	128.5
4	106.2	62	130.1
6	106.2	62	130.8
24	106.4	62	131.7
RECOVERY			
24	105.1	62	123.0
% of Original (3)	100.2	100	100

NOTES (1) - Connector: Burndy Part Number 8441.

(2) - Connector: Deutsch Part Number DS00-61-21P-12.

(3) - Neither the Burndy or the Deutsch electrical connectors showed any signs of physical degeneration as a result of being immersed in the PFC 265-141 and PFC 265-173 test solvents.

Test Protocol and Results for the Evaluation of Flush Solvents PFC 265-141 and PFC 265-173 with respect to Marking Label Compatibility

The purpose of this test was to see the effect of Petroferm's PFC 265-141 and PFC 265-173 flush solvent on adhesive strength or degradation of air conditioning labels. The substrates were .032"x 3"x 5" 2024-T3 Clad QQ-A-250/5, Alodined 1200, Primed with MIL-P-85582 TY1 CL C (SPRAYLAT). E-2C type air conditioning labeling tape used on Grumman aircraft was applied to the above substrates, one panel was immersed in the test solvent for 1 hour and a second panel was immersed in the fluid for 20 hours. Upon completion of the test, the panels were removed from the fluid and examined. See Tables 9A and 9B for test results.

TABLE 9A

TEST SOLVENT - PFC-265-141

SAMPLE	IMMERSION TIME HOURS	OBSERVATIONS
A	1	No loss of tape adhesion between label and substrate. No visual degradation was apparent.
B	20	Slight loss of tape adhesion between label and substrate No visual degradation was apparent.

TABLE 9B

TEST SOLVENT - PFC-265-173

SAMPLE	IMMERSION TIME HOURS	OBSERVATIONS
A	1	No loss of tape adhesion between label and substrate. No visual degradation was apparent.
B	20	Slight loss of tape adhesion between label and substrate No visual degradation was apparent.

Test Protocol for the Evaluation of Flush Solvents for Irradiated Modified Polyolefin Compatibility

The purpose of this test was to evaluate Petroferm's PFC 265-141 and PFC 265-173 flush solvents and its compatibility with irradiated modified polyolefin. Three samples of irradiated modified polyolefin identified as (GS830DR1, Sleeve Electrical, Insulating, Heat Shrinkable, Non-Burning, Flexible) were immersed in Petroferm's PFC 265-141and PFC 265-173. At periodic intervals the samples were removed from the solvent, weighed and reimmersed. After 24 hours immersion the samples were allowed to recover in air for 1 hour and then had weight and hardness readings taken. See Tables 10A and 10B for results.

TABLE 10A

SOLVENT PFC 265-141

SAMPLE	1	2	3
ORIGINAL WT. Grams	1.5	1.7	2.2
IMMERSION TIME HOURS	WEIGHT, Grams		
0.25	1.5	1.7	2.2
0.50	1.5	1.7	2.2
1	1.6	1.8	2.3
2	1.6	1.9	2.2
4	1.6	1.9	2.2
8	1.6	1.8	2.3
24	1.6	1.8	2.3
% of ORIGINAL	106.7	105.9	104.5
RECOVERY			
AFTER 1 HOUR % of ORIGINAL	1.5 100	1.7 100	2.1 100

TABLE 10B

SOLVENT PFC 265-173

SAMPLE	1	2	3
ORIGINAL WT. Grams	1.5	1.7	2.1
IMMERSION TIME HOURS	WEIGHT, Grams		
0.25	1.5	1.7	2.2
0.50	1.5	1.7	2.2
1	1.5	1.7	2.2
2	1.5	1.7	2.2
4	1.5	1.7	2.1
8	1.5	1.7	2.3
24	1.6	1.8	2.2
% of ORIGINAL	106.7	105.9	104.8
RECOVERY			
AFTER 1 HOUR	1.5	1.7	2.1
% of ORIGINAL	100	100	100

Test Protocol for the Evaluation of Flush Solvents for Compatibility with Electrical Wire and Markings

The purpose of this test was to evaluate various flush solvents with its compatibility with electrical wire markings and insulation. Marked electrical wires were placed into beakers containing the test flush solvents for a period of 24 hours. At the end of the test period, the wires were removed from the flush solvents and visually examined to see if the wire markings were removed or the insulation degraded. See Table 11 for test results.

TABLE 11

FLUSH SOLVENT	TEST RESULTS
HFE-7100	NO APPARENT DEGRADATION
HFE-71DE	NO APPARENT DEGRADATION
PFC 265-141	NO APPARENT DEGRADATION
PFC 265-173	NO APPARENT DEGRADATION
DUPONT Vertrel SMT	NO APPARENT DEGRADATION

Discussion

Screening Tests

The solvent screen testing protocol included both functional testing and material compatibility testing.

Solvent Functional Screening Tests

The initial functional testing protocol included screen testing of the test solvents for the removal of MIL-H-83282 and comparing the results against Freon. As described under the section Hydraulic Oil Flushing Test, a simple flush test was devised. Solvent materials such as pure unblended HFE 7100 did not meet the criteria for hydraulic oil removal. See Tables 1 and 2 for results. Generally flushing more than twice to remove the oil was considered a failure.

It was important that the selected solvent evaporate in a reasonable time so that the aircraft could be reactivated on the production line or flight ready in short order. Four hours was considered a reasonable criteria given current St. Augustine manufacturing flow times. Both the HFE 7100 and PFC 265-141 completely evaporated in less than four hours using the test protocol as described in the Evaporation Rate Test Protocol and Results section. See Table 3 for evaporation test results.
Laboratory flash point testing was conducted to establish at what temperature the material could flash. The PFC 265-141 demonstrated a flash point of approximately 40 degrees F. The PFC 265-173 would support combustion at room temperature or approximately 70 degrees F. The ideal solvent would be one with no flash point, however, the candidate solvents with no flash points had significant problems in the area of material compatibility with the exception of HFE 7100. Given that composition of the PFC 265-141 is mostly composed of HFE 7100, a solvent with no flash point, the PFC 265-141 solvent was not considered a high risk provided proper preventive measures are taken. These measures are called out in the concluding remarks.

Material Compatibility Screening Tests

Material compatibility testing included the use of the MIL-L-81352, acrylic topcoat. The acrylic topcoat, MIL-L-81352, was used for solvent material compatibility screening tests because the acrylic topcoat is attacked by most of the aggressive solvents. Solvents such as HFE 71DE,Vertrel SMT, Vertrel MCA, did not meet the requirements for material compatibility with the acrylic topcoat. In some cases such as the Vertrel SMT, the solvent stripped the acrylic coating down to the primer in short order. See Tables 6A and 6B for test results which indicate that the Vertrel SMT and HFE-71DE degraded the acrylic coating quite rapidly.
The Petroferm solvents PFC 265-141 and PFC 265-173 did no show any signs of degradation to the acrylic topcoat. See Table 6B and Table 7 for test results.

Material Qualification Tests

In addition to passing the screening tests for qualification testing, it was important that the selected solvent not degrade typical aerospace sealant, primers, topcoats, electrical wiring, electrical connectors, and wire markings. To test material compatibility the aforementioned materials and electrical components were subjected to immersion testing in the candidate solvents for a period twenty four hours. A twenty four hour time period was selected as a base line time in order to establish a wide margin of safety for the materials being tested. The actual material exposure times during a flushing operation would be on the order of minutes, unless drainage results in some local buildup of flush solvent. Local flush solvent pocket build ups of solvent greater than .9 inches would not be expected in an aircraft structure or fuselage which is normally designed to drain water. Table 3 summarizes the evaporation rate studies and indicates that the selected solvents PFC 265-143 and HFE-7100 would fully evaporate within a four hour time frame from a pool of solvent which is up to .9 inches in depth.

A summary of all the test results can be found in Tables 4 to Table 11. Where appropriate, the criteria of weight change, Durometer hardness, pencil hardness, and visual observations were selected to measure material degradation from the initial point.

A material recovery time of 24 hours was used in most cases to establish the final material properties. All the final the final measurements of the qualified solvents were considered acceptable with in the tolerances of the test protocol given the short term exposures expected in practice.

Conclusions

Extensive testing of the candidate solvents resulted in the selection of Petroferm's PFC 265-141 solvent for the removal of hydraulic oil followed by a final flush of 3M's HFE7100. The final flush was considered necessary in order to remove the contaminated PFC 265-141 solvent from the subassembly or fuselage structure.

Since the PFC 265-141 solvent does have a flash point all aircraft being flushed must be electronically grounded, powered down, and have adequate ventilation to avoid the lower explosive limit (LEL). Monitoring for the LEL is required and performed continuously down stream. An adequate airflow sufficient to ensure proper ventilation in order to prevent a potential vapor build up is required. The threshold for cessation of application of the solvent is ten percent of the LEL. After the flushing process is complete, the final flush with HFE 7100 (no flash point) essentially eliminates the flash point as an issue from this point on.

Evaporation rate studies indicate all PFC 265-141 and HFE 7100 solvents will be essentially evaporated from the fuselage, after four hours. Hence, after approximately four hours of the final HFE 7100 flush, the E2C and/or F-14 aircraft can be returned to the production environment.

Future Work

Future work will be concentrated on obtaining a lower cost flush solvent that does not have a flash point. The future environmental solvent must be compatible with aircraft materials such as acrylic paint (MIL-L-81352) used on the E2C and F-14 aircraft, while at the same time still be able to solvate hydraulic oil.

Acknowledgments

The authors would like to acknowledge John Munyak and Richard Zants of Grumman Technological Services, Inc. Mail Stop A01-001, Bethpage, NY 11714 for their technical support during this program.

Additionally, the authors appreciated the technical support from Beth Bivins and Michael O. Monaghan of Petroferm Inc., 5415 East Coast Highway, Fernandina Beach, FL 32034, for their expertise and sample solvent formulations.

Wiltech Component Cleaning & Refurbishment Facility CFC Elimination Plan at NASA Kennedy Space Center

Steve Williamson, Bob Aman, Andrew Aurigema
Wiltech
Kennedy Space Center, FL 32899

Orlando Melendez
NASA/Materials Science Division, LO-G3-C
Kennedy Space Center, FL 32899

The Wiltech Component Cleaning & Refurbishment Facility (WT- CCRF) at NASA Kennedy Space Center performs precision cleaning on approximately 200,000 metallic and non metallic components every year. WT-CCRF has developed a CFC elimination plan consisting of aqueous cleaning and verification and an economical dual solvent strategy for alternative solvent solution.

Aqueous Verification Methodologies were implemented two years ago on a variety of Ground Support Equipment (GSE) components and sampling equipment. Today, 50% of the current workload is verified using aqueous methods and 90% of the total workload is degreased aqueously using, Zonyl and Brulin surfactants in ultrasonic baths. An additional estimated 20% solvent savings could be achieved if the proposed expanded use of aqueous methods are approved. Aqueous cleaning has shown to be effective, environmentally friendly and economical (i.e.. cost of materials, equipment, facilities and labor).

Cleaning Facilities

Cleaning Facilities are divided into Pre-Clean and Precision Cleaning. Various forms of aqueous processes have been used in the Pre-cleaning area since the beginning of the program. Traditional pre-cleaning processes started with a solvent degrease followed by exposure to a variety of aqueous based solutions that were dependent upon the material being cleaned and its configuration. At Wiltech we have replaced the traditional solvent degreasing step with a purely aqueous one so that the entire pre-cleaning process is solvent free. The pre-clean degreasing facilities consists of the following systems. System A is a 260 gallon, 27 kHz ultrasonic tank filled with a 3% by vol.) solution of Brulin 815 GD and De-Ionized (DI) water heated to 140-180 °F. The ultrasonic generators are rated at approximately 9600 watts. The tank has a separate agitation and filtration system and is used for gross degreasing. System C consists of two separate systems: a surfactant tank and a DI water rinse tank. The DI water rinse tank is a 120 gallon, 40 kHz ultrasonic tank filled with DI water.

A Hydro-Air Gun is used to remove large deposits of surface contamination in the initial stages of pre-cleaning. The Hydro-Air Gun is a hand held pressure washer type spray gun used for spraying all the parts with high velocity heated (~ 140° F) DI water. The Hydro-4000 Gross Parts Washer is a polycarbonate glove box with a hand held pressure washer type spray gun used for degreasing parts with a high velocity solution of 1.5%-3% Brulin 1990 GD and DI water.

Precision cleaning at Wiltech consists of the Cascade DI Water Rinsing system and the Recycle DI water system. The Cascade DI Water Rinsing consists of 3 adjacent 30 gallon 40/25 kHz ultrasonic tanks filled with DI water at ambient temperature or heated to140° F. The supply water is filtered with a 10 micron filter prior to entering the system. The Recycle DI water system consists of 3 adjacent 30 gallon 40/25 kHz ultrasonic tanks filled with DI water at ambient temperature or heated to 140°F. Each tank has its own adjustable flow recirculation and filtration system for high volume low pressure flow. The recirculation system contains 5 micron filters.

New Aqueous Processes

Aqueous processes have also been developed to replace the CFC-113 Dip-cleaning , CFC-113 Flush cleaning and CFC-113 Filter cleaning methods. Vigorous Manual Agitation using Zonyl and water for Particulate Sampling is being used to replace the CFC-113 dip method. Parts are manually agitated in a solution of Zonyl and water at 140° F for 3 seconds. Parts cleaned by this method include piece parts such as fitting components and small valve parts of simple and complex geometries. A comparison test using more than 900 individual items showed that the method compares favorably with the CFC-113 dip cleaning method.

A Low Pressure Impingement Sampling Method using De-mineralized (DM) water was developed to replaced the CFC-113 flush method. The method applies to exposed metal surfaces of hard metals such as stainless steel. An Aqueous Filter Cleaning and Verification method has been developed at WT-CRCA to replace the CFC-113 Flush cleaning method. Wire mesh-stainless steel filter elements were precision cleaned and validated using a combination of degreasers, high pressure sprays and ultrasonic cleaning baths. Repeated cleaning and validation showed no significant degradation to the structural integrity of the filter elements. The new method employs nylon and Aclar bags in place of canisters. In the process, new aqueous filter cleaning and validation methods exceed performance expectations and have been implemented on GSE filters with only minor difficulties. A 25% - 35% solvent savings can be achieved if this method is approved by the program.

.

Dual Solvent Approach

Wiltech is proposing a dual solvent strategy using Vertrel MCA and HFE-7100 to eliminate CFC-113 usage. Only AK-225, Vertrel MCA and HFE-7100 are being added to SE-S-0073 as CFC-113 alternatives on a compatibility level, figure 1. Figure 2 is a comparison of the effectiveness of material removal for AK-225, Vertrel MCA and HFE-7100. AK-225 is not being considered for use in our CFC elimination plan at this time because of time and cost constraints imposed by facility modifications, strong toxicity concerns and currently mandated phase out of AK-225.

PROPERTY	*CFC-113*	*AK-225 **	*VERTREL MCA*	*HFE-7100*
Boiling Point - °C	48	54	39	60
Surface Tension - Dynes/cm	17.3	16.2	15.2	13.6
Vapor Pressure mmHg@20 C	331	290	375	210
Liquid Density	1.56	1.55	1.41	1.52
Solubility of H2O (ppm by wt)	110	420	490	95
Solubility in H2O (ppm by wt)	170	210	140	10
8 HR Exposure Limit (ppm)	1000	50	200	600
Category	CFC	HCFC	HFC	HFE
Ozone Depletion Potential (Max=1.0)	0.8	0.03	0.0	0.0
Global Warming Potential	High	Lo	Lo	Lo
Flammable	No	No	No	No
Auto Ignition Temperature Issue	No	No	Yes	No

** Scheduled for phase out in 2015; may be accelerated. Exposure limits may be lowered due to recent exposure incidents involving HCFC's..*

	Contaminant, Percent Removed					
FLUID	**DC-33**	**Braycote 601**	**Mil-H-83282**	**Mil-H-5606**	**Houghto-Draw**	**Titanlube**
None	3	0	0	78	0	1
CFC-113	80	91	100	100	100	100
AK-225	85	87	100	100	100	16
Vertrel MCA	60	12	100	92	100	51
HFE-7100	16	85	34	86	1	4
Dual Solvent Strategy ***(Vertrel MCA & HFE-7100)***	60	85	100	92	100	51

- Table reflects data extracted from BNA Laboratory Test Report, LTR 6887-4097, with the exception of the Dual Solvent Strategy data which is a combination of the solvency data of both the Vertrel MCA and the HFE-7100.

The Dual Solvent Strategy consists of using Vertrel MCA outside of the clean room where facility costs and exposure concerns can be minimized. Non Volatile Residue (NVR) verification can be performed with Vertrel MCA outside the clean room relieving medium to heavy hydrocarbon contamination concerns. HFE-7100 will be used for the verification fluid in the clean room for both particulate and NVR (Light Hydrocarbon Contamination). Aqueous

cleaning and verification techniques will continue to be employed whenever possible. Items being certified to an "A" Level NVR will be tested as follows: items solvent degreased and solvent verified will be NVR tested twice, once with Vertrel MCA in preclean and again with HFE-7100 in the clean room. Items aqueously degreased and solvent verified will be NVR tested once with HFE-7100 in the clean room. Suitable items may be completely processed aqueously and tested for NVR using the Total Organic Carbon (TOC) method.

The proof of concept will consist of defining Manpower and Equipment Requirements, selecting and testing the hardware, building a Test Plan and performing the Tests. The hardware will consist of complex parts with internal passages including dead-end bourdon tube gages Teflon lined flexhoses
convoluted flexhoses, Valve Assemblies, Quick Disconnects complex parts with no internal passages such as Omni Seals and Swivel fittings and simple parts with all surfaces exposed simple fittings softgoods.
The Test Plan consists of the following: Test solvent flush, flow and dip methods against appropriate test hardware start with a certified clean test specimen, contaminate the test specimen, clean the test specimen with the dual solvent process to level 100A, perform a rinse analysis with CFC-113 and compare the results to level 100A
test Both the Solvent-Solvent and the Aqueous-Solvent Plan

Elimination of Methyl Ethyl Ketone for Removal of Tenacious Contaminants

by
Catherine Clayton
USBI Co.
P.O. Box 21212
407-853-0523
Kennedy Space Center, Fl 32815

Mike Mason
USBI Co.
P.O. Box 1900
256-544-2789
Huntsville, Al 35807

Introduction

Over the last eight years, there has been a shift in environmental compliance methodology. That shift is from an "end of the pipe" strategy to one of prevention and elimination. This is especially true of the aerospace industry. EPA has classified MEK and toluene as hazardous air pollutants and has regulated the use of MEK and toluene in the aerospace industry through the Aerospace Manufacturing and Rework National Emission Standards for Hazardous Air Pollutants (NESHAPs). Although the Space Shuttle has been exempted from these regulations, USBI has taken a proactive stance in eliminating the use of MEK and toluene.

USBI is responsible for design, acquisition, assembly, test, and refurbishment of the nonmotor segments of the Space Shuttle Solid Rocket Boosters (SRB's) (1). In 1995, USBI replaced 1,1,1- trichloroethane, xylene, and perchloroethylene with more environmentally friendly cleaners for hand wipe cleaning operations. Although the new cleaners were compatible with the surfaces being cleaned, they were unable to remove the more tenacious contaminants. MEK and toluene continued to be used for removal of these tenacious contaminants. Since MEK and toluene are both hazardous air pollutants, USBI has sought to replace these cleaners with one or more cleaners that can remove the contaminants without significantly affecting the surface.

Test Matrix and Variables

The first step in finding alternatives for MEK and toluene was to select the variables to be used in the test program. The activity included a vendor survey and determination of the various substrates and contaminants. There are considerably fewer surfaces cleaned with MEK and toluene than with the present general hand wipe cleaners. Fifteen surfaces were selected for testing. See Table 1. The specific alloys and coatings listed below were chosen to represent the respective surface types on the SRB's which require hand wipe cleaning with MEK and toluene.

Table 1. SRB surfaces Selected for Testing

304 Stainless Steel	Briner Primer
4130 Low Alloy Steel	Briner Topcoat
2219 Aluminum	Crown Metro (443-3-1)
Inconel 718	Urethabond (3015 Mod 4)
Deft Primer (44-GN-7)	Carboline Primer
Deft Topcoat (03-W-127A)	Carboline Topcoat
Hypalon (HFR-2100)	Rust-Oleum Topcoat
Rust-Oleum Primer	(93-9525 white)
(zinc-sele 9334 green)	

Contaminants currently being removed by MEK and toluene may be found in Table 2. The contaminants, and the surfaces where they occur, are listed in the hand wipe cleaning requirements document.

Table 2. *Contaminants Selected for Testing*

Grease Pencil	PR1422 (partial cure)	Ink/Part marking
Loctite 410	PR 1770 (partial cure)	Ink/Sharpie
608 Epoxy	PS 870 (partial cure)	Ink/Machinist
EA 934 (partial cure)	RTV-60 (partial cure)	Deft Primer (over-spray)
Krylon (Clear)	Rubber residue (Neoprene)	Deft Topcoat (over-spray)

Candidate cleaners were identified through papers, corporate committee meetings, and conferences. After reviewing technical data sheets, Materials Safety Data Sheets (MSDS), and technical discussions with the vendors of over fifty-five cleaners, twenty-five cleaners were chosen for testing. See Table 3.

Table 3. *Cleaners Selected for Testing*

Cleaner	Vendor	Cleaner	Vendor
Acetone	per O-A-51	DS-104	Dynamold Solvents inc.
Tarksol HTF-60	Solvent Solutions	DS-108	Dynamold Solvents inc.
Tarksol HTF-90	Solvent Solutions	Safe Strip	Ecolink
Tarksol HTF-90 gel	Solvent Solutions	Positron	Ecolink
UBIX-0075	Enzymes Plus	NMP	ARCO Chemical
UBIX-0092	Enzymes Plus	Prepsolve	Ecolink
EP-921	Inland	Paint Remover-L	Huntsman
Foam Flush	International Specialty Coatings	ATTAR-C	Delta-Omega Technologies, inc.
FSX-3	Baragamo Corp.	FO 425 Q	Fine Organics
Ship Shape	International Specialty Coatings	Oxsol 100	Occidental
X-Caliber	Inland	Oxsol 10	Occidental
Enviosolve 655	Fine Organics Corp.	CT-320	Chem Tech International, inc.
PF-d'Ink NF	PT Technologies		

Methods

The MEK Replacement project consisted of three phases: screening, qualification, and implementation. Figure 1 shows the over-all methodology of the project.

Phase I, the screening process, included dry time determinations and performance evaluations of cleaners. Dry time testing was necessary to determine the length of time needed for dissipation of a candidate cleaner between surface cleaning, including dry wiping, and beginning the next process. Establishment of a cleaner's dry time parameters was needed before further testing could be conducted. The dry time was determined gravimetically, the length of time the weight of a cleasned coupon to reach equilibrium.

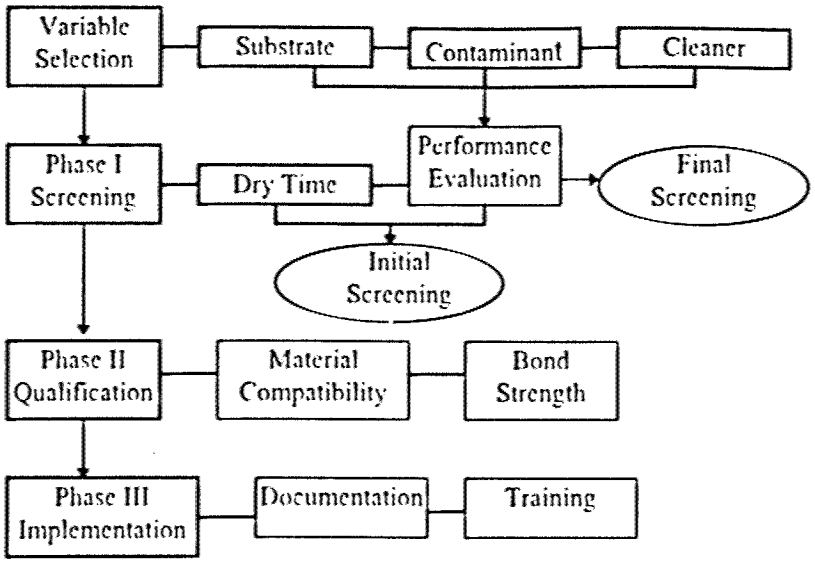


Figure 1. Project Flow Chart

Performance evaluation testing determined the cleaning ability of the candidate cleaners. This test measured the amount of residue left on a substrate coupon after applying a contaminant, then cleaning the coupon with a candidate cleaner. The residue was measured gravimetically. The coupon surfaces and contaminants are listed in Tables 1 and 2 respectively. MEK and toluene were used as controls in each set of three tests. Screening of the candidate cleaners took place throughout the dry time and performance evaluation testing. During initial screening, five cleaners were chosen for continued testing. The initial screening included test data evaluations and a second scrutiny of the chemical composition and hazards of the cleaners. By the end of Phase I, final screening of the cleaners was accomplished. The final screening included test data evaluations, worker safety, and environmental impact of the cleaners. Two cleaners were chosen for qualification from the final screening.

Phase II of the MEK replacement project was the qualification of the candidate cleaners for use on SRB hardware. This portion of the project included compatibility and bond strength testing. Compatibility of the candidate cleaners was determined for the substrates listed in Table 1. The metal surfaces were tested for compatibility using ASTM F 483 - 90: "Standard Test Method for Total Immersion Corrosion Test"(7) and ASTM F 1110: "Standard Test Method for Sandwich Corrosion Test"(4). There was a slight overlap in the beginning of Phase II and the end of Phase I, final screening of the candidates. Therefore, five candidate cleaners were tested, instead of two in the Total Immersion Corrosion test. The painted surfaces were tested for compatibility using ASTM F 502 - 83: " Standard Test Method for Effects of Cleaning and Chemical Maintenance Materials on Painted Aircraft Surfaces" (2). MEK and toluene were used as controls in all compatibility testing.

Bond Strength testing was conducted to determine if the candidate cleaners would have any adverse affects on the bond strengths of adhesive systems, thermal protection systems (TPS), or coating systems used on the SRB's. To determine any possible effects which the candidate cleaners might have on the adherence of coating systems, tests were conducted per ASTM D 4541-85 "Standard Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers" (3). To determine any possible effects which the candidate cleaners might have on the adhesive and TPS systems, flatwise tensile and lap shear testing were conducted. Lap shear testing was conducted per ASTM D 1002-72: "Standard Test Method for Strength Properties of Adhesives in Shear Tension Loading (Metal to Metal)" (5). Lap Shear testing was conducted using Scotch-Weld 2216 adhesive and RTV 133 sealant for material-

to substrate bonds. The flatwise tensile tests were conducted per ASTM D 1623: "Standard Test Method for Tensile and Tensile Adhesion Properties of Rigid Cellular Plastics" (6). Flatwise tensile tests were conducted to evaluate bond strengths of Marshall Convergent Coating 1 (MCC-1), Booster Trowelable Ablative (BTA), Cork, K5NA, PR-1422 (a polysulfide sealant), Insta-Foam, and Scotch-Weld 2216 epoxy. Tests were conducted at room temperature and at an elevated temperature of 150 degrees, Fahrenheit. In addition, some flatwise samples were contaminated with grease pencil prior to use of the cleaners. To evaluate long term exposure, flatwise tensile testing was conducted using Scotch-Weld 2216 epoxy after six months and after twelve months of exposure to a production environment. MEK and toluene were used as controls for all tests.

Results

In this project, the cleaners were chosen for their ability to remove inadvertant coatings, adhesives and other tenacious contaminants. Due to the cleaners ability to remove paints and other tough contaminants, some also attacked the paints being cleaned. All cleaners tested had relatively short dry times when used on bare metal. However, on coated systems, the dry times were much longer Some cleaners soaked into the coating and would not readily dissipate. N-methyl pyrrolidone and cleaners containing N-methyl pyrrolidone are examples of these types of cleaners. A fine line had to be found between removing the contaminants and not significantly harming the coatings.

Overall, most of the cleaners removed the contaminants tested as well as MEK and toluene. However, some cleaners were eliminated for their inability to remove contaminants. Five cleaners were chosen from the initial screening of the candidates. Those cleaners were: Paint Remover-L, HTF-60, DS-104, X-Caliber, and acetone. Two cleaners were chosen in the final screening of the cleaners. They are DS-104 and acetone.

Results of the Total Immersion Corrosion tests indicated that the metal surfaces were not affected by DS-104. Acetone was already an approved cleaner for use on the SRB hardware, and therefore, was not included in the compatibility testing. Results of the Sandwich Corrosion tests indicated that DS-104 was comparable to MEK and toluene. DS-104 was compatible with all of the coating systems with the exception of Briner topcoat. All cleaners tested, including MEK and toluene, significantly damaged the Briner topcoat. This coating is not yet approved for use on SRB hardware.

In the bond strength evaluation portion of the cleaner qualification, acetone was included to expand the database on that cleaner. DS-104 and acetone showed no detrimental effects to any of the bondlines tested.

Conclusions

The MEK replacement task successfully identified and qualified cleaners for the replacement of MEK and toluene. Of all the cleaners tested, two cleaners, DS-104 and acetone, passed all pre-qualification testing. DS-104 passed qualification for use on SRB hardware. Although, acetone was already a qualified cleaner for the SRB program, this project has shown that acetone was able to remove some of the more tenacious contaminants.

The implementation portion of this project will include assigning the right cleaner for specific contaminant removal processes. In many cases, either cleaner can be used. Additionally, implementation will also include changing all hand wipe cleaning requirements documentation and ensuring all employees are versed in the use of the new cleaners.

References

1. Clayton C. P. and Kovach M. P., "Environmentally Compatible Hand Wipe Cleaning Solvents," *Aerospace Environmental Technology Conference*, Huntsville, Al. 1994, pp. 491-498.

2. "Standard Test Method for Effects of Cleaning and Chemical Maintenance Materials on Painted Aircraft Surfaces," ASTM: D 502-83, *Space Simulation; and Aircraft; High Modulus Fibers and Composites*, Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 504-505.

3. "Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers," ASTM: D 4541-85, *Paints, Related Coatings, and Aromatics*, Section 6, Vol. 06.01, ASTM, Philadelphia, PA. 1992, pp. 791-797.

4. "Standard Test Method for Sandwich Corrosion Test," ASTM: F 1110-90, *Space Simulation; and Aircraft; High Modulus Fibers and composites*, Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 627-629.

5. "Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal to Metal)," ASTM: D 1002-72, *General Products Chemical Specialties and End-Use Products*, Section 15, Vol. 15.06, ASTM, Philadelphia, PA. 1993, pp. 59-63.

6. "Standard Test Method for Tensile and Tensile Adhesion Properties of Rigid Cellular Plastics," ASTM: D 1623, *Annual Book of ASTM Standards for Plastics Section 8*, Vol. 8.01, ASTM, Philadelphia, PA. 1993, pp. 494-499.

7. "Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals," ASTM: F 483-90, *Space Simulation; and Aircraft; High Modulus Fibers and composites*, Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 491-494.

Contamination Control Changes to the Reusable Solid Rocket Motor Program—A Ten Year Review

By

David M. Bushman, NASA Resident Management Office at Thiokol Propulsion
Robin J. Elliott, Thiokol Propulsion
P.O. Box 707 Attn: NASA K68
Brigham City, UT 84302

Abstract

During the post Challenger period, NASA and Thiokol implemented changes to the Reusable Solid Rocket Motor (RSRM) contract to include provisions for contamination control to enhance the production environment. During the ten years since those agreements for contamination controls were made, many changes have taken place in the production facilities at Thiokol, and these changes have led to the production of much higher quality shuttle solid rocket motors, and improved cleanliness and safety of operations in the production facilities. The experience in contamination control over this past decade highlights the value these changes have brought to the RSRM program, and how the system can be improved to meet the challenges the program will face in the next ten years.

Introduction

In 1987 NASA drafted a change to its contract for the Space Shuttle solid rocket boosters to "incorporate solid rocket motor process control requirements" (CO 966). This included contamination control, inspection and verification requirements. The implementation of these changes, known collectively as Change Order (CO966), started in 1988.

This paper will explore the contamination control tools implemented under CO966. To begin, an effort is made to understand contamination and contamination control. Highlights of CO966 changes are reviewed and findings from evaluating these changes are discussed. Finally recommendations are made in the conclusions concerning the development and implementation of contamination control.

Contamination

What is contamination?

Just about everyone has a opinion on the definition of contamination. According to Webster's Dictionary, contamination is defined as an unwholesome or undesirable element that makes something unfit for use (Webster). This definition actually captures the essence of the concern with contamination—that is when some undesirable material, the contaminant, finds it way into a material or onto a surface that can adversely effect the product. Certainly an unwholesome inclusion in a production material could preclude its use. Foreign material such as grease, dust, or other surface contaminants can adversely effect bonding. One important concept not included in Webster's definition is the quantity of contamination. For example, low levels of dust may not be a concern at all for bonding—in fact some tests have shown that low levels of dust may actually enhance the performance of some bonds (TWR-18229).

Not only can a contaminant make something unfit for use, it can negatively affect the fabrication as well as the performance of a product. Just as important as avoiding the rejection of a part due to contamination, the degradation in the performance of a part or material, even if it still meets requirements, is still undesirable and is a contamination issue. Some parts that are contaminated may be cleaned of contamination and rendered useful. This process however requires additional time, resources and should be avoided through contamination control.

In addition each system, or even each application, often has its own unique set of contaminants. A definition of contamination for shuttle solid rocket motors could be written as undesirable elements in sufficient quantity to adversely effect a product or process.

Contamination Control

Furthermore, from a quality perspective, which is necessarily conservative, the definition of contamination is any indication of an item foreign to the part or process which is not known to be benign. This means that when something unusual is discovered in a material or product, quality will assume it to be a contaminant and treat it accordingly, until it is proven to be otherwise. For example, clumps in insulation often turn out to be nothing more that odd-looking pieces of asbestos, where asbestos is a normal ingredient of insulation rubber. This is important because proper contamination control can reduce the number of "false alarms" and the associated investigation work by minimizing the list of potential contaminants.

Contamination can affect the appearance of the product, its performance, or both. When certain standards for appearance and performance for a product exist, contamination problems increase the rework or rejection of those products. For example, there are important appearance characteristics for the paint on the outside of the solid rocket boosters, and an uncontrolled contaminant that changes the appearance of the paint would generally require rework to reproduce the expected appearance of the booster.

A far more significant issue however, is that in the highly controlled production environment where the shuttle's solid rocket motors are made, contamination creates an increase in the level of uncertainty in the proper fabrication and eventually in the performance of the booster. Because the shuttle is a manned system, significant effort is made to minimize uncertainty and risk to enhance crew safety. Such an extensive effort would not be required on an unmanned system. In a complex system like the Space Shuttle, uncertainties cannot be eliminated, but are controlled in order to limit risk of failure to acceptable levels. When uncertainties are introduced by the discovery of contamination in the fabrication of the product, it becomes more difficult to analyze the risk factors, and efforts to do so can be expensive and time consuming.

An example of this problem is silicone. Silicone is used throughout the manufacturing world as a release agent. Obviously introducing a silicone release agent into a process (such as the bonding of rubber insulation to the metal cases) increases the possibility of a bond failure, and thus increases risk. Consequently, a moratorium on the use of silicone in any area where it could reach a bonding surface was imposed. Before long, testing showed silicone was nearly ubiquitous in the RSRM manufacturing environment. It was found on the gloves used to protect hardware from workers hands, in the brushes used to apply adhesives, on tapes used to mask parts, and even in the insulation itself as part of its manufacturing process.

What can be done? Steps can be taken to remove silicone from everything before it reaches the production floor. This was done with brushes and some other support items (used as a manufacturing aide). This approach was of limited use because the silicone found in the production materials could not be easily removed. Attempts were made to procure silicone free materials and products. This approach proved to be of limited success because silicone was used throughout industry to manufacture many products (brushes for example) and silicone free versions were not available. Another approach is to run a battery of tests for each item to determine if any silicone found had adverse effects on the appropriate bonding operations. The problem, however, was that each time a vendor changed their product, or a new vendor was selected, a new battery of tests would have to be run to test for the presence of silicone and its effects. The last approach is to perform an extensive array of tests to determine generically the sensitivity of each bonding operation to silicone. This would determine at what levels silicone adversely affected bonds, and manufacturing limits could be set to control to those levels. After this, tests performed at shipping and receiving would help ensure that silicone contamination found on new materials and products did not exceed safe levels.

Change Order 966 Implementation

Change Order 966 implemented modifications to facilities and processes to enhance the ability to monitor and control contamination in the production facilities. A portion of these changes was geared to make the facilities cleaner with improved control of the environment. Other changes refined cleaning and procedures to create a more consistent process and product. Tools to inspect and verify production processes were also added to ensure process and product integrity are maintained.

As a result of CO996 the following changes were adapted into the program.

Cleaning Facilities

Prior to implementing contamination control changes, the facilities were thoroughly cleaned inside, including cleaning rafters, floors, and walls. This cleaning removed layers of dirt and debris that had accumulated since the buildings were built for other programs.

Planning now requires that an annual cleaning of overhead structures take place to clear away any dust or debris that may have accumulated during the year.

Foreign Object Control

In addition to the annual cleaning, care is taken to ensure fasteners and other objects that could potentially get loose are secure in their proper place. In addition to the annual inspection, procedures in critical bonding areas require crews to examine all equipment directly over a bonding operation for loose or missing screws. The same inspection is done following the bonding process to ensure no foreign object (like a screw) got loose in the area during operations.

In addition, people in bonding areas are required to wear smocks and hairnets, empty pockets and remove jewelry. In some cases, personnel must wear Tyvek suits (coveralls made of tear resistant material) over their clothing.

Door Closure

Perhaps the first effort to control contamination in RSRM production was to close the facility doors. This may sound obvious, but previously outside doors remained open to allow air to circulate throughout the building. This was done primarily to keep the facilities cool and to vent vapors—which allowed outside debris inside.

To facilitate the shipment of hardware and materials in and out of the facilities, airlocks were established to control the movement of outside air into the facilities.

In addition, inside roll up doors were added and requirements were put into the planning to only open doors when hardware was moved from one area to another. This helped control airborne particulate from moving across areas—like grit blast dust migrating to bonding areas.

Sealing of Floors

Prior to the contamination control effort, the floors in the facilities were made of bare, finished concrete. To help control contamination, the floors were sealed with an epoxy coating. This coating sealed the small pores and cracks in the concrete and eliminated the chipping and deterioration inherent to concrete. The coating also provided a smooth, contiguous surface. This allowed for easier cleaning and improved air bearing operation (used to move hardware around). The new floor coating was lighter and more uniform in color. This significantly improved the lighting conditions and made it detect contamination and clean spills.

Floor Sweeps

To help keep the floors clean and particulate levels down, floor sweeps were procured and planning was added to have the floors cleaned on a regular basis. This was originally to be done daily, but in some cases it was done every shift. Over time however, floor cleaning is done on a less frequent basis.

HVAC

Once the production personnel were required to close the doors, it was clear that temperature in the buildings would rise. A heating, ventilation, and air conditioning (HVAC) system were installed with HEPA filters to reduce the size and amount of particulate that entered the facilities. The HVAC system has not only kept the building comfortable for manufacturing personnel, the system has also provided greater control year round of the temperature which has provided a more uniform environment for production. It has also provided a somewhat limited control on humidity as part of the air conditioning system operation. The system, as mentioned, also reduced the particulate level by cleaning the air that entered the facility.

The HVAC system was designed to replenish the air in each area every ten minutes. This air exchange limits the effect a "particulate event" would have on a facility to ten minutes or less.

Controlled Operations Requirements

The primary concern has been to control contamination in bonding areas and during bonding operations. Extra controls were established to ensure a clean environment in the immediate vicinity of bonding operations. These include cordoning off bonding areas and limiting access to select personnel; often requiring the use of tacky mats, gloves, hair nets, empty pockets, no jewelry, Tyvek suits and booties, and tool and material accountability. There are also particulate monitors that will be discussed later that have blue lights to warn crews when particulate exceed a preset level. If a blue light activates, then the bonding crew needs to investigate the cause and take care of it before starting a bonding operation.

Contamination Control Teams

An important element of controlling contamination is the participation of personnel at all levels in following contamination control practices. To elevate contamination issues to level visible throughout the program, Thiokol established a contamination control team (CCT). The team addresses contamination issues from all areas of production and ensures that relevant information is shared between the different manufacturing facilities. The CCT also evaluates proposed actions or changes that may cause or effect contamination. The team gives a semiannual report to management to status contamination activities and issues.

In addition to the CCT, work centers also establish local contamination control groups to monitor and address local concerns. These teams meet regularly to address cause and corrective actions from discrepancy reports, to provide contamination control training, and to perform periodic contamination audits of their work areas.

Hand Cleaning

Although hand cleaning was performed prior to CO 966, the process was standardized and incorporated in production planning to ensure parts were cleaned uniformly and consistently. Hand cleaning is done with a solvent, typically 1,1,1-trichloroethane (methyl chloroform), commonly referred to as TCA, and a lint free cloth made of cotton or polypropylene fibers. The hand wipe procedure is available throughout the processing of RSRM hardware and is used if the hardware has not been cleaned for 144 hours, or as needed to clean contaminated areas. To clean and prepare rubber surfaces for bonding, methyl ethyl ketone (known as MEK) is used.

TCA is listed as ozone depleting compound, therefore its use requires an essential use waiver and its availability is greatly restricted. Work is underway to find an acceptable, environmentally friendly substitute for TCA.

Vapor Degreaser—Spray-In-Air

The vapor degreaser was used to remove grease and contaminants from the bare metal surfaces. Grease was used to protect the bare metal from contamination and from rusting. This process also removed grit blast residue. The degreaser provided a final cleaning before bonding.

Because it used TCA, the vapor degreaser was recently replaced with a spray-in-air (SIA) cleaning system that uses a hot, high-pressure water based solution to clean the cases. Also, instead of covering the cases with grease when shipping them to the insulation lining facility (as was previously done), new environmentally sealed segment shipping containers were made that protect the hardware during shipment. This eliminated the major use of grease and reduced the need to vapor degrease hardware. The SIA effectively cleans the metal surfaces, but there have been problems with flash rusting that creates stains on the case surfaces. These stains are now being removed by hand, but glass beading is being considered as an alternative method for stain removal.

Witness Panels

One of the most significant changes to the program from CO966 was the addition of the witness panel program. This program creates panels that are processed along with the hardware and replicate as close as possible the processing the hardware goes through, including using the same materials. Some of the panels are then subjected to various tests to ensure a bond strength that meets engineering requirements and performs within historical limits. Other panels are put into archive and reserved in case they are needed for later testing. This program has been very useful in verifying that parts are consistently produced to requirements, to identify deviations in materials and processes, and to evaluate what to do with discrepant parts. These tests are destructive and allow for an accurate prediction of the actual hardware's performance.

Pull Tests

Pull tests are also very valuable because they directly test the performance of the flight part itself. The pull test on the floor plates for the systems tunnels is an example of a direct test on the flight hardware. After the floor plates are attached to the motor, they are mechanically pulled to a predetermined level to ensure that they meet the minimum strength requirements. While pull tests are valuable because they give direct measurement of a bond's strength, there application is limited to tests that will not damage the hardware tested..

Statistical Process Control

An important part of CO966 is the collection of data. Data is gathered from various processes and used to develop a historical database for statistical process control (SPC). As sufficient data are gathered on a process, upper and lower SPC limits are established to flag personnel when something shifts too far from what is expected from the historical data.

Particulate Monitors

To keep track of particulate levels in bonding areas, particulate monitors were installed. The monitors continuously tracked particulate levels at and above 5 micron in size; testing showed that smaller particles did not cause a problem with bonding. Alarm levels were set for each monitor to alert crews with

99a flashing blue light that particulate levels have risen above normal background levels. Crews would then identify the source of elevated particulate, take corrective action, and when done, resume operations. Data from the monitors were also collected and archived via a computer system to provide historical records of area levels.

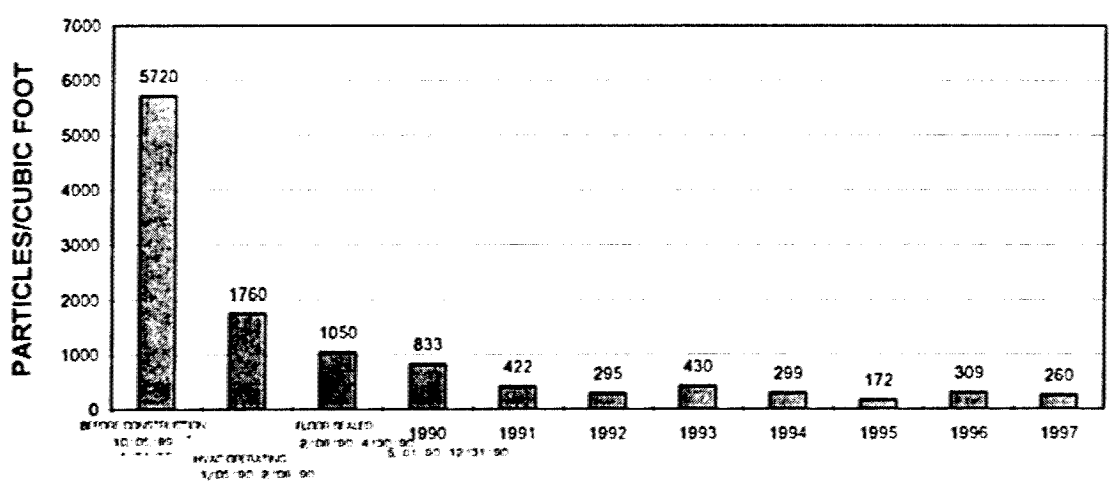
Over time additional environmental characteristics were added to the monitoring effort. These are items that typically have been identified to have an influence on certain processes. Humidity and temperature are two examples.

Conscan Inspection

Conscan stands for contamination scanning, but the technology is known as optically stimulated electron emission (OSEE) which uses a UV light to stimulate photo-emission of electrons from the surface of the material --typically a steel casing. These emissions are detected and measured. The value of the current measurement determines the cleanliness of the surface. Anything that effects the surface also effects the Conscan reading. Conscan therefore fills a niche and detect things that other inspection methods like visible and black light inspections do not. Conscan however also picks up non-contaminants. These non-contaminants include allowable levels of oxidation, and even changes in the angle that the grit blast impinged on the case. Since Conscan picks up both contaminants and non-contaminant variations, Conscan works best as a process control tool to monitor changes in the way hardware is produced.

Findings

The initial steps taken to improve facilities made a significant difference in both contamination control and production. The changes included the initial building cleaning, sealing the concrete floors, adding and closing doors, and installing HVAC systems with HEPA filters. These changes provided a clean work environment with improved lighting and environmental control. Work crews also benefited from the clean, environmentally controlled environment, and the focus on cleaning up the facilities led to improved work practices and habits which aided in maintaining the cleanliness of the facilities. Figure 1 illustrates how particulate levels showed a marked decrease with the facility improvements.



AVERAGE PARTICULATE LEVELS
FIGURE 1

One of the most significant contributions of CO966 was the creation of witness panels and pull tests. Unlike other components of the Shuttle program, like the orbiter and the liquid engines, that are tested at component and system levels, there is no way to directly test and validate the performance of the solid rocket motor outside firing it on the pad. Some components, like the igniter, are statistically tested by firing one igniter from each manufactured lot. Again, this is a destructive test that uses up a part, not a direct test on the components that will fly. The systems tunnel pull test is a rare opportunity to directly test a bond on flight hardware. Witness panels provide an excellent alternative to direct testing of flight hardware by processing them along with hardware to represent the hardware in destructive tests that verify the motors are indeed built as they are supposed to be, and therefore should perform as expected. This verification provided by witness panels is not only key to sustaining production rates, but also an indispensable tool in resolving discrepancies that occur in the course of building hardware.

The standardization of processes, such as hand cleaning, has made an important contribution to the program. By standardizing procedures and processes, manufacturing improved the repeatability of parts and activities that reduced variability between operators, established expectation standards for what the part is supposed to look like, and simplifies production scheduling. Currently efforts are being made to further clarify processes by eliminating discrepancies between engineering requirements, production planning, and actual production practices to ensure that parts are fabricated in compliance with manufacturing and engineering requirements, and that compliance can be verified through inspection. This lends itself to streamlining of manufacturing and inspection, and simplifies verification. This also reduces opportunities for contamination and error. Statistical process control was also incorporated to collect data to monitor and understand the manufacturing processes. Limits are set to reflect normal operations, normal materials, and normal conditions. When these values are exceeded, an investigation is triggered to determine why there is a shift from what is expected. The particulate monitors also play a key role in monitoring and understanding the particulate levels in production areas.

Inspection and cleaning techniques that have been added have increased confidence in the cleanliness of the hardware to ensure consistent acceptable results (such as bond strength). Prior to the addition of conscan inspection, black light and white light inspections were performed. These were effective inspection methods for surface cleanliness, but they were not complete—there were some potential contaminants that were not identified with these methods alone. Conscan filled in the gap by detecting any change to the surface (case or nozzle hardware). The drawback is that conscan will detect allowable changes to the surface as well, such as allowable levels or rust or dust, or a change in the angle of grit blasting. Because of this sensitivity, conscan has become an excellent device to detect changes in production, which lends itself to SPC limits on hardware conditions to ensure the process remains the same.

Initially, there was cautious compliance from the production crew for contamination control because it meant the control of debris that used to blow into the facility. The crews obviously benefited from stopping the dust and eliminating the debris, and from the HVAC system that cleaned the air and regulated to some degree the temperature. The sealing of the floors provided also benefited the crew by brightening up the work areas. With direct benefits to the personnel in the work areas, it was obvious that they would be supportive of contamination control.

Not all contamination efforts were perceived positively. For example, a decision was made to incorporate a blue light warning system with the particulate monitors to alert crews when particulate levels picked up. The blue lights were purposely set at levels to activate several times a week to remind crews to keep their work areas clean. When the monitors activated, however, crews had to drop what they were doing, determine what caused the problem, resolve the problem, reset the monitors, and record the information—all before they could resume their work. It didn't take long before the effort to use contamination control equipment to enforce work area cleanup backfired. This was especially true when the blue lights repeatedly activated during normal operations such as moving hardware around on air bearings. Because of the numerous false alarms, crews often discounted the blue light warnings in order to do their work. Because these warning lights were connected to the contamination control equipment, work crews developed a negative attitude toward contamination control, even though the issue in the aforementioned case was work area cleanup.

Recently management has taken a renewed interest in contamination control and efforts are being made to re-educate the work force on contamination control and its implementation. Contamination work teams have formed involving production workers, and interest and effort in contamination control have been renewed in some areas. This paper is part of this renewed interest and efforts to control contamination.

While the initial goals that were explicitly spelled out in CO966 were quickly and effectively implemented, the underlying purpose of reducing uncertainty by controlling contamination was not as obvious. This is because it is easier to complete goals with explicit steps than general goals like "make the product better."

Perhaps the greatest challenge in evaluating the success of CO966 was finding an appropriate "measuring stick." While it is clear that the initial implementation goals were readily achieved, finding a means to measure their long-term impact proved difficult. Without a clear overall long-term goal derived from CO966, each area based their efforts upon their interpretation of the long-term needs. A clear, long term objective at the beginning would reduce the dilution as each area pursued their understanding of contamination control.

Conclusions

- Contamination control efforts should have clear long term goals that can be translated by organizations and individuals into short-term goals.
- The involvement of personnel, from the production line to the management leadership must be incorporated and maintained into the effort —everyone must understand the value of the effort, what contribution is expected from them, and what the benefits will be to them and the company.
- Use contamination control to reduce uncertainties in manufacturing processes by minimizing sources of contamination and by creating an environment that supports the identification of contaminants.
  - eliminate sources of contamination
  - know what is in the facility
  - understand how contaminants effort processes and products
- Use statistical process control to establish a history of operation to identify shifts in production or products
- With an accurate understanding that contamination control is a win/win situation - the customer has increased confidence in the product and the producer has greater value to the customer - communicating concerns will be a team effort with both sides eager to improve.

References

1. NASA Change Order 966, 1987
2. Webster's 9th New Collegiate Dictionary, 1984
3. Whitworth, C., SRM Bonding Contamination Study-Interim Report, Thiokol Wasatch Report (TWR)-18229, pages 12-18

DEVELOPMENT AND IMPLEMENTATION OF ENVIRONMENTALLY COMPATIBLE SOLID FILM LUBRICANTS

Howard L. Novak
USBI Co.
P.O. Box 21212; USB-IRD
Kennedy Space Center, Florida 32815

Phillip B. Hall
National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Department EH-14
Marshall Space Flight Center, Alabama 35812

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. Future launch systems 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 trade 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. 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.

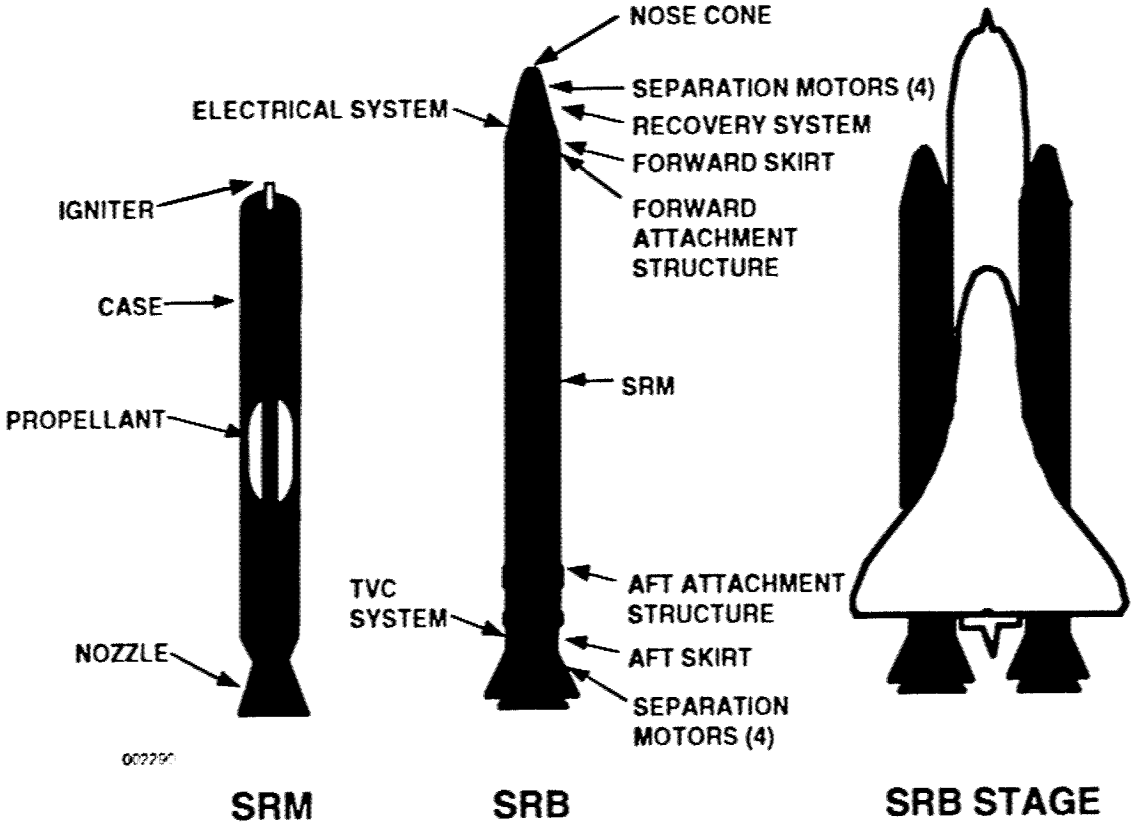


Figure 1. Space Shuttle's SRB

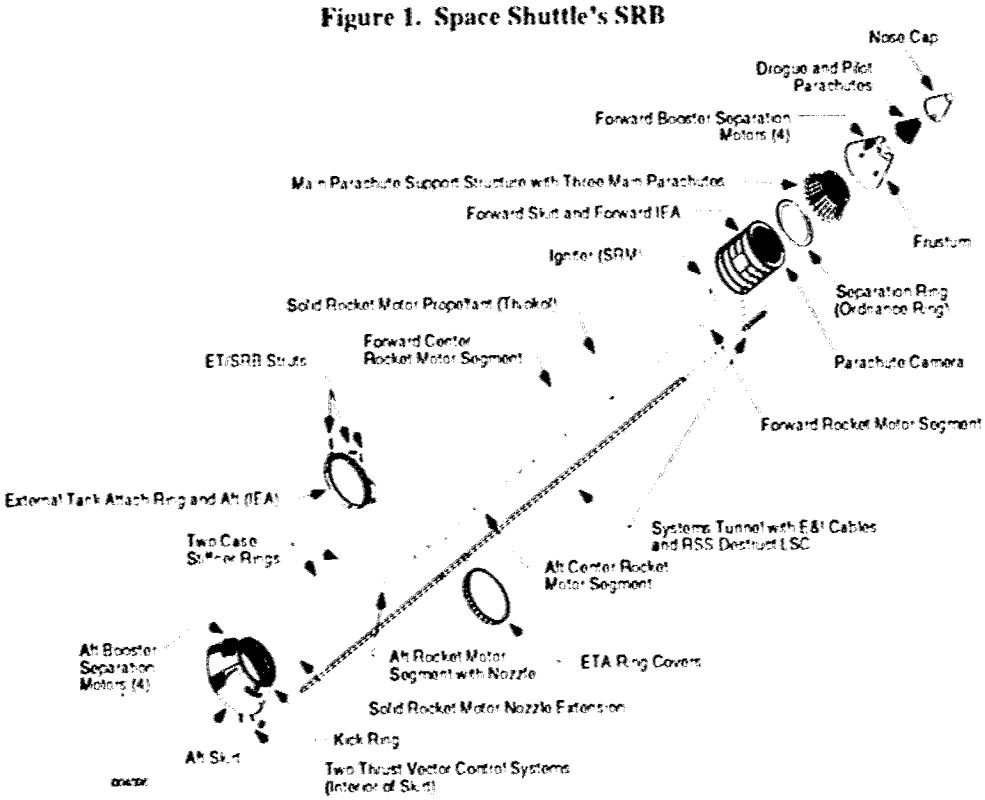


Figure 2. Solid Rocket Booster

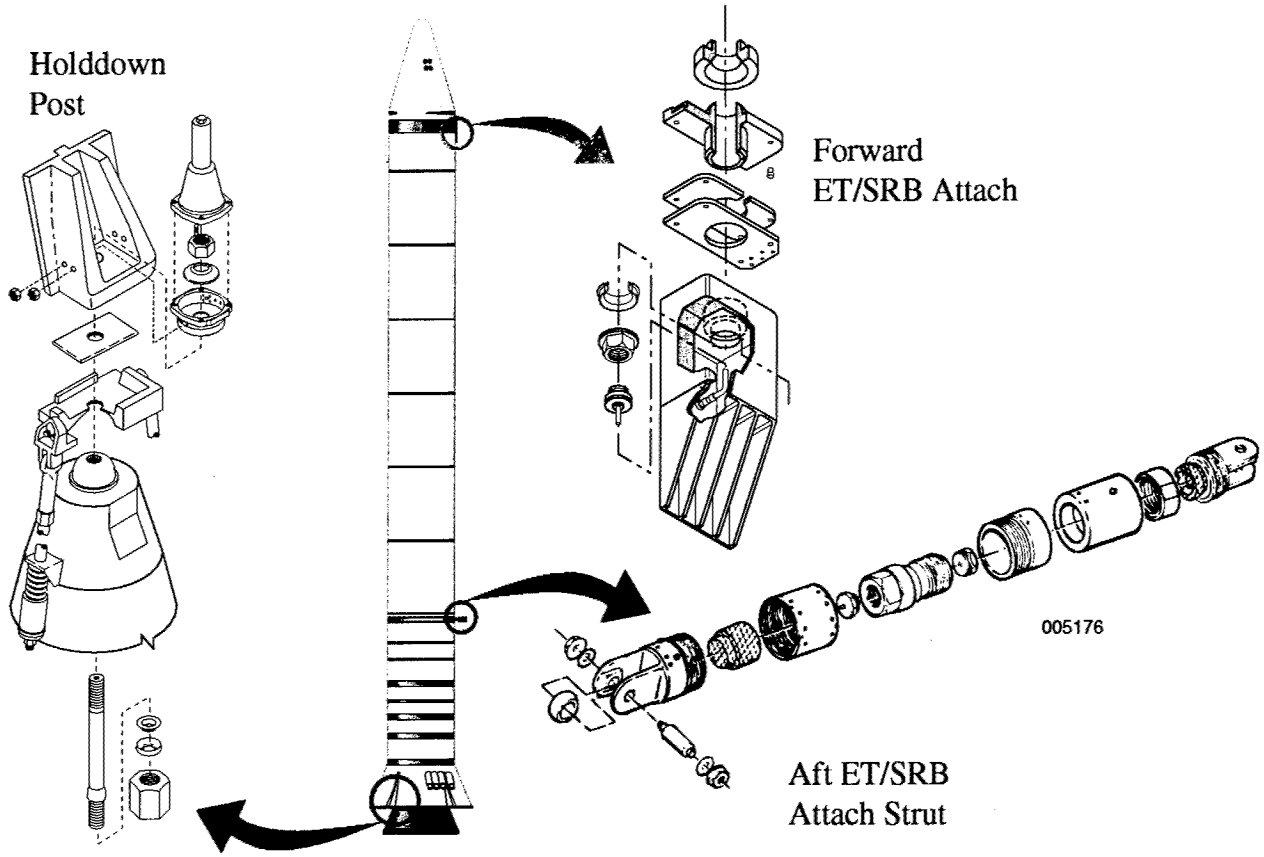


Figure 3. Typical Areas of Lubricant Application on SRB Flight Hardware

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 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.

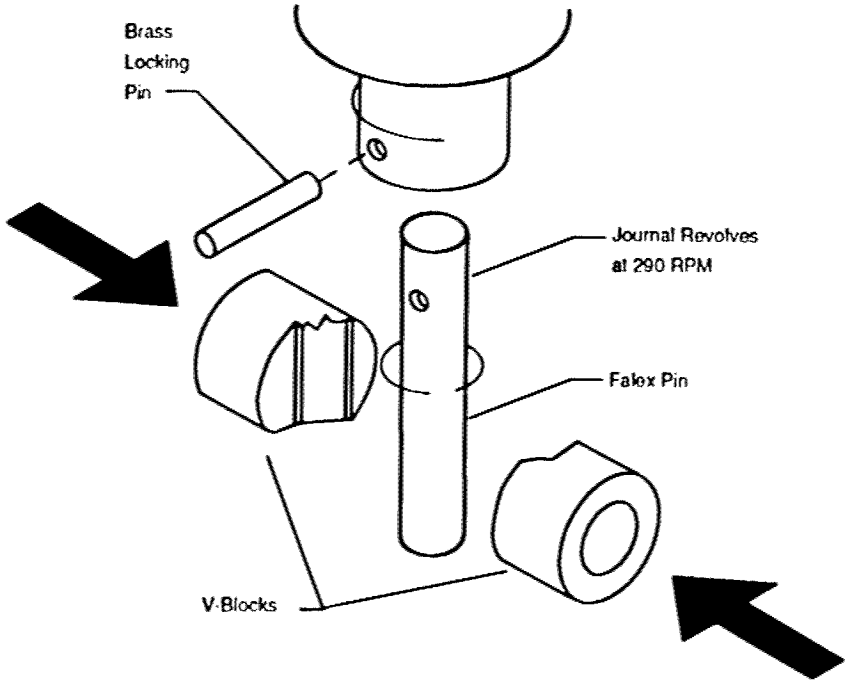


Figure 4. Standard Falex Pin and V-Blocks for Lubrication Tests

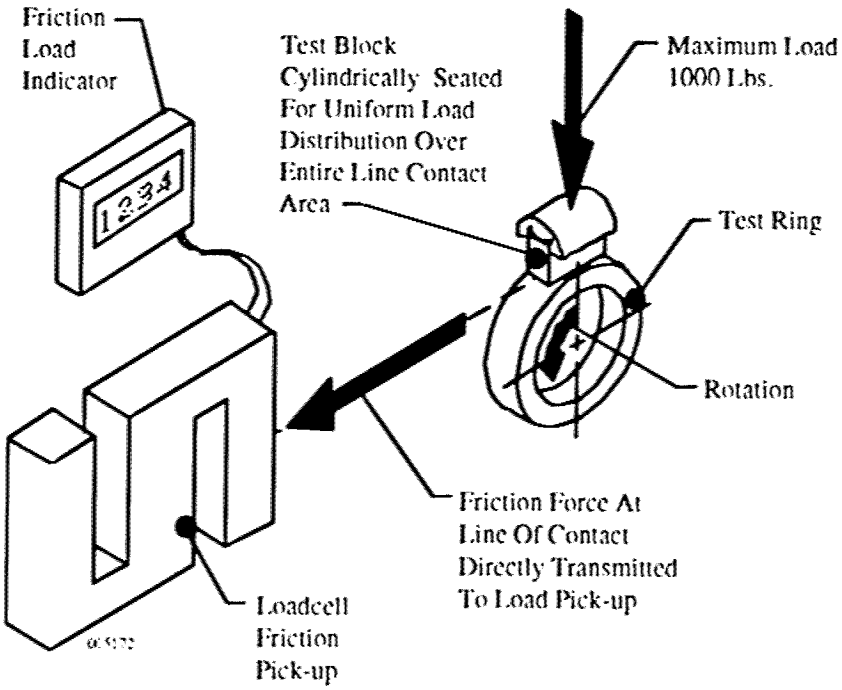


Figure 5. Function Diagram of the Falex Block-On-Ring Testing Machine

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 an 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 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. 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 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, a material that also contains lead and hazardous air pollutants.

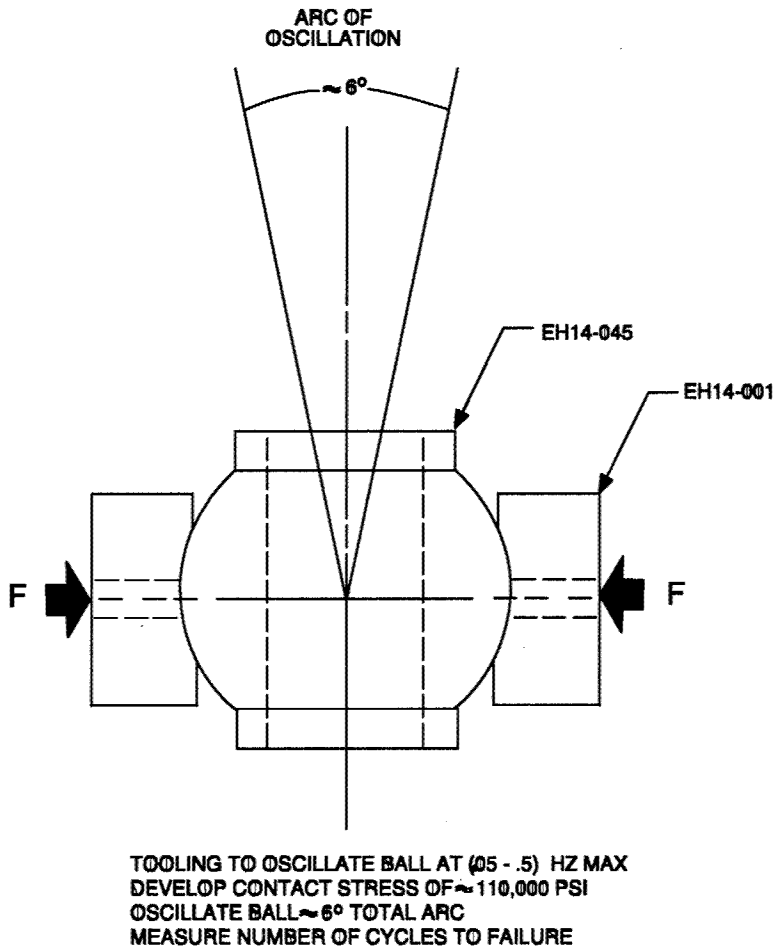


Figure 6. MSFC/EH14 High Load Test (110 KSI)

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. Additional thanks are given to E/M Co. management and laboratory personnel who helped make this program a success.

REFERENCES

(1). Annual Book of ASTM Standards, Vol. 05.02, "Petroleum Products and Lubricants," ASTM, Philadelphia, PA 1992.

CORROSION EVALUATION OF AIRCRAFT DEPAINTING CHEMICALS

Preston McGill
Pablo Torres
Metallic Materials Division
George C. Marshall Space Flight Center
Marshall Space Flight Center, AL 35812

Introduction

The National Aeronautics and Space Administration is participating in an interagency task agreement with the Environmental Protection Agency and the United States Air Force to evaluate alternative technologies for aerospace depainting operations that do not adversely affect the environment (Reference 2). An element of this study is directed towards the evaluation of environmentally advantaged chemical paint strippers, specifically, paint strippers that do not contain methylene chloride. Eight environmentally advantaged, or alternative, chemical paint strippers and two methylene chloride, or baseline, paint strippers were obtained from various manufacturers and incorporated into the depainting study. In addition to being evaluated on their ability to remove paint, the potential of these chemicals to promote corrosion and hydrogen embrittlement was evaluated. The corrosion and hydrogen embrittlement potential of the chemical paint strippers are presented in this report.

The tests conducted in this study are a subset of the prescribed corrosion evaluation tests listed in the SAE Aerospace Standard, MA4872, "Paint Stripping of Commercial Aircraft – Evaluation of Materials and Processes." This document was generated to outline technical requirements for the evaluation of materials and processes for stripping organic finishes from commercial aircraft (Reference 4). Specifically, three standard test procedures were implemented to determine the corrosion potential of these chemicals on clad and non-clad 2024-T3 aluminum substrates and the hydrogen embrittlement potential of these chemicals on AISI 4340 high strength steel. These procedures are summarized below.

- ASTM F483-90, "Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals," was conducted to determine the corrosiveness of these chemicals on aircraft metals (Reference 1). The test requires that a substrate material totally immersed in a test chemical for a specified amount of time be examined for weight change and surface damage.
- ASTM F1110-90, "Standard Test Method for Sandwich Corrosion Test," was conducted to determine the corrosiveness of these chemicals on aluminum alloys commonly used in aircraft structures (Reference 1). The test requires that filter paper saturated with the test chemical be place between substrate material for a specified amount of time. The extent of corrosion of the substrate is rated according to scales provided in the specification.
- ASTM F519-93, "Standard Test Method for Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals," was conducted to evaluate any hydrogen embrittlement potential that may arise from the introduction of hydrogen from the chemical paint stripper into the substrate (Reference 1). This test requires that preloaded high strength tensile specimens be immersed in the chemical and monitored for failures over a period of 150 hours. The hydrogen embrittlement potential is based on the number of failed specimens that occur during the exposure time.

The chemicals evaluated in this study and their classification based on the manufacturers reported pH levels include, Gage Stingray 874B (neutral), Turco 6813 (alkaline), Turco 6813-E (alkaline), Turco 6840-S (alkaline), McGean-Rohco Cee-Bee E-1004B (acidic), Calgon EZE 540 (acidic), Eldorado PR-2002 (acidic), and Turco 6776 (acidic). Two methylene chloride chemicals, McGean-Rohco Cee-Bee R-256 (alkaline) and McGean-Rohco Cee-Bee A-202 (acidic) were also included in the study. Manufacturers provided the chemicals reported in this study for evaluation. Mention of trade names or specific commercial products does not constitute endorsement or recommendation for or against their use. The clad aluminum tested in this study was purchased per AMS 4041 and QQ-A-250/5 specifications. The non-clad aluminum tested in this study was purchased per AMS 4037 and QQ-A-250/4 specifications. All aluminum substrate tested was 1.6mm (0.064 in) thick.

Corrosion Testing

Many aircraft maintenance chemicals are used on components and structures that would be adversely affected by corrosion (Reference 1). Loss of material due to corrosion in a component can contribute to fatigue problems as well as reduce strength capability. Total immersion corrosion and sandwich corrosion are two test methods used in the qualification and approval of compounds employed in aircraft maintenance operations to evaluate the corrosion potential of aircraft maintenance chemicals.

Total Immersion Corrosion Testing

The total immersion test method is used to evaluate the corrosiveness of aircraft maintenance chemicals on aircraft metals. The test is conducted by immersing the substrate in the chemical for a prescribed time. Corrosiveness of the chemical is determined quantitatively by weight change and a visual qualitative assessment. Total immersion test coupons were fabricated from 1.6 mm (0.064 in) thick clad and non-clad 2024-T3 aluminum alloy. The non-clad material was anodized per MIL-A-8625C, Type 1 for chromic acid. All chemicals were tested in the as received condition. The total immersion corrosion tests were conducted per ASTM F483-90. Per specification, the samples were weighed prior to testing, after 24 hours, and again after seven days of exposure.

Average weight loss rates for each of the chemicals is provided in Table 1. These measurements represent average weight loss divided by total coupon area (28.2 cm^2) expressed as loss in milligrams per square centimeter per 24 hours. Acceptable weight loss rates as provided in the SAE MA4872 specification are 0.2 $mg/cm^2/24hr$ for non-clad 2024-T3 and 0.3 $mg/cm^2/24hr$ for clad 2024-T3. An assessment of these data suggests that almost no weight loss was exhibited over the test period by coupons treated with alkaline/neutral strippers. Alkaline/neutral chemicals that did exhibit weight loss were well within acceptable rates. Negative numbers indicate weight gains most likely due to the presence of remnant surface deposits since these test coupons were not electrolytically cleaned. Significantly higher weight loss rates were seen for coupons treated with acidic strippers. Three of the five acidic strippers, including the methylene chloride baseline, exhibited weight loss rates for non-clad material exceeding the acceptable rate. For the clad material one of the five chemicals, an alternative paint stripper, exhibited a weight loss rate exceeding the specification limits.

Summaries of the visual observations after 168 hours of exposure are shown in Tables 2 and 3 for non-clad and clad substrate respectively. Visual requirements set forth in the SAE MA4872 specification requires that no evidence of corrosion be present on the samples. The alkaline/neutral strippers produced no visible etching, pitting or accretions (corrosion product) on any samples. The acidic strippers demonstrated signs of etching on all samples, clad and non-clad. All but one chemical, an alternative stripper, promoted pitting and localized attack of non-clad substrate. With respect to the clad substrate, two chemicals, both alternative strippers, showed no signs of pitting or localized attack. No accretions were noted on any samples.

Sandwich Corrosion Testing

Sandwich corrosion testing was performed to evaluate the corrosion potential of chemicals entrapped in faying surfaces. Sandwich corrosion test coupons were fabricated from 1.6 mm (0.064 in) clad and non-clad 2024-T3 aluminum alloy. The non-clad material was anodized per MIL-A-8625C, Type 1 for chromic acid. Testing was performed per ASTM Specification F1110-90. Four test coupon sandwiches were tested per chemical per alloy each comprised of two individual test coupons sandwiched together in pairs of the same alloy and surface treatment. Both clad and non-clad sandwiched pairs were used to test all chemicals and all chemicals were mixed thoroughly to ensure uniformity before being applied to the test coupons. Four coupon sandwiches were tested with reagent deionized water as controls for comparative purposes. In each case, a piece of glass fiber filter paper was fit over one coupon of the sandwiched pair. The filter paper was then saturated with the as-received test solution and the wet paper was covered with the second coupon of the sandwiched pair. The specimens were exposed to alternate warm air and warm humid air for seven days. Each set was exposed individually (not stacked) in a horizontal position. After exposure, the panels were cleaned and examined under 10x magnification. They were then assigned a qualitative rating per ASTM F1110-90 as shown in Table 4. Corrosion ratings were then compared between

Table 1 - Average Corrosion Rates for Clad and Non-Clad 2024-T3 Test Coupons During Total Immersion Corrosion Testing				
Chemical Tested	Corrosion Rate ($mg/cm^2/24hr$)			
	Non-Clad 2024-T3		Clad 2024-T3	
	Exposed for 24 Hrs	Exposed for 168 Hrs	Exposed for 24 Hrs	Exposed for 168 Hrs
Turco 6813 (Alkaline)	0.0035	-0.0005	0.0000	-0.0025
Turco 6813-E (Alkaline)	0.0071	-0.0015	0.0000	-0.0020
Turco 6840-S (Alkaline)	0.0000	-0.0010	-0.0071	-0.0020
Stingray 874B (Neutral)	0.0000	-0.0005	0.0000	-0.0010
Cee-Bee R-256 (Alkaline baseline)	0.0000	0.0015	0.0000	-0.0015
Turco 6776 (Acidic)	0.3121	0.4189	0.2092	0.3440
EZE 540 (Acidic)	0.2943	0.2771	0.2624	0.2036
PR-2002 (Acidic)	0.0319	0.0709	0.0000	0.1054
Cee-Bee E-1004B (Acidic)	0.1986	0.1717	0.1773	0.1327
Cee-Bee A-202 (Acidic baseline)	0.2979	0.2594	0.1950	0.1753

coupons tested with chemicals and coupons tested with reagent water. These comparisons only considered the surfaces under the filter paper and any corrosion at the edges was disregarded. Per ASTM specifications, any corrosion in excess of that shown by the deionized water is considered cause for rejection.

Test results (ratings) from the sandwich corrosion testing are presented in Table 5. The coupons tested with reagent water showed significant discoloration and spotting over the surface. Pitting on coupons in reagent water was also evident. As a result the coupons tested in reagent water were given a corrosion rating of 3. All alkaline/neutral chemicals performed better than the reagent water. On the non-clad material three of the four alternate alkaline/neutral chemicals performed better than the methylene chloride baseline. On clad material, the methylene chloride baseline performed better than the alternate alkaline/neutral chemicals. With respect to the acidic chemicals, on the non-clad material the chemicals caused more corrosion that the reagent water. However, the alternate chemicals performed better than the methylene chloride baseline on the non-clad material. On clad material, four of the five acidic chemicals, including the methylene chloride baseline, performed as well or better than the reagent water. However, only one of the four alternate chemicals performed better than the methylene chloride baseline.

Mechanical Hydrogen Embrittlement Testing

Hydrogen embrittlement testing was performed to evaluate the potential of the paint stripping chemicals to embrittle cadmium plated high-strength AISI 4340 steel. Testing was conducted per ASTM F519-93. Test specimens were Type 1A notched round tensile specimens fabricated from AISI 4340 steel that was heat treated per

MIL-H-6875 to obtain a hardness of 51 to 54 HR_c with an ultimate tensile strength of 1800 to 1930 MPa (260 to 280 ksi). The sensitivity of the 4340 steel to embrittlement was determined using the methodology presented in ASTM F519-93. After machining, the notched round tensile specimens were degreased, dry abrasive blasted with alumina, rinsed with tap water and immediately electroplated using a low-embrittlement cadmium cyanide bath. After electroplating the specimens were baked at 191 ± 14 °C (375 ± 25 °F) for 23 hours.

Table 2 - Visible Changes in Non-Clad 2024-T3 Test Coupons After Total Immersion Corrosion Testing (168-Hour Exposure)

Chemical Tested	Coupon Number	Discoloration or Dulling	Etching	Accretions Presence and Relative Amounts	Pitting	Selective or Localized Attack
Turco 6813 (Alkaline)	1	yes	no	no	no	no
	2					
	3					
Turco 6813-E (Alkaline)	4	yes	no	no	no	no
	5					
	6					
Turco 6840-S (Alkaline)	7	no	no	no	no	no
	8	small spots				
	9	no				
Stingray 874B (Neutral)	10	very little	no	no	no	no
	11	a little				
	12	no				
Cee-Bee R-256 (Alkaline baseline)	13	very little	no	no	no	no
	14	very little				
	15	no				
Turco 6776 (Acidic)	16	yes (coupons whitened)	yes	no	no	no
	17					
	18					
EZE 540 (Acidic)	19	yes	yes	no	some	yes
	20					
	21					
PR-2002 (Acidic)	22	yes (many spots)	yes	no	yes	yes
	23					
	24					
Cee-Bee E-1004B (Acidic)	25	yes	yes	no	some	yes
	26					
	27					
Cee-Bee A-202 (Acidic baseline)	28	yes	yes	no	yes	yes
	29					
	30					

Each chemical was tested in the as-received condition at 20 to 30 °C (68 to 86 °F). The containment chamber was isolated around the test specimens and the specimens were completely submerged in the chemical. Three specimens per chemical were assembled and loaded in tension to 45% of the notched ultimate tensile strength. Constant strain test fixtures (as opposed to constant load test fixtures) were used to conduct the tests. To ensure that no load relaxation occurred during the test, the recovered strain upon unloading the non-failed

specimens was measured and compared to the initial strain required to load the specimen to confirm that the initial load was maintained. The loaded specimens were immersed in the chemicals and the time to failure recorded. The test was discontinued after 150 hours. Per ASTM F519-93 specifications, a chemical is considered non-embrittling under the conditions tested if no specimens fail within 150 hours after immersion in the chemical at 45% of the notch tensile load. A chemical is considered embrittling under the conditions tested if two or more break in less than150 hours.

Table 3- Visible Changes in Clad 2024-T3 Test Coupons After Total Immersion Corrosion Testing (168-Hour Exposure)

Chemical Tested	Coupon Number	Discoloration or Dulling	Etching	Accretions Presence and Relative Amounts	Pitting	Selective or Localized Attack
Turco 6813 (Alkaline)	49	some	no	no	no	no
	50	very little				
	51	some				
Turco 6813-E (Alkaline)	52	some	no	no	no	no
	53					
	54					
Turco 6840-S (Alkaline)	55	very little	no	no	no	no
	56					
	57					
Stingray 874B (Neutral)	58	no	no	no	no	no
	59					
	60					
Cee-Bee R-256 (Alkaline baseline)	61	some	no	no	no	no
	62	very little				
	63	very little				
Turco 6776 (Acidic)	64	yes (coupons whitened)	yes	no	no	no
	65					
	66					
EZE 540 (Acidic)	67	yes	yes	no	no	no
	68					
	69					
PR-2002 (Acidic)	70	yes	yes	no	yes	yes
	71	some			no	no
	72	yes			yes	yes
Cee-Bee E-1004B (Acidic)	73	yes	yes	no	almost none	no
	74					
	75					
Cee-Bee A-202 (Acidic baseline)	76	yes	yes	no	yes	yes
	77					
	78					

Table 4 - Rating Scale for Sandwich Corrosion Testing	
Rating	**Condition**
0	No visible corrosion
1	Very slight corrosion or discoloration (up to 5% of the surface area corroded)
2	Slight corrosion (5 to 10% of the surface area corroded)
3	Moderate corrosion (10 to 25% of the surface area corroded)
4	Extensive corrosion or pitting (25% or more of the surface area corroded)

Results of the hydrogen embrittlement testing are presented in Table 6. Numbers listed in parentheses represent the time interval in which the specimen failed. The failure ratio is the number of specimens that failed over the number of specimens tested under the same conditions. The acidic chemicals, including the methylene chloride baseline, failed this test. All specimens failed within 48 hours of exposure. However, all of the specimens exhibited average failure times exceeding the methylene chloride baseline. Scanning electron microscopy of failure surfaces revealed a large region of intergranular fracture. Metallographic cross sectioning of these samples revealed secondary cracking below the failure surface indicative of grain boundary attack. Two out of three specimens tested in the neutral chemical (Group 1) failed between 98 and 145 hours. Microscopy and metallography of these specimens also revealed a region of the failure surface exhibiting an intergranular fracture with secondary cracking. The remaining specimen that passed the test was loaded to failure and exhibited a ductile failure surface. Since other laboratory data indicated acceptable performance of a neutral chemical three additional samples were tested and are listed in Table 5 as Group 2 specimens (Reference 3). All of these specimens met the 150 hour exposure requirement. The exposure time was extended beyond 150 hours and one specimen failed after 191 hours. The reason for the Group 1 and Group 2 failures for the neutral chemical may be related to the pH of the chemical. The pH of the neutral chemical was measured as 5.7. This is in contrast to the manufacturers reported pH of 6.5. The lower pH of the chemical as tested may be responsible for the failures in the neutral Group 1 and Group 2 specimens. All specimens tested in the alkaline chemicals passed the test with no failures noted. Test specimens loaded to failure post test exhibited ductile failure surfaces.

Conclusions

Total immersion corrosion, sandwich corrosion, and hydrogen embrittlement testing on ten chemical paint strippers has been performed. Testing was conducted on two methylene chloride baseline chemicals, one alkaline and one acidic. Testing was also conducted on eight non-methylene chloride alternate chemicals, three alkaline, one neutral, and four acidic. The test data indicates that alternate alkaline and neutral chemical paint strippers perform as well or better than a methylene chloride baseline with respect to corrosion requirements. These alternate alkaline/neutral chemical paint strippers also, in general, meet corrosion acceptance criteria as specified in SAE MA 4872. All alkaline chemical paint strippers and one group of the neutral chemical paint stripper met specification requirements for hydrogen embrittlement. Alternate acidic chemical paint strippers have been identified that, with respect to corrosion and hydrogen embrittlement requirements, perform as well or better than a methylene chloride baseline. However, these chemicals do not generally meet corrosion acceptance criteria for non-clad material or hydrogen embrittlement acceptance criteria as specified in SAE MA 4872.

Table 5 - Sandwich Corrosion Test Results				
Chemical Tested	Non-clad 2024-T3		Clad 2024-T3	
	Sandwich Number	Rating	Sandwich Number	Rating
Deionized Water (per ASTM D1193, Type IV)	1	3	121	3
	3	3	123	3
	5	3	125	3
	7	3	127	3
Turco 6813 (Alkaline)	9	1	129	3
	11	2	131	3
	13	2	133	3
	15	3	135	3
Turco 6813-E (Alkaline)	17	2	137	2
	19	2	139	3
	21	2	141	2
	23	2	143	3
Turco 6840-S (Alkaline)	25	3	145	2
	27	3	147	3
	29	2	149	2
	31	2	151	3
Stingray 874B (Neutral)	33	3	153	3
	35	3	155	3
	37	3	157	3
	39	3	159	3
Cee-Bee R-256 (Alkaline baseline)	41	2	161	1
	43	3	163	2
	45	2	165	2
	47	3	167	1
Turco 6776 (Acidic)	49	4	169	3
	51	4	171	3
	53	4	173	3
	55	4	175	3
EZE 540 (Acidic)	57	4	177	3
	59	4	179	4
	61	4	181	3
	63	4	183	3
PR-2002 (Acidic)	65	4	185	3
	67	4	187	3
	69	4	189	3
	71	4	191	3
Cee-Bee E-1004B (Acidic)	73	4	193	3
	75	4	195	2
	77	4	197	3
	79	4	199	2
Cee-Bee A-202 (Acidic baseline)	81	4	201	3
	83	4	203	2
	85	4	205	2
	87	4	207	3

Table 6 - Results of the Hydrogen Embrittlement Test		
Chemical Tested	**Failure Ratio**	**Time to Failure, Hours**
Turco 6813 (Alkaline)	0/3	No Failures
Turco 6813-E (Alkaline)	0/3	No Failures
Turco 6840-S (Alkaline)	0/3	No Failures
Stingray 874B – Group 1 (Neutral)	2/3	(98-145), (128-143)
Stingray 874B – Group 2 (Neutral)	1/3	(191-198)
Cee-Bee R-256 (Alkaline baseline)	0/3	No Failures
Turco 6776 (Acidic)	3/3	4.5, 6, (28-48)
EZE 540 (Acidic)	3/3	0.5, (8-24), (8-24)
PR-2002 (Acidic)	3/3	0.5, (7-23), (31-47)
Cee-Bee E-1004B (Acidic)	3/3	1.75, 1.75, 1.75
Cee-Bee A-202 (Acidic baseline)	3/3	0.5, 0.5, 0.5

Acknowledgments

The investigators would like to acknowledge the cooperation of those companies whose products were evaluated in this study, Gage Products Company, Turco Products, Inc., McGean-Rohco, Inc., Calgon Corportion, and Eldorado Chemical Company. The investigators would also like to thank James Coston and Wendell DeWeese for performing the microscopy and metallography on the test samples and Gary Green, Brian Hurless, and James Hodo for the mechanical testing.

References

1. *Annual Book of ASTM Standards, Space Simulation; Aerospace and Aircraft; High Modulus Fibers and Composites*, Volume 15.03, 1996.
2. *Joint EPA/NASA/USAF Interagency Depainting Study*, Fifth Progress Report, November 1997.
3. *Scientific Material International, Inc.*, Test Report, 9801039, February, 1998.
4. *Society of Automotive Engineers International, Aerospace Standard, MA4872*, SAE MA 4872, 1996.

Phase II ODC Elimination: Hand-Wipe Cleaning

June 3, 1998

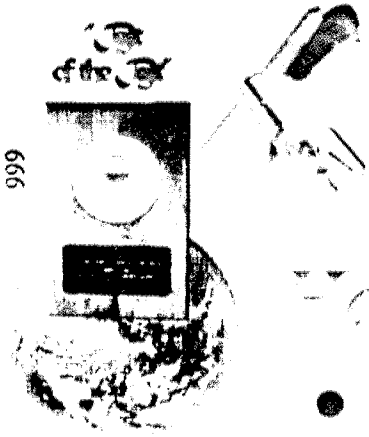
Presented by:

Dan Danieu

50 YEARS OF SOLID PROPULSION

981187.ppt

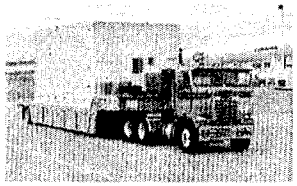
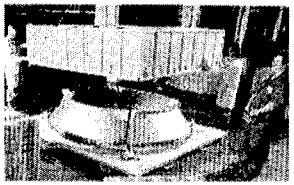
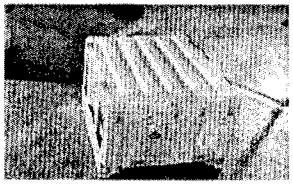
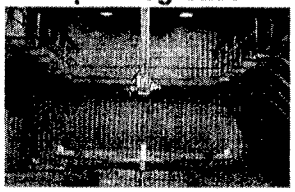
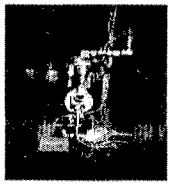
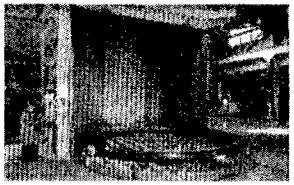
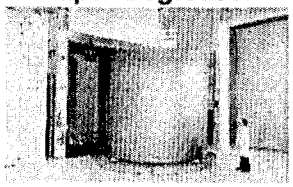
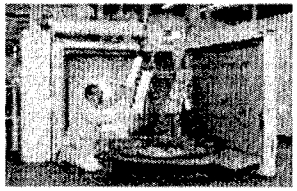
THIOKOL PROPULSION



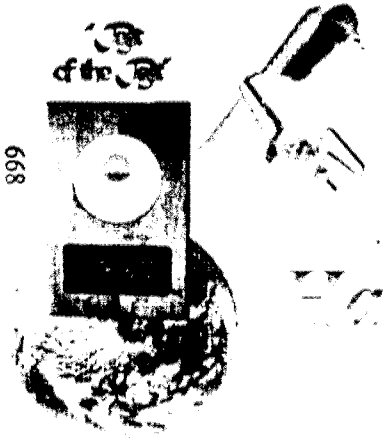
Phase II ODC Elimination Hand-Wipe Cleaning

- **Introduction**
  - Ozone depleting compounds (ODC) elimination through 3 phases over 9 years
    - Facility design and installation
    - Process changes
    - TCA stockpile
    - Eliminated over 1.2 Mlb per year
  - Phase II hand-wipe cleaning eliminates last 10%
    - Essential use exemption (EUE) expiration December 2001
    - Approximately 140 critical cleaning operations
    - Extensive coupon and full-scale testing
    - Three full-scale static tests
  - EUE extension requested throughout Space Shuttle life

Phase II ODC Elimination: Hand-Wipe Cleaning

PHASE 0	PHASE I		PHASE II
	Step 1	Step 2	
Greaseless Shipping  Environmental Shipping Trailers  Nozzle Environmental Shipping Containers  Igniter Environmental Shipping Containers	Replace Refurbishment Vapor Degreaser  3-Axis Case Bay High-Pressure Water Blast  5-Axis Nozzle High-Pressure Water Blast  H-7 Aqueous Wash Systems	Replace Production Vapor Degreaser  M-52 Large Aqueous Wash Systems  Small Aqueous Wash Systems Propellant Mix/Cast Tooling Cleaning	TCA handcleaning elimination No major facilities/ tooling anticipated at this time Ventilation modifications Dispensing equipment Storage facilities

981187.ppt



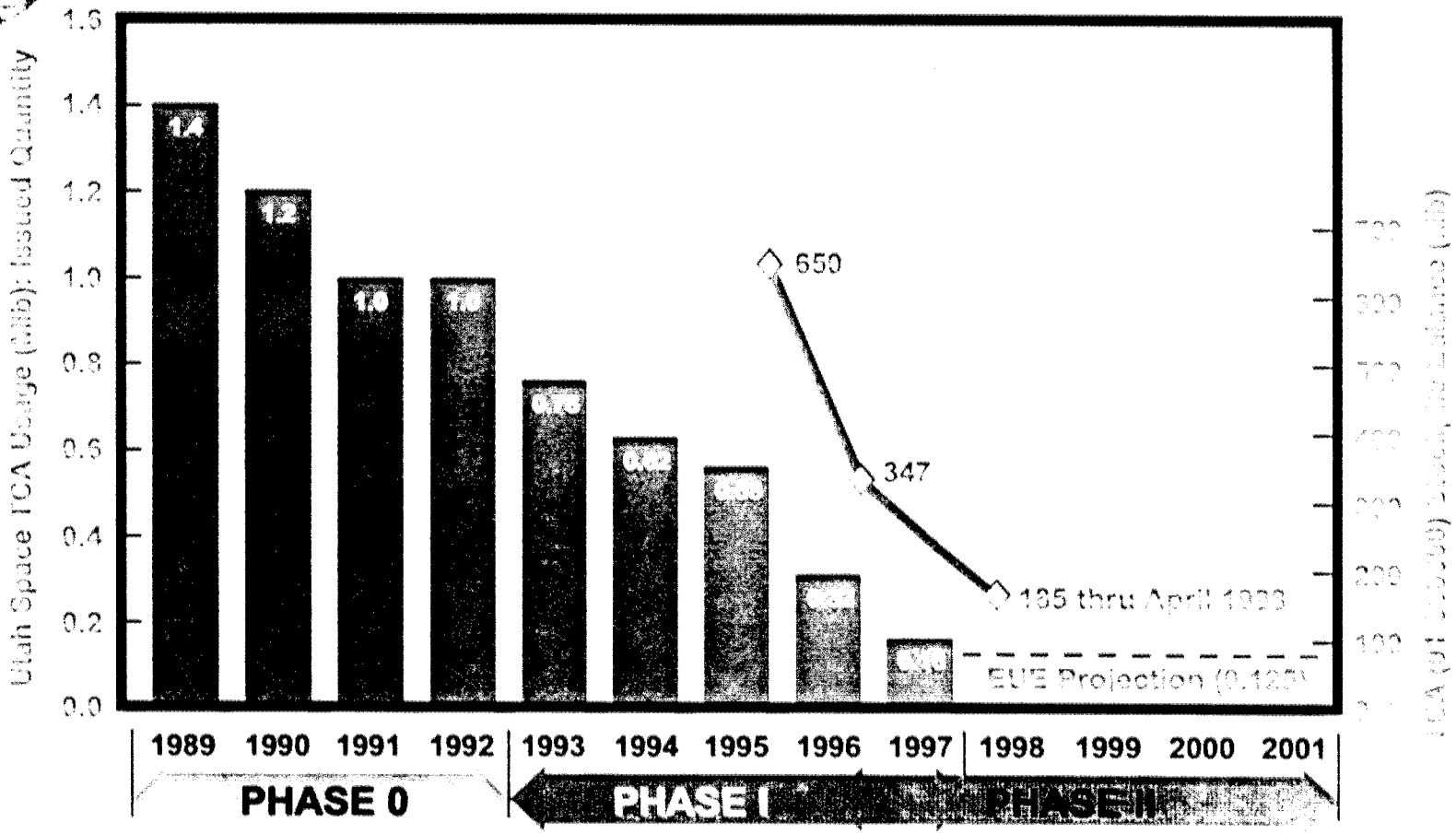
Phase II ODC Elimination: Hand-Wipe Cleaning

- **Phase I update summary**
  - ODC-free aqueous processes and materials are qualified and are being implemented into flight program
  - Production efficiency fine tuning under way
    - Aqueous spray-in-air (SIA) bath life extension studies in progress for Brulin 1990®

Phase II ODC Elimination: Hand-Wipe Cleaning

- **TCA use reduction and projections**
  - RSRM program continues to meet or exceed our TCA use reduction projections (see following graph)
  - EUE awareness training completed for all Thiokol personnel involved with TCA use video segment, posters, and labels on drums and bottles
    - EUE TCA use controlled via specific shop planning callouts using exclusive lot number
    - EUE TCA use monitored on a daily/monthly basis through full-time material control coordinator

Actual TCA Usage/Stockpile Balance vs. Calendar Year



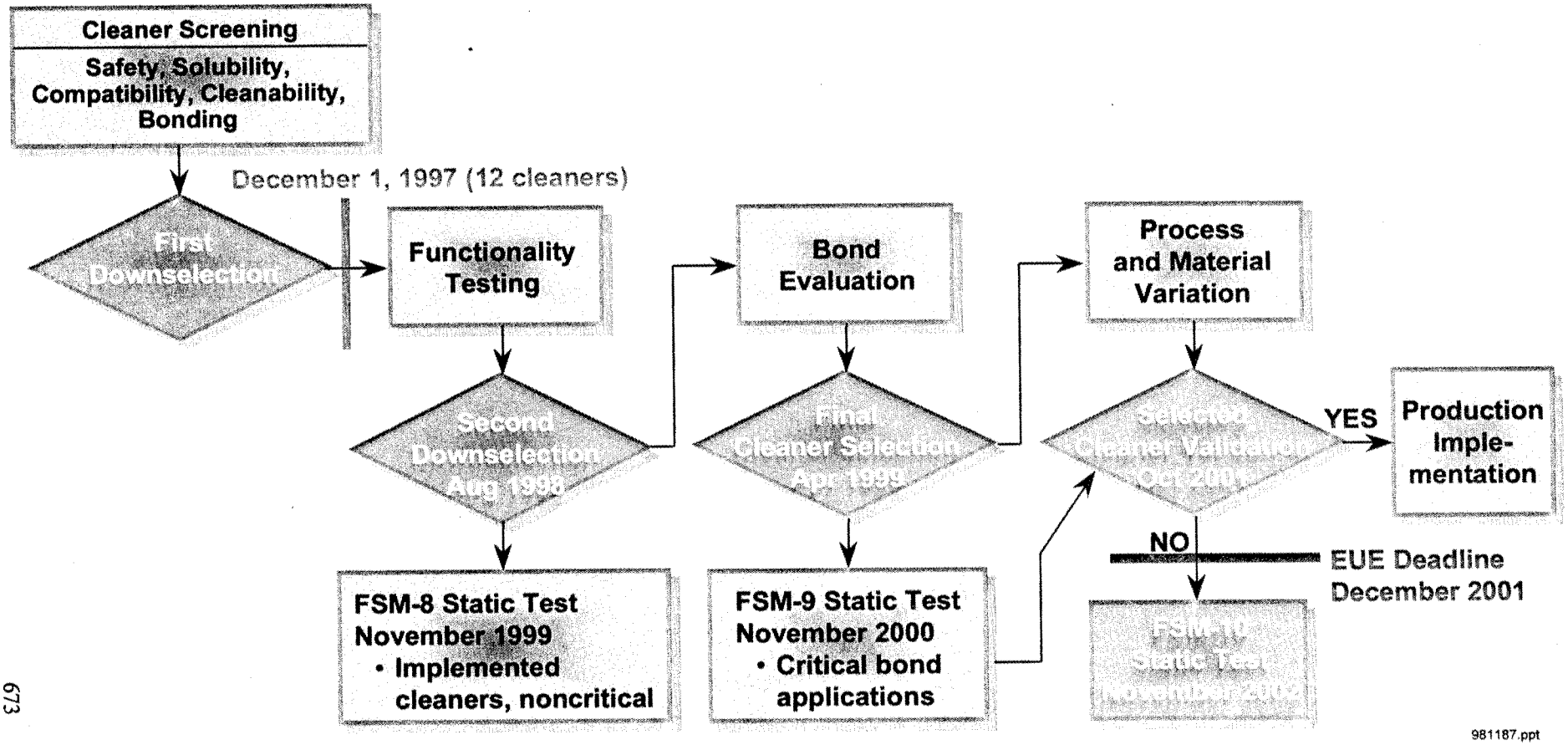
Phase II ODC Elimination: Hand-Wipe Cleaning

- **ODC Elimination Phase II**
  - ODC Elimination Plan Phase II addresses the remaining 10% of total TCA usage
    - Usage comes from variety of operations including hand-wipe bond preparation cleaning and rubber activation
    - Many more substrates, contaminants and bondlines are affected by the remaining 10% TCA than the initial 90% TCA usage
    - No production bonds can be 100% NDE or proof tested
  - Extensive coupon and full-scale testing
    - Cleaner screening
    - Functionality, i.e., surface cleanliness and rubber activation
    - Critical bond preparation cleaning effects on bond strength
    - DoE for process and material variability
    - Full-scale implementation and static test

Phase II ODC Elimination: Hand-Wipe Cleaning

- **ODC Elimination Phase II (cont)**
  - Test matrix alpha code
    - **SS**: Testing to determine effect of solvents on substrates, process materials, and soils
    - **BF**: Validation testing to determine if 7 downselected cleaners are adequate in bond performance testing
    - **FF**: Tests cleaning ability of 7 downselected cleaners using surface analysis techniques (FTIR,ESCA,GC/MS,SE)
    - **FB**: Bond test with 3 downselected cleaners to optimize cleaning techniques and test material degradation
    - **BB**: Bond tests with 3 downselected cleaners on critical bond systems
    - **BI**: Bond testing of every conceivable bond system

Phase II ODC Elimination: Hand-Wipe Cleaning

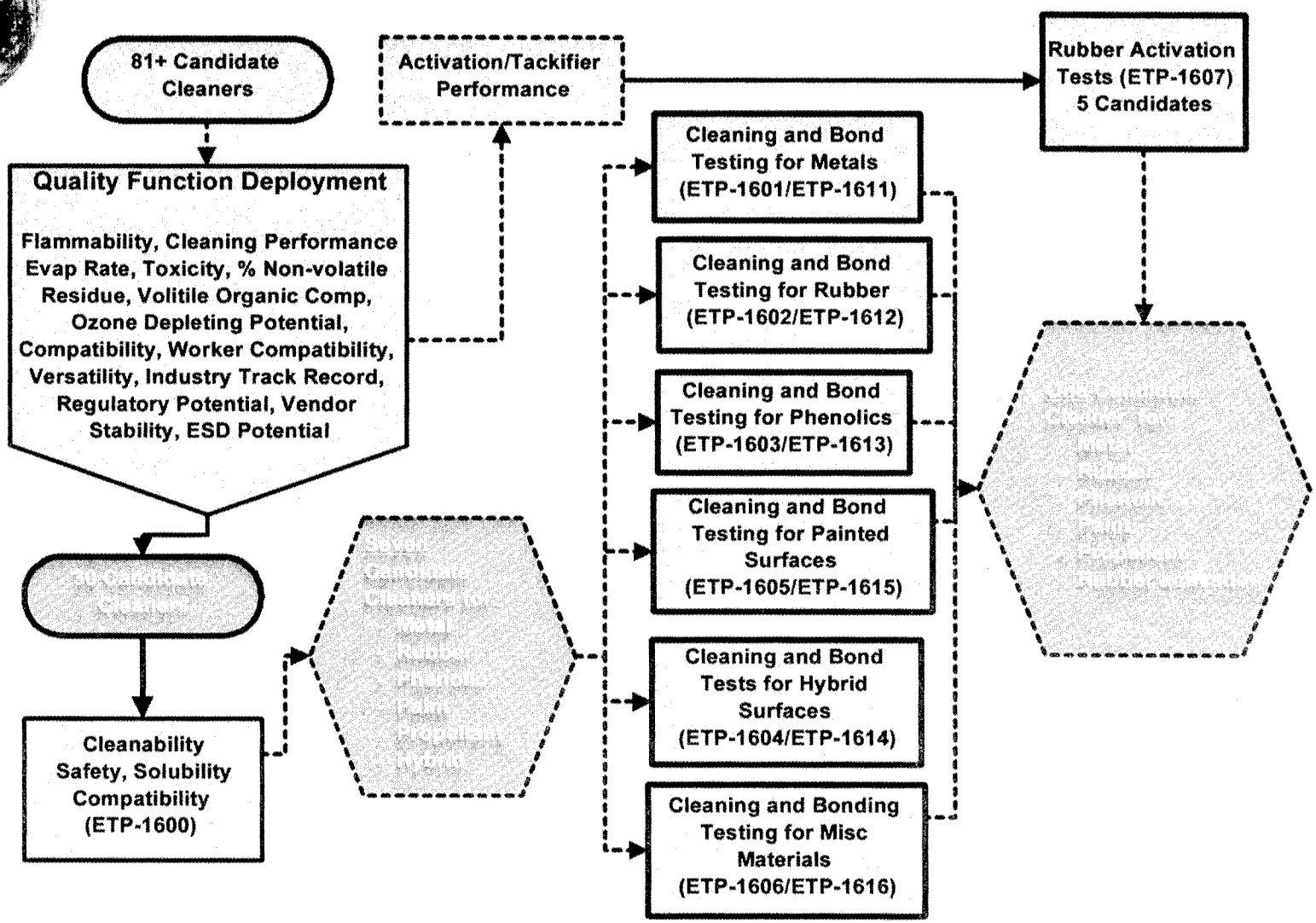


981187.ppt

Phase II ODC Elimination: Hand-Wipe Cleaning

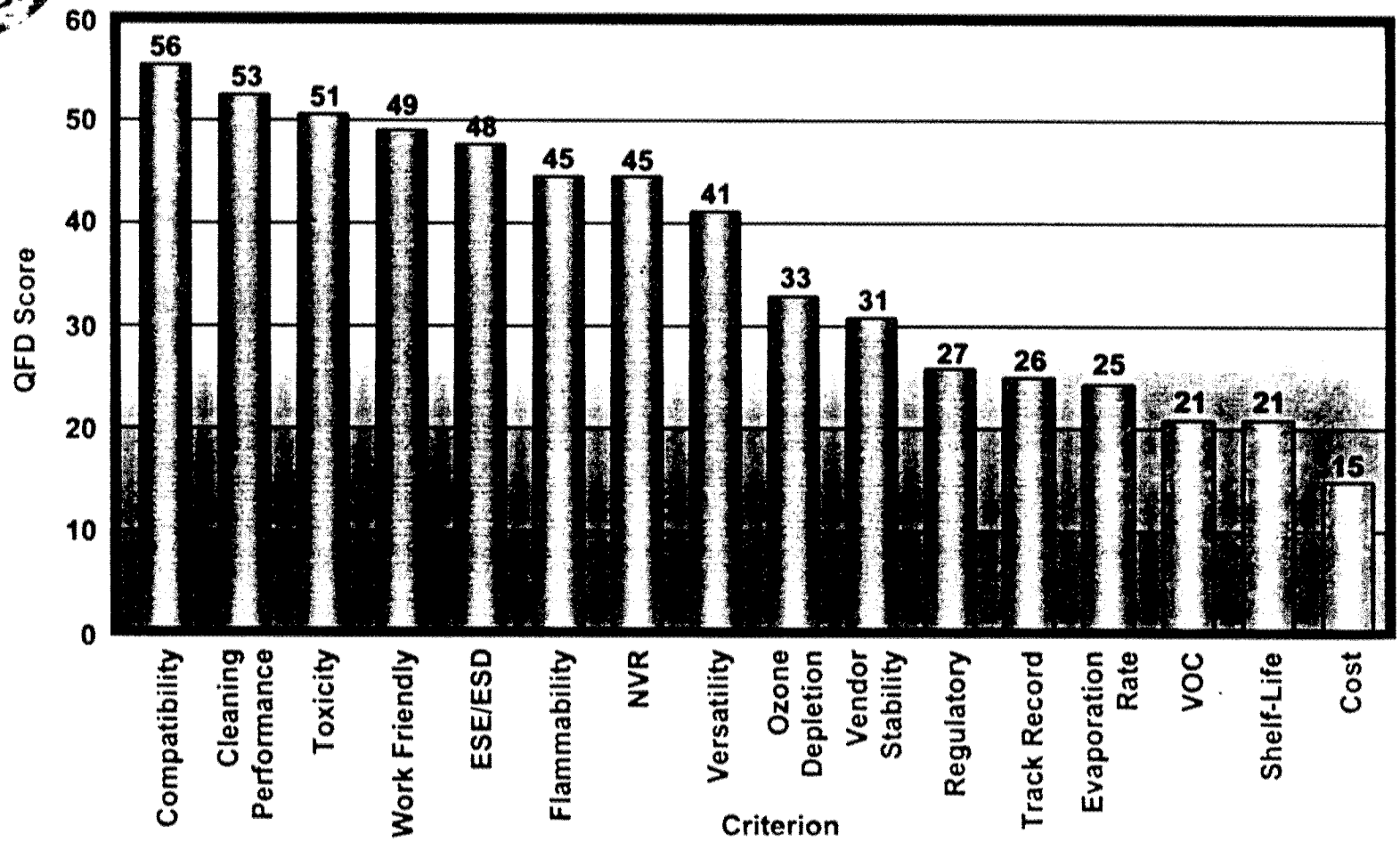
- **ODC Elimination Phase II (cont)**
  - Approach
    - A list of substrates and contaminants representative of those encountered in RSRM processing was developed
    - A literature search and vendor-contacts established cleaners matching the substrate and contaminant chemistries
    - A Quality Function Deployment matrix was developed and information on candidate cleaners was processed through the matrix and scored

Phase II ODC Elimination: Logic Flow



981187.ppt

QFD Matrix Results

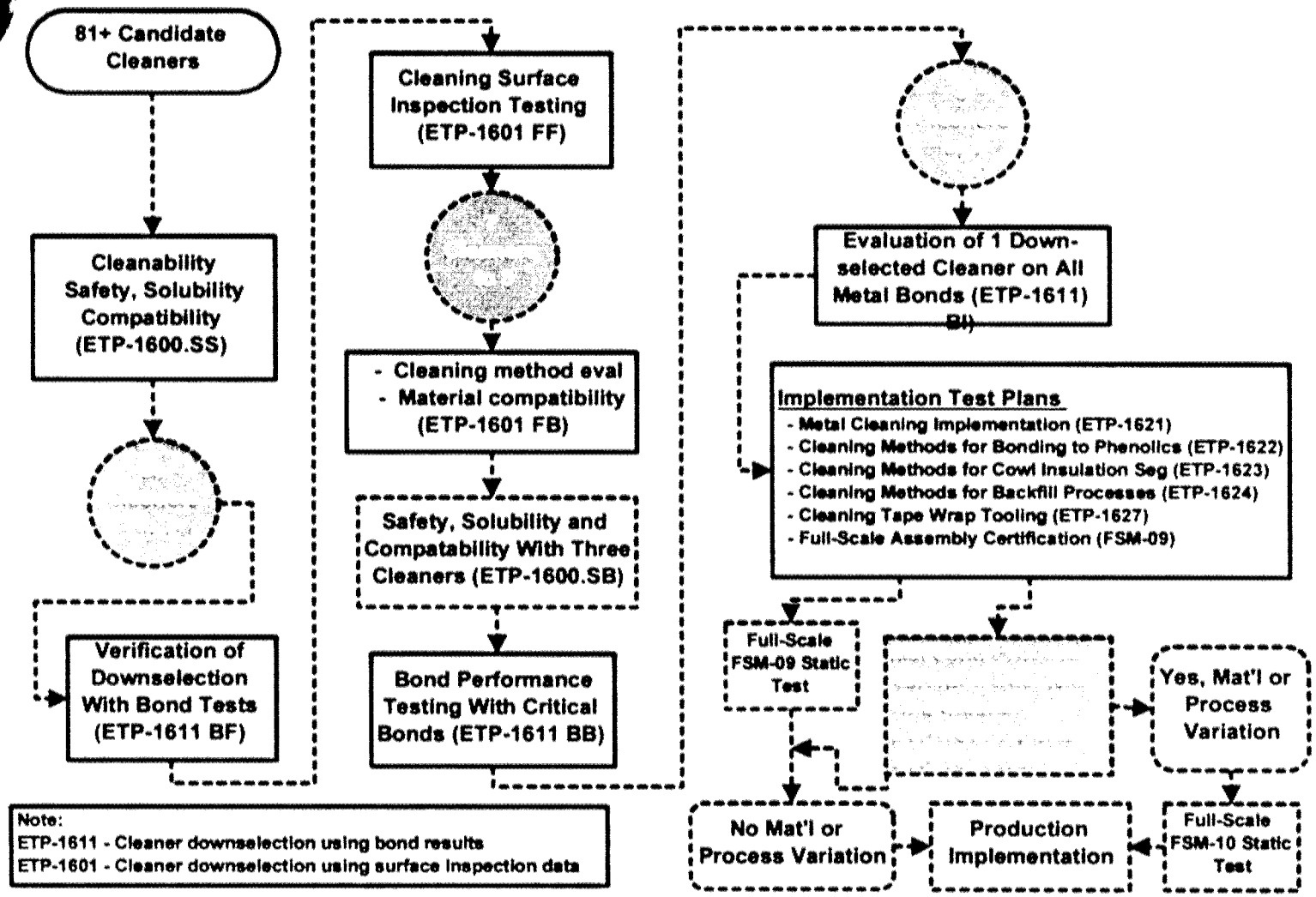


981187.ppt

Phase II ODC Elimination: Hand-Wipe Cleaning

- **ODC Elimination Phase II (cont)**
  - Approach (cont)
    - The top-scoring cleaners were considered for testing along with industry information and vendor recommendations for RSRM specific needs
    - 30 cleaners were selected and tested
    - Cleanability testing proved to be the most beneficial test for the first downselection

Phase II ODC Elimination: Logic Flow



981187.ppt

Phase II Cleanability Results

● = Performed Better than TCA
■ = Performed Comparable to TCA
▲ = Performed Worse Than TCA
A = Did Not Affect CL233
B = Removed Some of CL233
C = Removed All of CL233
Red Cleaners/Totals = Top Performing Cleaners

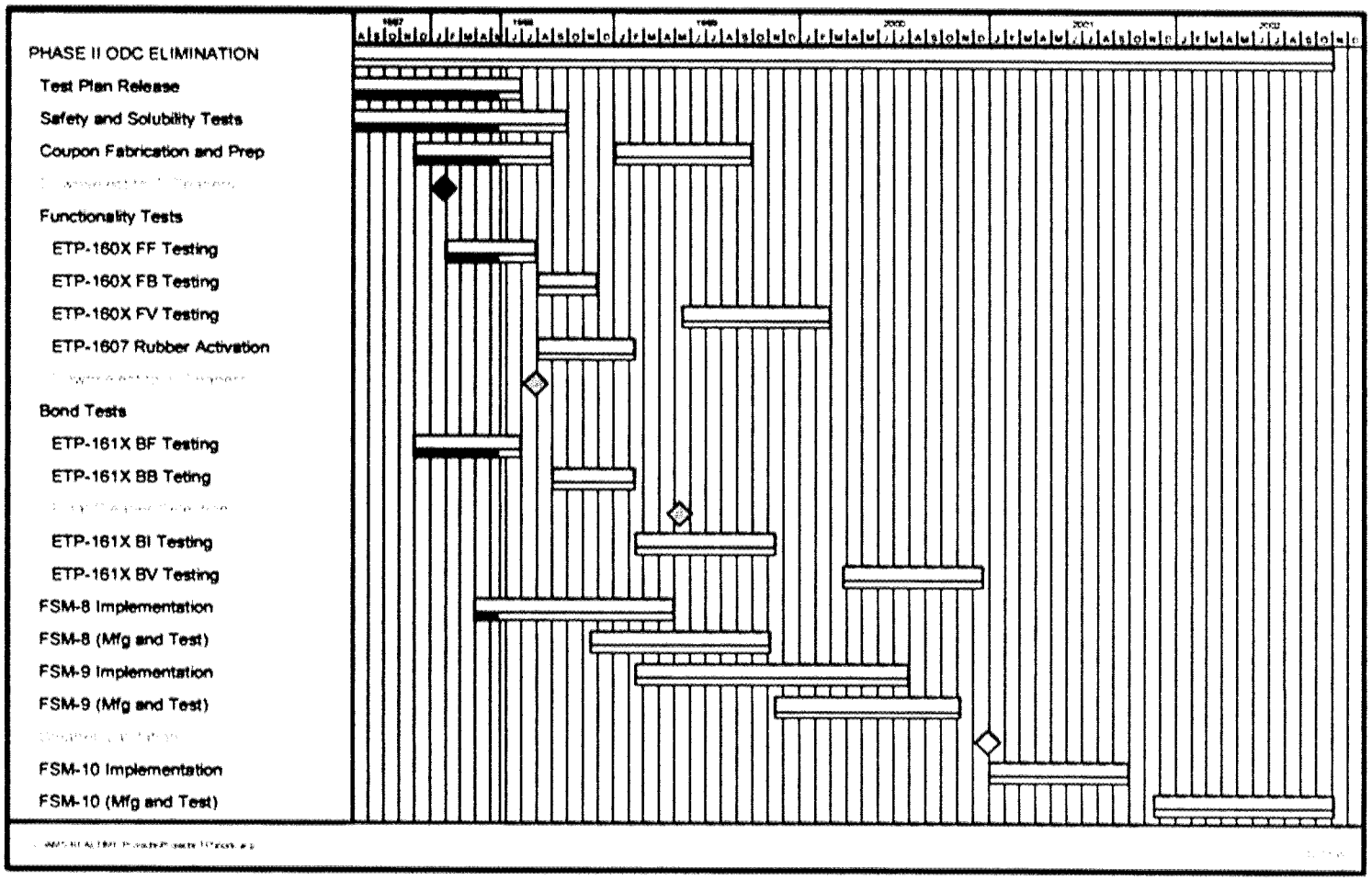
TCA = 1,1,1-trichloroethane
REV = Reveille
PFD = PF Degreaser
ION = IONOX BC
BA1 = Bio-Act 113
BA4 = Bio-Act 145
BTE = Borothene e

DG5 = Degreeze 500 LO
DS1 = DS-108
EC5 = Ecosolve 5
EXT = Ensolv XT
MCA = Vertrel MCA Plus
KZA = K-9200
OX1 = Oxsol 100

PCG = Bio-Act PCG
PFH = PF 145 HP
PFI = PF Ionsol
PFK = PF d'Ink
PL4 = Plus-4
TEP = Teksol EP

SOILS	TD-66 ETP-1698				PHASE II ETP-1600															
	TCA	REV	PFD	ION	BA1	BA4	BTE	DG5	DS1	EC5	EXT	MCA	KZA	OX1	PCG	PFH	PFI	PFK	PL4	TEP
Liner	1	0	1	0	2	2	2	0	0	2	2	1	1	2	1	2	1	2	2	1
Propellant	1	0	0	3	2	3	1	0	1	2	1	1	1	2	2	3	2	2	2	0
EA-946	1	0	0	2	2	2	0	2	3	3	0	1	1	1	0	0	0	2	2	0
HD-2 Grease	2	3	2	0	2	2	1	2	0	2	1	1	1	2	3	2	2	3	2	2
Silicone Adhesive	1	3	0	0	3	3	2	2	3	3	1	2	1	3	3	3	2	3	2	0
Chemlok 205/233	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0
NOTES	C	A	A	C	A	B	C	A	B	C	B		C	B	A	C	A	C	C	A
Nonsilicone Tape A	1	0	1	0	2	2	1	1	0	2	1	0	1	1	2	2	3	2	1	1
HYCAR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Molykote	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NOTES					■	●	■	■	■	●	■		■	▲	■	■	●	■	■	●
PR-1422	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NOTES				●																
Celvacene Grease	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NOTES				●																
RTV 90-006	1	0	0	0	1	1	0	1	1	2	1	0	0	1	3	2	2	2	2	1
Vacuum Putty	2	2	2	0	1	3	1	2	1	1	2	1	3	2	3	2	3	1	1	1
TOTAL	10	8	6	5	15	18	8	10	9	17	9	7	9	14	17	16	15	18	15	6

Phase II ODC Elimination: Schedule



981187 ppt

WHAT IF WE COULD PURIFY AND REUSE OUR WASTE AIRCRAFT HYDRAULIC FLUID?

1Lt Dennis O'Sullivan
AFRL/MLQ
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403
(850) 283-6239
DSN 523-6239

Mr. Edward B. Seaman
BDM International
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403
(850) 283-6290
DSN 523-6290

Mr. Neal C. Werner
Pall Aerospace Company
5775 Rio Vista Drive
Clearwater, FL 34620
(813) 539-8448

INTRODUCTION:

The United States Air Force (USAF) spends approximately $30 million per year in the disposal and replacement of used hydraulic fluid. This estimate is based on Tyndall AFB consumption and disposal costs times the number of worldwide Air Force bases with flying missions. Most of this money could be saved if the hydraulic fluid were purified and reused. The Air Force Research Laboratory, Materials and Manufacturing Directorate, Airbase and Environmental Technology Division (AFRL/MLQ), Tyndall AFB, Florida, is sponsoring a project that will enable the Air Force to realize these savings.

Routine USAF aircraft operations generate large quantities of waste hydraulic fluid each year. Through regular use, accumulation of particulate matter and water requires the disposal or incineration of the fluid. The Air Force generated a need to evaluate economical equipment and/or processes that would allow the USAF to reuse the contaminated hydraulic fluid (USAF Environmental, Safety, and Occupational Health Need 95-530, Recycling and Verification of Hydraulic Fluid for Reuse). In response, AFRL/MLQ began a hydraulic fluid purification project.

Researchers chose to evaluate a portable hydraulic fluid purifier manufactured by Pall Aeropower Corporation. The Pall purification equipment was selected because it uses a vacuum dehydration, spinning disc process to remove water, air, and volatile organic solvents; not desiccants, heat distillation, or high vacuum that could break down the properties of the base oil. It also incorporates a filtration system to remove particulate matter.

Initial testing revealed the PALL Purifier did not cause any adverse effects on the hydraulic fluid. However, continued testing was needed to evaluate the impact of using purified fluid in aircraft hydraulic pumps. The following text provides information on the testing to date.

BODY:

INITIAL EVALUATION

In 1995, AFRL/MLQ evaluated the Pall purifier at Tyndall AFB, in an environmentally controlled facility. New hydraulic fluids from Velsicol Chemical Corporation, Castrol Specialty Products Division, and Royal Lubricants, and used hydraulic fluid from Moody AFB, Eglin AFB, and Dover AFB were evaluated. Each of the new hydraulic fluids was deliberately contaminated with measured amounts of deionized water (1200 ppm) and one gram of AC fine test dust (particulate) at hourly intervals. The Pall purifier was operated for a total of 18.5 hours, for each of the six hydraulic fluids evaluated. Three hydraulic fluid samples for each fluid included: unpurified (baseline), after 8 hours, and after 18.5 hours. The fluid samples were analyzed for degradation at AFRL/ML, Wright-Patterson AFB, OH, in accordance with Military Specification MIL-H-83282C. The fluid was analyzed for

viscosity, acid number, rubber swell, water content, lubricity (four-ball wear), evaporation, and oxidation-corrosion. The initial evaluation indicated that the Pall purifier did not degrade the fluids processed.

Based on these encouraging results, AFRL/ML recommended that wear testing be accomplished on aircraft hydraulic pumps to determine the impact of fluid purification on pump life/performance. The F-16 emergency power unit (EPU) pump and the main hydraulic fluid pump were selected for these tests because they are common aircraft piston pumps and could be mounted on the test equipment. AFRL/MLBT was tasked to accomplish the tests.

PUMP WEAR TEST #1

The first pump wear test, sponsored by the B-2 Program Office, compared pump wear between two F-16 EPU pumps, operated under load, with both purified and unpurified MIL-H-5606F hydraulic fluid. The two pumps were operated for 1500 hours, each at 3000 psig, with flow rates cycled between 12 gpm and 3 gpm every minute. Each pump was then disassembled and inspected for wear. During the tests, fluid samples were extracted and evaluated for viscosity, water content, lubricity, foaming, metal content, and particle count. At the conclusion of the tests, there was no apparent difference in pump performance and no significant difference between fluid properties, with either purified or unpurified fluid. However, it was noted that there was an equal viscosity change in both the purified and unpurified fluids, which was attributed to the behavior of MIL-H-5606F hydraulic fluid and not the purification process. Again, the results encouraged further testing, this time with MIL-H-83282C hydraulic fluid.

PUMP WEAR TEST #2

The second pump wear test (in progress) is sponsored by the Ogden Air Logistics Center. The objective is to compare pump wear between aircraft pumps, operated under load, with both purified and unpurified MIL-H-83282C hydraulic fluid. However, each fluid will be intentionally contaminated with measured amounts of distilled water. The two F-16 main hydraulic pumps will be operated for 2000 hours each, at 3100 psig, with flow rates cycled between 28 gpm and 6 gpm every minute. During the tests, fluid samples will be extracted and evaluated for viscosity, water content, lubricity, foaming, metal content, and particle count. Each pump will be disassembled and inspected for wear. This test is scheduled for completion in December 1998.

OPERATIONAL UTILITY EVALUATION

Headquarters Air Mobility Command is currently conducting an operational utility evaluation on the Pall purifier at McChord AFB, WA. They plan to determine if the purifier is capable of sufficiently cleaning hydraulic fluid without degrading fluid characteristics and determine if the purifier is logistically supportable. This will be accomplished by purifying new MIL-H-5606, MIL-H-83282, and MIL-H-87257 that has been contaminated with measured amounts of AC fine test dust, deionized water, and PD-680 (solvent). They will also validate procedures to connect the Pall unit to a portable hydraulic test stand, an in-shop hydraulic test stand, and C-141 aircraft hydraulic systems. The estimated completion date is December 1998.

CONCLUSION:

It is widely recognized that water and particulate contamination can degrade critical physical properties of hydraulic fluid, impair pump performance, and cause premature failure of the pump. By removing the water and particulates through filtration and purification, users can reuse the hydraulic fluid. The results of the initial evaluation and Pump Wear Test #1 should encourage consumers of large quantities of hydraulic fluid to consider purifying contaminated hydraulic fluid for reuse instead of immediate disposal. **Note:** Hydraulic fluid contaminated with other oils or fuel cannot be purified and reused through this process because it will not separate them.

Commands and Air Logistics Centers wanting to save money could benefit by extending the service life of hydraulic fluid without degrading the fluid's working properties. The average Air Force base can expect to invest less than $50K to reap full benefits of this process, which can be expected to reduce waste hydraulic fluid by 75 percent. The estimated annual Air Force savings of $30 million from use of this process can be multiplied several times, if the process is extended to the Department of Defense and the private sector. This is a truly transferable technology.

Anaerobic Treatment of Glycol Based Deicing Fluid Runoff

Robert Hickey[1], C. Weinert[2], S. Komisar[2], S. Veltman[3], M. S. Switzenbaum[3]

[1]EFX Systems, Inc., Lansing, MI
[2]Rensselaer Polytechnic Institute, Troy, NY
[3]Dept. of Civil & Environmental Engineering, University of Massachusetts, Amherst, MA

Introduction

Deicing or removal of snow, ice and frost from aircraft and anti-icing for the prevention of ice from reforming on the aircraft is generally accomplished using ethylene and propylene glycol based fluids. With chemical oxygen demand (COD) equivalents of 1.29 g COD/g and 1.68 g COD/g for ethylene glycol and propylene glycol respectively, deicing wastes have a high oxygen demand. Depending upon the method of collection and precipitation at the time of fluid application, glycol concentrations in the runoff from deicing operations may range from 2,000 – 300,000 ppm. The treatment of airport deicing fluid runoff is necessary to avoid the potential for severe oxygen depletion in receiving waters. Often the combination of flow rate and high oxygen demand represents too high a mass of oxygen demand for the local wastewater treatment plant. Pretreatment to reduce the oxygen demand down to typical sewer discharge limits is sufficient in many cases to render the water discharge acceptable.

Aerobic processes, which are widely used for wastewater applications, convert organic constituents to carbon dioxide and cell mass. The high cell yield and high power requirements associated with oxygen transfer makes these processes expensive for treating high-strength wastewaters such as aircraft deicing fluid (ADF) runoff. In contrast, anaerobic systems require significantly less energy to operate and produce much less sludge.

Anaerobic Treatment Fundamentals

The biological conversion of organic carbon accomplished under anaerobic conditions is typically performed by a methanogenic mixed culture consisting of four trophic groups of bacteria. These include: (1) hydrolytic acidogens that hydrolyze and ferment the ethylene and propylene glycols to organic acids, hydrogen and carbon dioxide; (2) hydrogen producing acetogens that convert longer chain volatile fatty acids to acetate and hydrogen; (3) methanogens which convert acetate to methane and carbon dioxide; and (4) methanogens that use hydrogen to reduce carbon dioxide to methane.

A stable process rests on maintaining each group in balance with the overall population. This is done by maintaining a minimum mean cell residence time (sludge age) so that the slowest growing organism has sufficient time to reproduce and maintain a viable population capable of keeping pace with the other groups.

Advantages of Anaerobic Treatment

Treating wastes anaerobically as opposed to aerobically offers distinct advantages:

- No oxygen (aeration) is required,
- Cell synthesis is low,
- Nutrient requirements are relatively low, and
- Methane gas is produced.

Although these advantages have been well known for many years, the process has not been widely applied due to the widespread impression that anaerobic systems are unreliable, difficult to control and require excessively long hydraulic residence times and reactor sizes. This was due in part to a lack of information concerning the fundamentals of anaerobic digestion and therefore, the lack of effective process control. Conventional anaerobic systems do, however, require rather large reaction vessels and hydraulic retention times. This is because for a completely mixed digestor, the mean cell retention time and hydraulic residence time cannot be effectively separated. Therefore, system design is based on the biological growth rate rather than the removal capabilities of the organisms. The minimum mean cell retention times required at 35° and 24°C have been calculated to be 4 and 8

days, respectively. The use of a fixed film process, such as the anaerobic fluidized bed reactor system, allows separation of hydraulic residence time from mean cell retention time allowing treatment times to be reduced to hours.

Anaerobic Fluidized Bed Reactor Process Description

Water is pumped upwards through a bed of granular activated carbon, fluidized the media. Treatment of the organic carbon in the water is achieved by a thin film of microorganisms that coats each particle, producing harmless end products: methane, carbon dioxide and some new biomass.

A schematic of the system is provided as Figure 1.

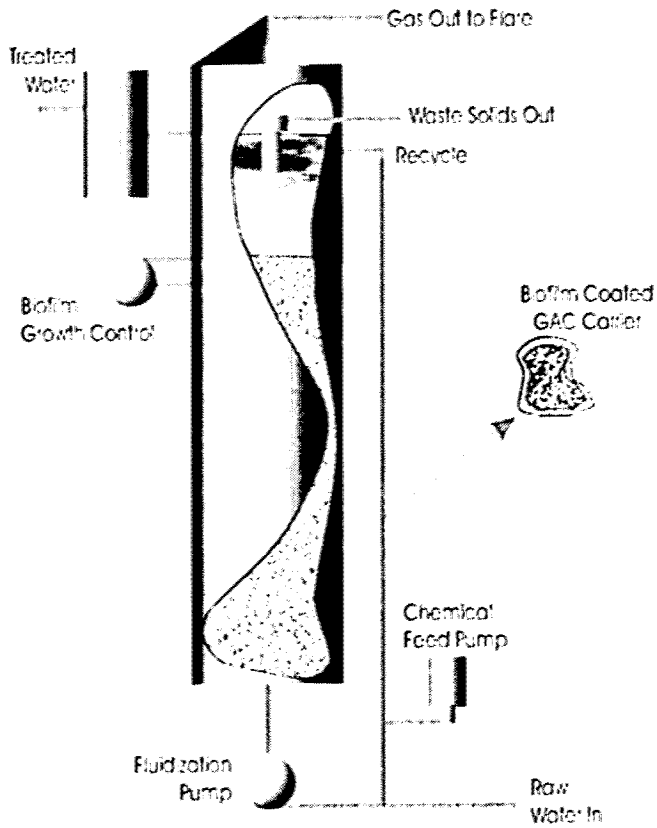


Figure 1. Schematic of Anaerobic Fluidized Bed System.

The high biomass concentrations achieved in biological fluidized beds results in high volumetric removal efficiency, which, combined with the vertical configuration, yields a small reactor footprint. A uniform influent flow distribution manifold, coupled with the fluidization properties, prevents short-circuiting and plugging of the system from biomass accumulation and gas entrapment. To keep a thin and highly active biofilm, media at the top of the bed is sheared of excess biomass and returned to the bed. This shearing device controls the bed height at a predetermined level.

The EFX anaerobic fluidized bed reactor, using granular activated carbon (GAC) as the biomass carrier, has proven to be more stable and reliable than strictly biological anaerobic processes. This is because the GAC biomass carrier is available to absorb slugs of materials that could be potentially inhibitory to the process (i.e., fuel spills) or remove compounds that could have an adverse effect on the environment (i.e., additives to the glycol solutions).

Successful applications of the process include low-cost treatment of food processing, chemical, brewery, soft-drink bottling, pulp and paper and agricultural wastewaters. Recent applications include pollution prevention efforts associated with high-strength storm water runoffs at airports, using anaerobic treatment of waters contaminated with deicing fluids.

A nine-month demonstration was conducted at an upstate New York airport to determine the technical and economic potential of anaerobically treating propylene glycol based deicing fluid runoff. The anaerobic fluidized bed process was able to reduce the COD (and BOD) concentration down to typical sewer discharge limits. Results are presented below.

Results of Pilot System Operation

The pilot-scale anaerobic GAC-FBR system at Albany County Airport was operated at three different steady-state periods. The applied organic loading rate (OLR), a measure of mass of oxygen demand per reactor volume per day, was varied from 5 to 24 kg COD/m^3-d.

Steady-state Period No. 1

The results obtained during the first steady-state period are presented in Figures 2 and 3 for COD and propylene glycol, respectively. These results are summarized in Table 1. In all instances, effluent propylene glycol was consistently degraded to below detection limits of the Gas Chromatographic techniques used (<3 mg/L).

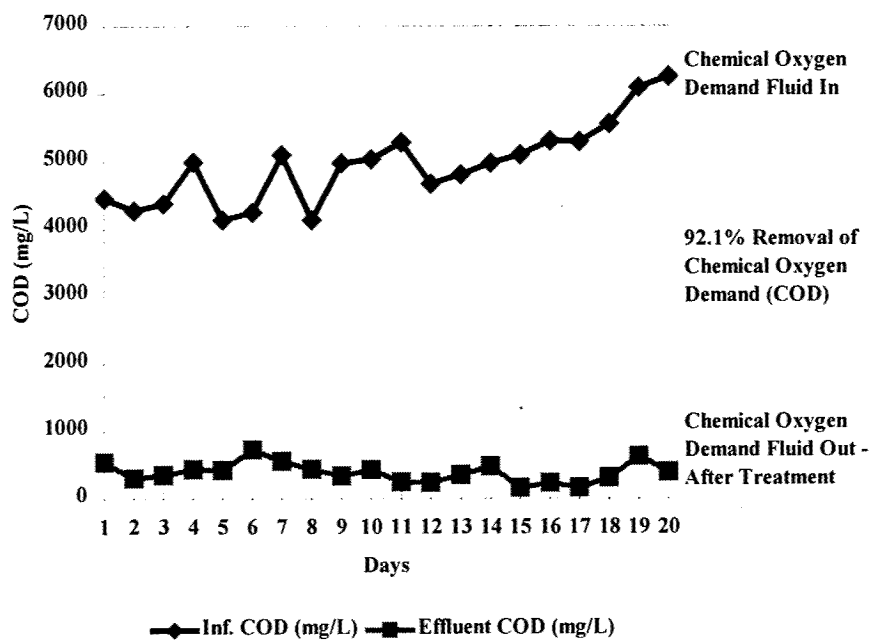


Figure 2. Chemical Oxygen Demand (COD) Removal from Deicing Runoff Anaerobic Fluid Bed Reactor System at Albany County Airport.

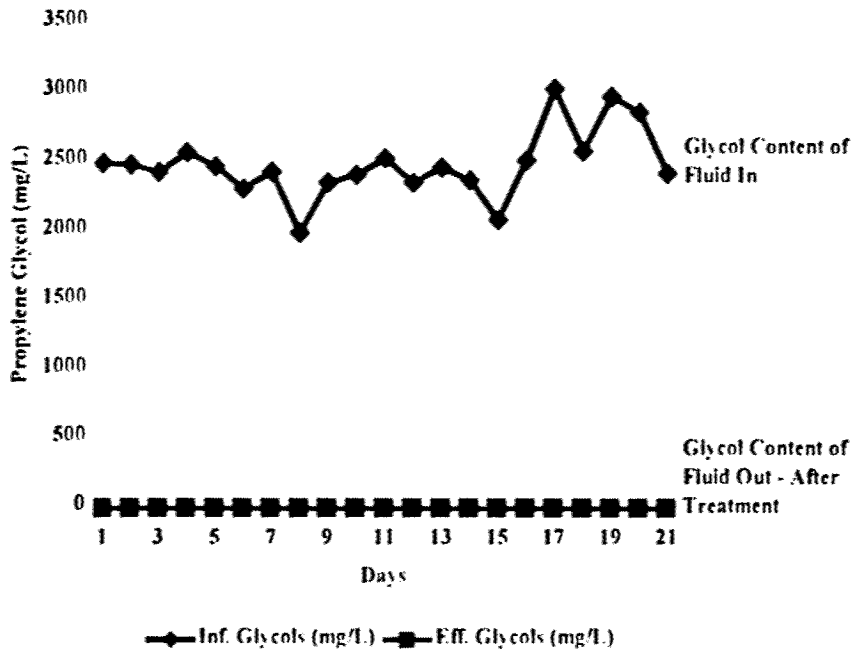


Figure 3. Propylene Glycol Removal from Deicing Fluids at the Albany County Airport.

Table 1. Summary of Results for Operational Period No. 1.

Constituent	Influent	Effluent	% Removal
COD (mg/L)	4,752	394	92
Propylene Glycol (mg/L)	2,454	BDL	>99
OLR @ 14.2 kg COD m³-d (0.89 lb COD CF-d) Temperature = 90°F HRT = 8.7 hours			

Steady-state Period No. 2

The organic loading rate was increase to 24 kg COD/m3-d following the conclusion of Period No. 1. After several weeks, performance reached a new steady-state. Results of the following 3 weeks (18 sample events) are presented in Table 2. Removal efficiency for COD decreased to 82%; PG was removed to below detection limits as before. The major source of COD in the effluent was due to accumulation of volatile fatty acids, propionate and acetate.

Table 2. Summary of Results during Steady-state Operational Period No. 2.

Constituent	Influent	Effluent	% Removal
COD (mg/L)	8,143	1,429	82
Propylene Glycol (mg/L)	4,421	BDL	>99
OLR @ 24.2 kg COD/m³-d (1.51 lb COD CF-d) Temperature = 90°F HRT = 8.2 hours			

Steady-state Period No. 3

The performance of the anaerobic GAC-FBR at a lower OLR was examined after the conclusion of steady-state period No. 2. Again, several weeks were allowed for performance to stabilize. Results of 11 consecutive days of sampling at an OLR of 5.2 kg COD/m3-d are presented in Table 3. A COD removal efficiency of 97%, was achieved. The effluent COD averaged 87 mg/L; average effluent PG was below detection limits (<3 mg/L by the GC method). Samples tested using the NYS DOH method APC44 showed glycol levels in the effluent at <0.5 mg/L.

Table 3. Summary of Results of Steady-state Operational Period No. 3.

Constituent	Influent	Effluent	% Removal
COD (mg/L)	3,332	86	97
Propylene Glycol (mg/L)	1,509	BDL	>99
OLR @ 5.15 kg COD/m^3-d (0.32 lb COD/CF-d) Temperature = 90°F HRT = 15.6 hours			

Full-scale System Design

Based on the results obtained, a design for a system to handle all the deicing fluid runoff at Albany County airport was prepared. The design criteria was:

- 46 acres of catchment
- 31 million gallons of runoff
- 100,000 gallons of propylene glycol used
- 72% recovery of glycol
- >90% COD removal
- effluent PG <1 mg/L

Albany already has collection and 8 million gallons (MG) of storage for ADF runoff on-site. They also had an agreement with the local POTW to discharge a certain mass of oxygen demand per day. During the summer/spring, the runoff remaining in the lagoons was biologically treated and spray irrigated to reduce sewer discharge fees. The design developed took advantage of these existing capacities and attempted to reduce costs while enhancing flexibility of operation.

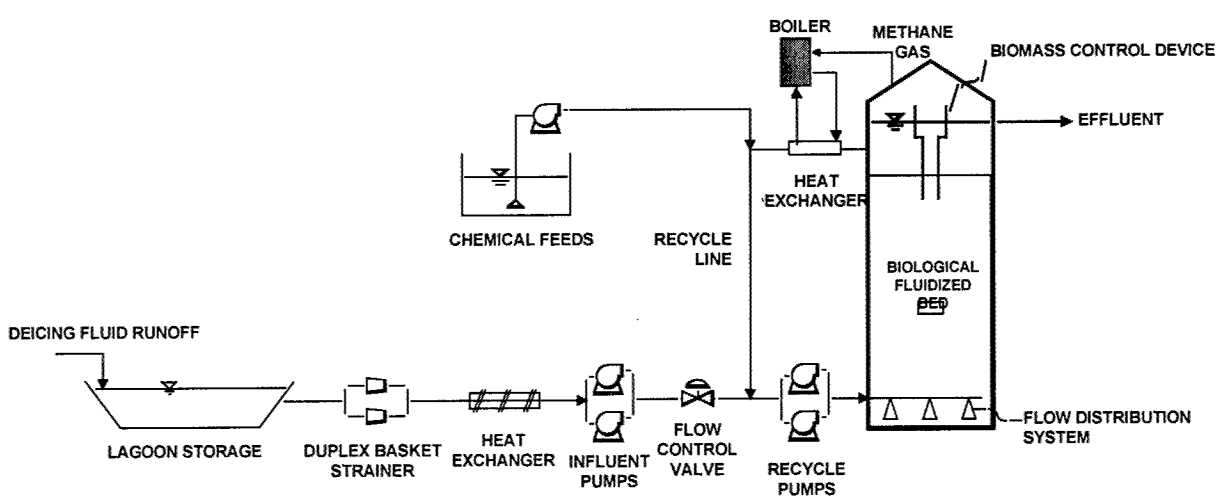


Figure 4. Simplified Process Flow Diagram of Anaerobic Fluid Bed System at Albany County Airport.

A simplified process flow diagram for the treatment system is presented in Figure 4. An overview of operations is presented in Figures 5 through 7.

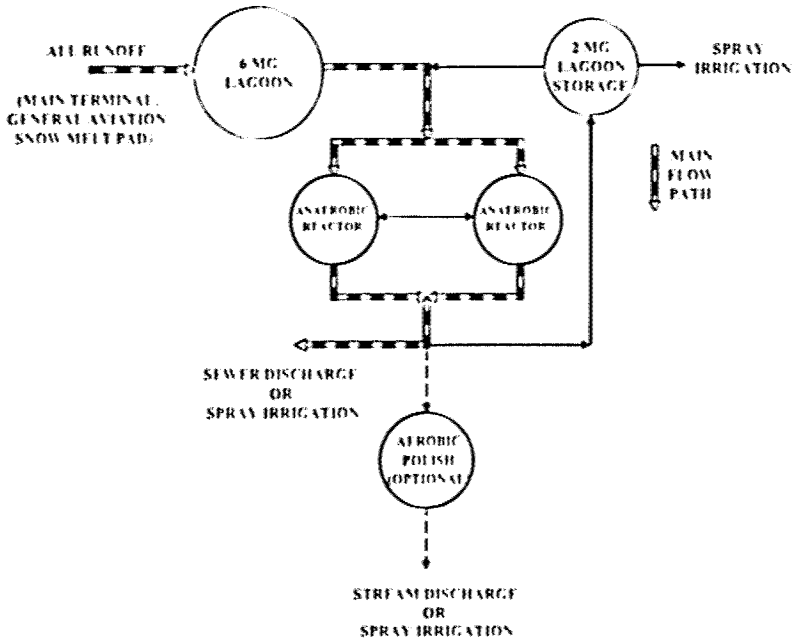


Figure 5. Proposed Flow Scheme for Treatment of all Deicing Fluid Runoff using Existing Lagoon Storage and Anaerobic FBR.

The system consists of two 14' diameter reactors with a height of 35 feet. The system design was based on 46 acres of catchment, 10-year rainfall event conditions, and 100,000 gallons of propylene glycol (pure product usage). Design calls for maintaining the OLR below the maximum tested during the pilot study.

The overall system has a small footprint (the entire process, including a control building occupies less than 3500 square feet at the airport). It produces less than 10 percent of the sludge of an aerobic process and is contained in a sealed reactor, eliminating odors. Energy and operating costs are relatively low. The effluent is suitable for discharging into a sewer system or for further processing such as the spray irrigation.

Proposed Operation

The proposed operation is for all water to flow to the large (6 MG) lagoon. Water from this lagoon is treated in the anaerobic GAC-FBR at 70 to 150 gallons per minute. Between 90 and 95 percent COD reduction is achieved; propylene glycol is removed to less than 1 mg/L. Effluent from the anaerobic system can be discharged directly to the sewer. Effluent can alternately be discharged to the small (2 MG) lagoon, for later discharge or spray irrigation.

During the winter months, treated water will be discharged to the local POTW. The ability to ultimately polishing the pretreated waters to stream discharge criteria will be considered in the future.

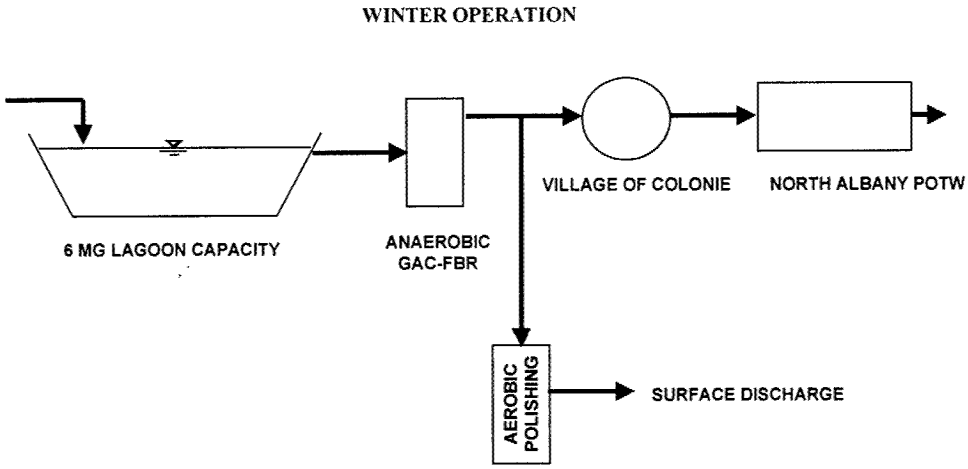


Figure 6. Deicing Runoff Disposal Options Available with Anaerobic Fluid Bed Reactor at Albany County Airport – Winter Months.

During the spring/summer months, it is anticipated that most of the treated water will be disposed of via spray irrigation to reduce disposal costs.

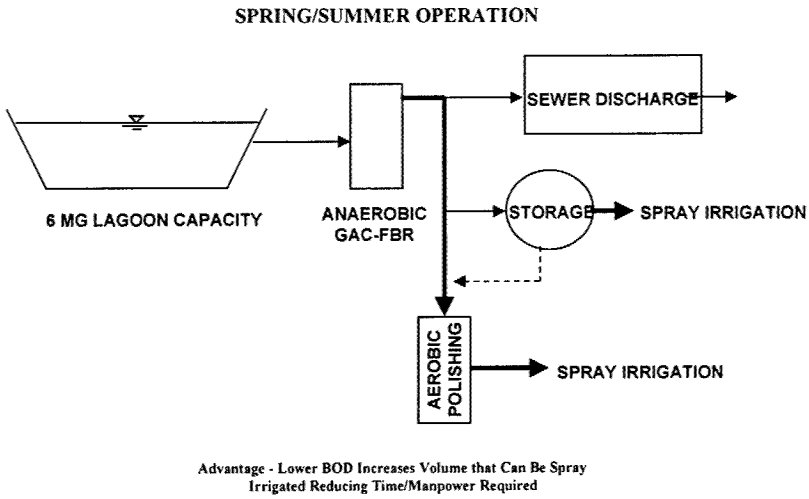


Figure 7. Deicing Runoff Disposal Options Available with Anaerobic Fluid Bed Reactor at Albany County Airport – Spring/Summer.

Economics

Annual savings in operating costs are anticipated to be a minimum of 17%, equivalent to a present worth savings of $3,000,000 over an on-site aerobic treatment alternative examined. The cost of current operations at expanded flow handling needs is even greater. At a time when airports are facing more stringent standards, more limited or expensive options at local publicly owned treatment works and frustration with technological approaches that have fallen short of complete solutions, this technology holds the promise of providing an important element in an overall flexible, cost-effective solution to the glycol disposal problem.

Report of the Biodegradability and Toxicity Studies of Ethoxylated Aqueous Surfactant and Utilization of the Aqueous Surfactant Wastewater as a Carbon and Energy Source in Biological Industrial Wastewater Treatment Facilities

Ken L. Ball
Thiokol Corporation Propulsion Group
PO Box 707, M/S 860
Brigham City, UT 84302-0707
435/863-8365

New environmentally acceptable aqueous surfactants are utilized as a replacement for 1,1,1-trichloroethane in the manufacture of Reusable Solid Rocket Motor (RSRM). A study to find an effective, low cost method of disposing of the wastewater generated from the alternative aqueous cleaners was completed. The study investigated the biodegradability, toxicity and potential utilization of the waste aqueous surfactant solutions as a carbon and energy source. Due to the proprietary nature of the surfactant, chemical compositions and structure of the surfactant will not be identified.

History

As a result of the elimination of 1,1,1-trichloroethane (TCA) due to environmental regulation a new environmentally acceptable aqueous cleaner was needed to replace 1,1,1-trichloroethane in the manufacture of Reusable Solid Rocket Motor (RSRM). Literature studies and toxicity events at local publicly owned treatment works had shown that replacement solvents containing nonylphenolethoxylates (NPE) constituent were contributing to whole effluent toxicity test failures of the Ceriodaphnia dubia and Pimephales promela species. An alternative aqueous cleaner B2 was identified. Testing to find an effective, low cost method of disposing of the wastewater generated from alternative aqueous cleaners was completed. Due to the proprietary nature of the new surfactant the new surfactants name, chemical composition, and structures will not be identified.

The newly identified aqueous cleaner, B2, contained numerous different types of general chemical compounds as well as proprietary surfactants. At the time of the study limited information on the biodegradability and toxicity of B2 or the individual chemical constituents was available. Large quantities of high (10wt%) and low (0-35 mg/l) concentration B2 wastewater were to be generated. It was estimated that approximately 250,000 gallons of low concentration wastewater approximately 20,000 gallons of high concentration wastewater would be generated annually. New construction of biological industrial waste water treatment facilities (IWWTF) was approaching completion on site where the bulk of B2 wastewater was to be generated. It was desired to treat the B2 wastewater onsite. Onsite treatment of B2 wastewater was dependent upon the biodegradability and toxicity of the B2 wastewater.

A three-phased test plan to quickly and cost effectively evaluate the biodegradability and toxicity of the B2 wastewater was proposed.

In Phase I, three objectives were identified. 1. Identify all surfactants and chemical constituents of the B2. 2. Predict the potential biodegradability of the identified surfactant constituents by utilizing a computer biodegradability model. 3. Evaluate the toxicity and treatability for the low concentration B2 wastewater utilizing analytical and acute-whole-effluent-toxicity testing.

Phase II included bench top laboratory testing of identified surfactant in a controlled biological system. Three objectives were identified. 1. Validate the biodegradability of the surfactants. 2. Estimate the acclimation period for the biological system. 3. Obtain a laboratory half-life value for each of the four surfactants and the four surfactants combined.

Phase III had two objectives. 1. Evaluate treating B2 wastewater at a full-scale biological industrial waste water treatment facility (IWWTF). 2. Implement a full-scale test to introduce and treat high concentration B2 wastewater at full-scale biological (IWWTF).

Since completion of testing, B2 wastewater has been utilized as a carbon and energy source in the biological IWWTF. Gradual and continual acclimation of the biomass has proven to be a key parameter in the effective treatment of the B2 wastewater. In 1997 a second biological IWWTF began to utilize the B2 wastewater as a carbon and energy source replacing the use of commercial dog food as carbon and energy source during low influent BOD/COD periods.

Phase I.

Compound Identification

A proprietary agreement was signed with the manufacture of the B2 surfactant and a completed disclosure of constituents in the B2 surfactant was obtained. The constituents were ranked in regards to potential toxicity based upon the chemical structures supplied. Chemical structures for four potentially toxic surfactants, D8 (anionic polyether), D22 (proprietary anionic compound), D26 (nonionic surfactant), and D30 (nonionic polyglycol), were identified to be evaluated to predict biodegradability.

Computer Modeling of the Biodegradability of the Surfactant

The B2 surfactant constituents were evaluated utilizing computer biodegradability modeling. The model was developed, executed, and evaluated by Dr. Robert Okey, Ph.D. The model was based upon a regressive equation (Equation 1.) for an unacclimated model that assigned an index value to predicted biodegradability of solution.

$$\text{Index Value} = -0.030\,({}^{6}\chi^{v}) - 0.123\,({}^{3}\chi^{v}_{c}) - 6.420\,({}^{5}\chi^{v}_{ch}) + 1.386\,({}^{6}\chi^{v}_{ch}) + 0.198\,(\text{Growth}) + 0.337\,(\text{Aliph}) - 0.482\,(NH_2) + 0.029\,(OH) - 0.344\,(HAL) - 0.407\,(COOH) - 0.012\,(SO_3) - 1.430\,(NO_2) - 0.234\,(HET) + 1.765.$$

Equation 1.

Equation 1. utilized the connective indices (χ terms) that describe the size and complexity of the molecules. The "Growth" term as a descriptor to describe the impact of the growth substrate. The "Aliph" term to identify an aliphatic structure present. The " HET" term to identify a heteroatom present. The NH_2, OH, HAL (Halogen), COOH, SO_3, and NO2 terms are utilized to identify the number of denoted functional groups present. Based upon the index value computed, the model predicted the intact molecules, despite the presence of the ester linkage, would degrade at a calculated rate of 1.0-2.0 mg COD/hr.g MLSS (mixed liquor suspended solids). The rate predicted would not be sufficient to maintain a biological system and therefore would not degrade as a sole carbon source. The model revealed the toxic constituents could potential degrade if other carbon sources were present. When hydrolysis at the ester linkage was assumed the characteristic fatty acid carbon chain was predicted to rapidly degrade. The model predicted the hydrolyzed toxic constituents would degrade at a rate of 12.0-mg COD/hr.g MLSS. This rate was sufficient to assure degradation of the materials as a sole carbon source and that the surfactant and byproducts of the degradation would adsorb into the biological system.

Based upon the biodegradability model result, Phase II, laboratory biodegradation study on four surfactant constituents D8, D22, D26, and D30 was indicated.

Acute Whole Effluent Toxicity Testing of Low Concentration B2 wastewater

The majority of B2 wastewater to be generated was to be low concentration. The aqueous cleaning systems utilized a two-step rinse. The first rinse cycle was recycled deionized water and the second was single pass, non-recycled deionized water. Testing was completed to ascertain the toxicity and treatability of wastewater. Granular activated carbon (GAC) was chosen as the method of treatment due to the low concentration and ionic characteristic of the B2 rinse waters. A commercial granular activated carbon (GAC) was utilized in the treatability testing.

The treatment apparatus consisted of a 550-gallon storage tank and a commercially available 55 gallon, 2 ½ cubic foot GAC vessel. The GAC vessel was conditioned and purged of carbon fine by passing potable water through the vessel at a rate of four gallons per minute for approximately 8 hours. After the conditioning was completed, approximately 500 gallons of recycled rinse water follows by 500 gallons of non-recycled rinse water were circulated through the GAC unit at approximately three gallons per minute. Test samples of the rinse waters were collected before and after the GAC vessel. Analytical and acute whole effluent toxicity testing was completed.

Results
The results of the testing are shown in Table 1.

	D-30 (mg/l)	D-26 (mg/l)	D-22 (mg/l)	D-8 (mg/l)	Pimephales Promela LC50	Ceriodaphnia dubia LC50
Non-recycled Rinse Carbon Treated	u	8	u	u	> 100%	> 100%
Non-recycled Rinse	u	21	11.9	5.6	22%	21%
Recycled Rinse Carbon Treated	u	11	0.24	u	> 100%	> 100%
Recycled Rinse	29.9	113	127	57.2	5.30%	4.90%
Detection limit (mg/l)	28.2	1	0.2	2	u - undetected	

Table 1.

Conclusion
Test results revealed that recycled and non-recycled B2 low concentration wastewaters were toxic. Acute whole effluent toxicity testing LC50 of 5.3% and 4.9 % for Pimephales promela (Fathead minnow) and Ceriodaphnia dubia (Ceriodaphnia) reported on recycled B2 rinse wastewater and LC50 of 22 % and 21% for Fathead minnow and Ceriodaphnia reported on non-recycled rinse wastewater.

Granular activated carbon treatment was found to be effective in eliminating acute toxicity in the low concentration B2 wastewaters. LC50 test results of >100% for Fathead minnow and Ceriodaphnia for GAC treated rinse water as reported.

Phase II. Laboratory Testing

Laboratory Test Methods
Prior to laboratory testing, a method for quantifying surfactant concentrations in activated sludge was developed. The extraction procedures suggested by Standard Methods (1989) were inadequate for activated sludge samples. Dr. Robert Okey, Ph.D., developed a procedure suitable for testing surfactants in activated sludge (adsorbable species). A modification of a procedure from "The Measurement of Nonionic Surfactants in Aqueous Environments," by Tabak and Bunch (1984) was used. To determine the residual surfactant in the activated sludge, a method to assure the adsorbed surfactants was dissolved in solution was developed. The test utilized was similar to that reported for cobalt thiocyanate active substances. The basic procedure of capturing the surfactant was to extract the surfactant first with ethylacetate and reduce the volume by low temperature evaporation, and then the surfactant was extracted into a methylene chloride phase. Test results provided the total quantity of surfactant remaining in the biological culture after a specific period of time. The D26 surfactant was utilized as a standard.

Laboratory Testing of Biological System
The laboratory testing involved testing of surfactant constituents, D8, D22, D26, and D30. Three cultures were established. The activated sludge was developed from soil and sewage inoculum and was reinoculated frequently from both sources during the first month of development. The activated sludge was fed a synthetic sewage which consisted of glucose, castile soap and beef extract. Additional inorganic nutrients were supplied through the addition of phosphate and ammonium salts. The organic nutrients created an activated sludge substrate, which was buffered at about pH 7.5 and in which the organics contained in the synthetic sewage were all degraded. At approximately 45 days, the system was switched from synthetic sewage. The cultures were than converted entirely to influent from the new industrial wastewater treatment facility over a period of one week. Once the biological systems were acclimated the constituents were tested in the biological systems receiving only the influent wastewater as its sole inorganic nutrient and organic carbon source. Acclimation of the biological system to the introduction of

the surfactant was estimated to have been achieved within 1-2 days. A 10-day sludge retention time (SRT) was utilized for the laboratory testing. All the surfactants were fed at concentrations ranging from 1.0, 5.0, and 10.0 mg/L in the activated sludge systems. The general procedure for testing was to extract and analyze the activated sludge system at various periods of time.

Results

An insufficient number of tests were analyzed to determine a statistically precise half-life of each of the surfactants. However, all surfactants tested were degraded completely in less than seven days beyond the 0.5 to 1.0 mg/l. range of detection limit of the procedure. Acclimation of the biological system to the introduction of the surfactant was estimated to have been achieved with 1-2 days. Results found that all four surfactants degraded with half-lives of less than two days, indicating that all four surfactant studies were fairly biodegradable. Based on the analytical information developed of the individual surfactant, the half-life for the combined B2 wastewater mixture was estimated to be one-half to two days.

Conclusion

It was concluded that all tested materials were easily degraded and did not create a foaming, scum operation in the culture. The results were similar to findings of Kravetz (1990). Kravetz noted that like compounds were degraded fairly rapidly with half-lives of the same order. Ahel *et al.* (1994) also reported the half-life of similar material to be of the order of 1 to 3 days. Based upon the laboratory and literature results, Phase III evaluation and full scale testing of treating B2 wastewater was suggested.

Phase III Full-Scale Testing.

Phase III had two main objectives, first; to evaluate treating high concentration B2 wastewater and second; implement a full-scale test to introduce and treat high concentration B2 wastewater at a full-scale biological industrial waste water treatment facility (IWWTF).

Evaluation

During the evaluation items of concern were reviewed. It was feared that the high concentration B2 wastewater could possibly have an impact of the biological and physical operation of the full-scale plant. The biological industrial wastewater treatment facility, was a newly constructed 0.260 million-gallon aerobic oxidation ditch that utilized ozonation as a disinfecting/detoxification tertiary treatment. The IWWTF influent contained low biological oxygen demand (BOD) and high chemical oxygen demand (COD). (See Table 2). For approximately 72 hours out of the week the IWWTF influent consisted in large part of boiler blow down and cooling water from manufacturing equipment. This was a result of a 4-day workweek for the majority of employees that the IWWTF serviced. The lack of nutrient inhibited biological cell growth in the oxidation ditch

IWWTF Parameters

	COD mg/l	BOD mg/l	Flow Rate (GPD)
Monday-Friday (96 hours)	200-850	20-100	60000
Friday-Monday (72 hours)	20-40	<5	40000

Table 2.

The facility utilized large surface aerators and pumps in the operation. It was feared excessive foaming in the oxidation ditch and/or cavitation of the pump would occur. The B2 surfactant was formulated to be stable in temperatures greater than 100 degree F. No documented foaming problem was noted in the laboratory bench studies. It was anticipated that foaming would not pose a significant problem if the B2 wastewater was gradually and continuously introduced into the facility.

The fact the surfactant half-life was longer than the treatment plant hydraulic detention time was addressed. It was assumed the bulk of the surfactant would associate with the cell tissue and not with the aqueous phase. Synthetic and natural surfactants usually primarily associated with the solid phase in wastewater treatment. The calculated sludge retention time (SRT) of the IWWTF was in excess of 100 days. The SRT was maintained at the 100+ day SRT to meet the high influent COD demand. If the surfactant associated with the solid phase, a 100+ day SRT would allow ample time for biodegradation.

Concerns about the effect high levels of surfactant would have on the COD removal was evaluated. Phase II. laboratory tests investigating the COD removal revealed the presence of modest levels of surfactants did not appear to have any impact. A literature search found a study by Rouse *et al.* (1994) in which the influence of surfactants on biodegradation is reviewed. Rouse found in most cases biodegradation has been enhanced in the documented report. If Rouse's study was accurate, and biodegradation was enhanced, it was possible that surfactant could be utilized and a carbon and energy source for the IWWTF. Testing to monitor the affect of the B2 wastewater on the COD removal at the IWWTF oxidation ditch was indicated.

It was unknown at the time what effect the ozonation system would have on surfactant remaining in the IWWTF effluent. No literature was available on the effect ozonation would have on residual surfactants. Testing on the effluent was indicated to assess the effect ozonation would have on the anionic and nonionic surfactants.

Full-Scale Testing

Results from the laboratory testing verified that all four constituents would degrade with approximately the same half-life of ½ -2 days. D22 surfactant was chosen as the analytical constituent for testing. The D22 had a nominal half-life of the reported half-lives, made up the greatest fraction of the B2 constituents, and had a low level of detection (<0.5 ppm). It was assumed the other constituents would degrade similarly. Based upon the characteristic composition of the B2 solution the concentrations of the three constituents remaining could be estimated.

Full-scale testing was completed over a 30-day period in September and October of 1995. During the full-scale test, high concentration B2 wastewater was introduced into the IWWTF. The B2 wastewater was introduced continuously into the facility at a rate of 10 to 100 gallons per day. Visual observation and operation data was collected during the test. The IWWTF was acclimated to low concentration of the wastewater over a 14 day period. Total surfactant influent concentrations ranged from 2.5 to 7.9 parts per million (ppm) and D22 concentration ranged from 0.82 to 2.56 ppm during the 14-day acclamation period. Over the next 12 days the total surfactant concentration level was increased from 7.78 to 26.26 ppm which corresponded to a D22 influent concentration of 2.32 to 8.5 ppm. Samples of IWWTF effluent water were taken one day after maximum amounts of high concentration B2 wastewater was introduced. Two samples were taken, one prior to and one after the ozonation-contract-basin.

Results

Visual observations revealed no abnormal foaming in oxidation ditch. Facility aeration and pump operations were unaffected. On the sixth day of low concentration acclimation an oil sheen was visible on the clarifiers. It was observed that the grease and scum deposit on the clarifier and oxidation ditch walls began to diminish. It was assumed that this phenomenon was a result of the surfactants, no such incident had been experienced prior. Visually, the oxidation ditch biomass appeared initially stressed. Within six days the biomass appeared healthy and thrived for the duration of testing. The 5-day moving average mixed liquor suspended solids (MLSS) increased (12.45%) from 1895 mg/l prior to testing to 2131mg/l at the end of the B2 wastewater addition. Ammonia concentrations in the IWWTF effluent were monitored. Ammonia concentrations in effluent samples tested during the test did not exceed 0.2 ppm and were within normal operating parameters. Effluent COD was monitored and averaged 26.0 ppm and ranged from 7- 41 ppm. These COD levels were higher than the previous monthly average of 21.4 ppm. This increase in COD coincided with the appearance of the oil sheen and was believed to be attributed to the release of oil scum from the facility.

Samples of effluent water taken before and after the ozonation contact basin were less than the detection limit (<0.5 ppm) of D22 surfactant. Analytical test results of the effect ozonation would have on the surfactant was not possible due to insufficient concentration of constituents remaining in the effluent solution. Oil and grease levels were reduced from 60mg/l, for samples collected before the ozone contact chamber, to 35mg/l for sample collected exiting the ozone contact chamber.

Conclusion

Based upon the results of full-scale testing, B2 wastewater is treated very effectively in a Biological IWWTF. Acclimation of the oxidation ditch biomass was achieved in approximately 6 days. Addition of the B2 wastewater results in a "cleansing" of oil and grease scum deposit in the clarifiers and oxidation ditch. Greater than 93.5% of D22 constituent was removed when treated by acclimated biological means. The 5-day morning average of the MLSS in the oxidation ditch rose 236 gm/l, during the test. Based on the results of testing, it was postulated that the B2 wastewater could be utilized in an acclimated biological system as a carbon and energy source.

Since completion of the full-scale test, B2 wastewater has been utilized as a carbon and energy source in the biological IWWTF when available. Gradual and continual acclimation of the biomass has proven to be a key parameter in the effective treatment of the B2 wastewater. In 1997 a second biological IWWTF began to utilize the B2 wastewater as a carbon and energy source replacing the use of commercial dog food as carbon and energy source during low influent BOD/COD periods.

Summary

A newly identified aqueous cleaner, B2, contained general chemical compounds and proprietary surfactants. Limited information on the biodegradability and toxicity of B2 or its individual chemical constituents was available. It was desired to treat the B2 wastewater onsite at biological industrial waste water treatment facilities. A three-phased test plan to quickly and cost effectively evaluate the biodegradability and toxicity of the B2 wastewater was completed.

In Phase I computer modeling of the biodegradability of the surfactants and acute whole effluent toxicity testing of low concentration B2 wastewater was completed. The computer modeling was based upon a regressive equation of an unacclimated model to predict biodegradability of solution. Based upon the results, the intact molecules would degrade at a rate of 1.0-2.0 mg COD/hr.g MLSS (mixed liquor suspended solids). The model predicted the toxic constituents would degrade at a rate of 12.0-mg COD/hr.g MLSS if other carbon sources were present and hydrolysis at the ester linkage was assumed.

Acute whole effluent toxicity testing of low concentration B2 wastewater was completed to ascertain the toxicity and treatability of low concentration B2 wastewater. A commercial granular activated carbon (GAC) unit was chosen as the method of treatment. Testing results revealed the low concentration B2 wastewater was toxic to Fathead minnow and Ceriodaphnia. GAC treatment of the wastewater was found to be effective in eliminating acute toxicity.

Phase II laboratory testing involved testing four identified B2 surfactant constituents, D8, D22, D26, and D30. Three biological cultures were established and activated sludge was developed. All constituents were fed at concentrations ranging from 1.0, 5.0, and 10.0 mg/L in the activated sludge systems. The constituents tested were degraded completely in less than seven days beyond the range of detection limit of the procedure. The test method was capable of noting active substances at a concentration of <0.5 to 1.0 mg/L. It was found that all four constituents and combined mixture degraded with half-lives of less than two day.

Phase III testing evaluated treating and implementing full-scale biodegradability testing of high concentration B2 wastewater at a biological industrial waste water treatment facility (IWWTF). The evaluation implied that full-scale testing could be performed safely. Full-scale testing revealed B2 wastewater is treated very effectively in a biological IWWTF. Acclimation of the oxidation ditch biomass was achieved within 6 days . A greater than 93.5% removal efficiency for D22 constituent achieved by acclimated biological means. The 5-day morning average of the MLSS in the oxidation ditch rose12.45% (236 gm/l) during the test. Based on the results of testing, it was postulated that the B2 wastewater could be utilized in an acclimated biological system as a carbon and energy source.

Since completion of the full-scale test, B2 wastewater has been utilized as a carbon and energy source in the biological IWWTF when available. Gradual and continual acclimation of the biomass has proven to be a key parameter in the effective treatment of the B2 wastewater. In 1997, a second biological IWWTF began utilizing the B2 wastewater as a carbon and energy source replacing the use of commercial dog food as carbon and energy source during low influent BOD/COD periods.

Acknowledgment

A special thanks to:

Dr Robert Okey Ph.D., and his staff

Jeff Hollingsworth, Thiokol Corporation

Andy Poriot, Thiokol Corporation

References

Ahel, M., D. Hršak, and W. Giger. (1994) "Aerobic Transformation of Short-Chain Alkylphenol Polyethoxylates by Mixed Bacterial Cultures," Arch. Environ. Contam. Toxicol., **26**:540-548.

Kravetz, L. (1990) "Biodegradation Pathways of Nonionic Ethoxylates," in Agricultural and Synthetic Polymers, Biodegradability and Utilization, J.E. Glass and G. Swift, Eds., ACS Symposium Series 433, Chapter 9, 96-109, American Chemical Society, Washington, DC.

Rouse, Joseph D., David A. Sabatini, Joseph M. Suflita, and Jeffrey H. Harwell. (1994) "Influence of Surfactants on Microbial Degradation of Organic Compounds," Critical Reviews in Environ. Sci., **24**(4):325-370.

Standard Methods for the Examination of Water and Wastewater. (1989) 17th Ed., Washington, DC: American Public Health Association.

Tabak, Henry H., and Robert L. Bunch. (1984) "Measurement of Nonionic Surfactants in Aqueous Environments," 36th Purdue Industrial Waste Conference, 888-907, Purdue University, West Lafayette, IN.

MICROTOX TOXICITY TEST COMPARED WITH THE DAPHNID, FLATHEAD MINNOW ACUTE LETHALITY TEST FOR USE IN MONITORING WASTEWATER EFFLUENT AT NASA, MARSHALL SPACE FLIGHT CENTER

Donald C. Obenhuber and Tim Huff,
Microcraft Inc. , Marshall Space Flight Center,
Huntsville, AL 35812

The Microtox Toxicity Test is a new bioanalytical method for determining the toxicity of aqueous samples. Microtox measures the light output of fluorescent bacteria (Vibrio fischeri) before and after exposure to a toxic sample. The Microtox Test was compared with the EPA approved Daphnid, Flathead Minnow Acute Lethality Test for use in monitoring wastewater effluent.

The Daphnid, Flathead Minnow Acute Lethality Test indicated toxicity of the system effluent consistently on quarterly samples for 2 years. The results of Microtox Chronic Testing indicate toxicity at a concentration between 12.5 and 50 percent based on a Lowest Observable Effective Concentration (LOEC). Microtox Acute Basic Test yielded no significant toxicity at the Effective Concentration of a 50% Light reduction (EC50). The use of the Microtox Acute Comparative and Inhibition Tests and an increase in sensitivity of the Basic Test by using an EC20 produced toxicity data which was comparable and significant relative to the Daphnid, Flathead Minnow Test.

General Information

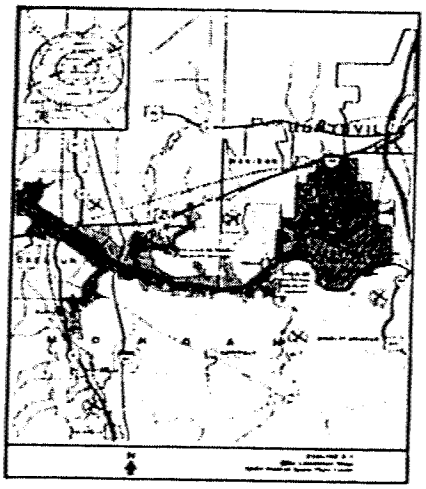
National Aeronautics and Space Administration (NASA)
George C. Marshall Space Flight Center (MSFC)
Huntsville, Alabama

The George C. Marshall Space Flight Center is one of NASA's largest centers, occupying 800 acres in Huntsville, Alabama. Its primary mission is to lead the Agency to develop and maintain space transportation and propulsion systems and conduct microgravity research.

Marshall hosts NASA's Centers of Excellence in science research in materials, biotechnology, global hydrology and climate studies, astrophysics, and payload utilization. In addition, Marshall houses Centers of Excellence in propulsion, avionics, space environment and optics technologies. Marshall's employees and facilities constitute a national resource, readily adapting to the changing needs of space exploration.

The Marshall Center was established in 1960 under the leadership of Dr. Wernher von Braun. Highlights of the early years included building the Mercury-Redstone vehicle that boosted America's first astronaut, Alan B. Shepard, into suborbital flight and developing the Saturn rockets which took the first man to the Moon in 1969.

Throughout its history the Marshall Center has managed many significant space projects including the Lunar Roving Vehicle, 1971; Skylab, 1973; Space Shuttle main engines, external tank and solid rocket boosters, 1981; the Hubble Space Telescope, 1990; and 23 Spacelab missions since 1983, most recently, the Life and Microgravity Spacelab mission, 1996.



MSFC is located on approximately 1,840 acres surrounded by the U.S. Army Redstone Arsenal (RSA), which occupies 38,309 acres of property in the southwestern portion of Madison County, Alabama. The Tennessee River forms the southern boundary of RSA. The City of Huntsville surrounds RSA on the eastern and northern sides, as well as on most of the western side of the facility. The Wheeler National Wildlife Refuge borders RSA on the southwest. A substantial portion of RSA, including most of the lands to the south and west of MSFC, is a part of the refuge. A small portion of the Wheeler National Wildlife Refuge extends onto property controlled by MSFC.

MSFC is located within RSA on a site previously occupied by the U.S. Department of the Army (DA). The RSA area, which shares a common boundary with MSFC, originally was established to produce conventional and chemical munitions for use during World War II. From 1942 to 1945, Army operations were used to manufacture raw materials for toxic agents and incendiary materials, and to assemble, store, and ship the final products. Onsite waste disposal activities included disposal of construction debris, drums, and chemical munitions, and open burning of combustible materials. After the war, RSA became a center for the receipt, storage, and demilitarization of Allied and German chemical agents.

In 1949, RSA's mission was changed to research and development of rocketry and guided missile systems. In 1960, civilian rocketry and missile activities were transferred to NASA's MSFC. Since then, the area known as MSFC has been used to develop, test, and manufacture space vehicles and components. A renewable 99-year land grant transferred buildings, land, and space projects from the U.S. Army to NASA.

Objective

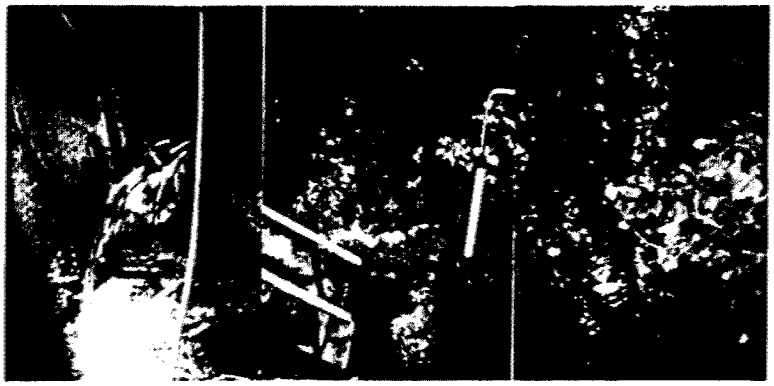
Plating Facility, Building 4760

Environmental protection is an important part of the nationwide operations of the National Aeronautics and Space Administration.

The Marshall Center has high level of industrial activity on site and therefore has a well managed chemical acquisition and disposal program and a carefully monitored industrial sewer system. No environmentally hazardous materials are permitted in the industrial sewer system. The Alabama Department of Environmental Management (ADEM) regulates the discharge of waste water and according to current permits discharge sites are monitored periodically.

Discharge site DSN-001 was routinely monitored for chemical discharge as well as toxicity. The site had recently been failing the Bioassay procedure required for permit compliance. The bioassay used was the method required by the US Environmental Protection Agency (US EPA). After several attempts to determine the chemical nature and cause of the toxicity, no cause could be found. It was decided that an intensive study of the problem was necessary but due to the expense of using the standard EPA Bioassay method and alternative bioassay method was sought to allow for a more rapid determination of the problem. The Microtox Toxicity Test was selected due to it's microbiological nature and rapid turn around time of analysis. The system was purchased and setup in the Environmental Chemistry Laboratory, formally the Microbial Ecology Facility.

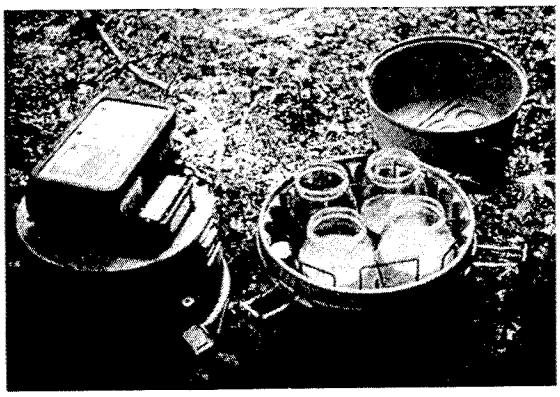
Discharge site DSN-001



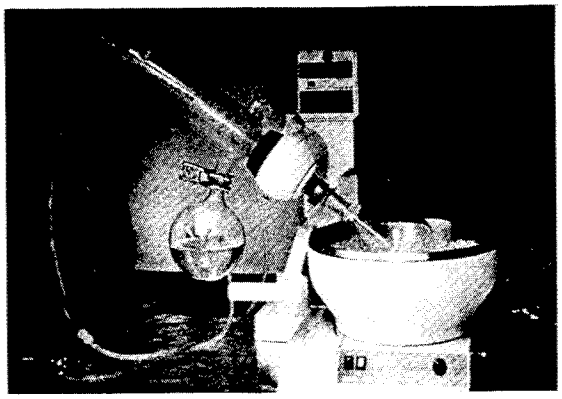
Initial tests were performed on the discharge water to determine the level of toxicity present.

Methods

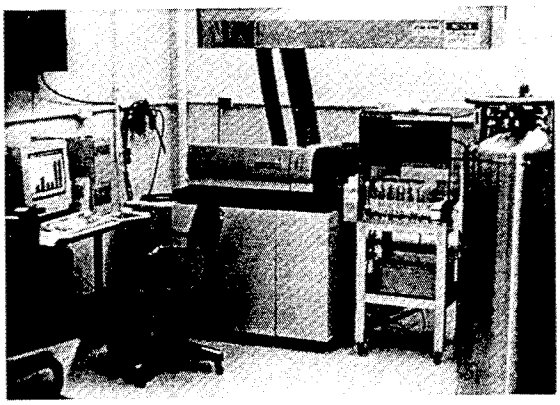
Samples were collected at the site either as grab or composite samples. SPMD's (Semipermeable membrane device) were used as In-situ bioaccumulators to concentrate toxic compounds. Laboratory analysis consisted of metals analysis using ICP-MS and toxicity analysis using the Microtox System.



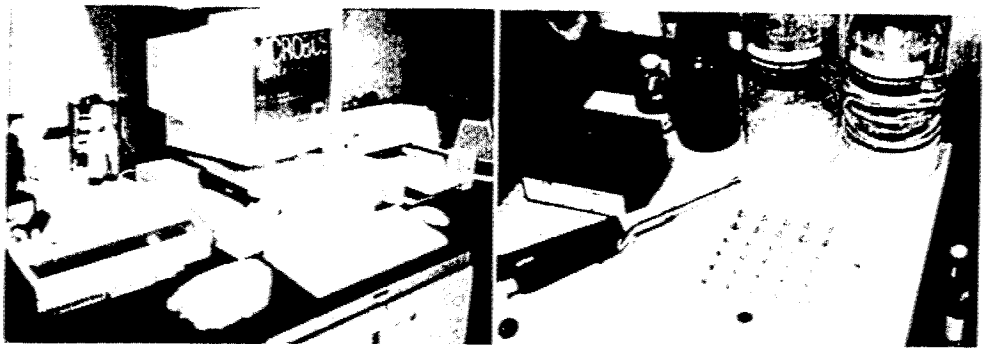
Composite samples were taken every 6 hours for analysis.



Initially samples were concentrated before analysis to improve sensitivity

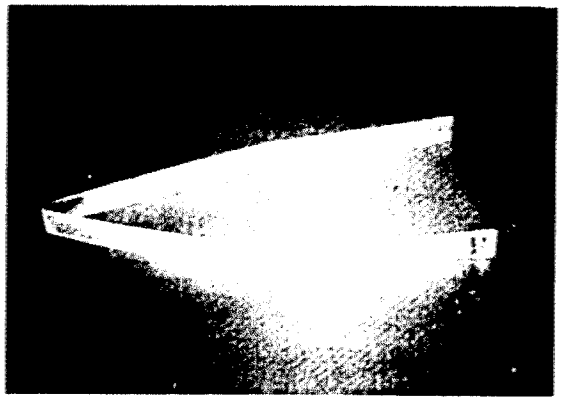


Inductively Coupled Plasma - Mass Spectrometry was performed on some samples to determine metal concentrations.



The Microtox Toxicity System is a relatively new bioanalytical method for determining the toxicity of aqueous samples. The Microtox Test was used to supplement the EPA approved Daphnid, Flathead Minnow Acute Lethality Test for use in monitoring wastewater effluent.

Microtox measures the light output of fluorescent bacteria (Vibrio fischeri) before and after exposure to a toxic sample.

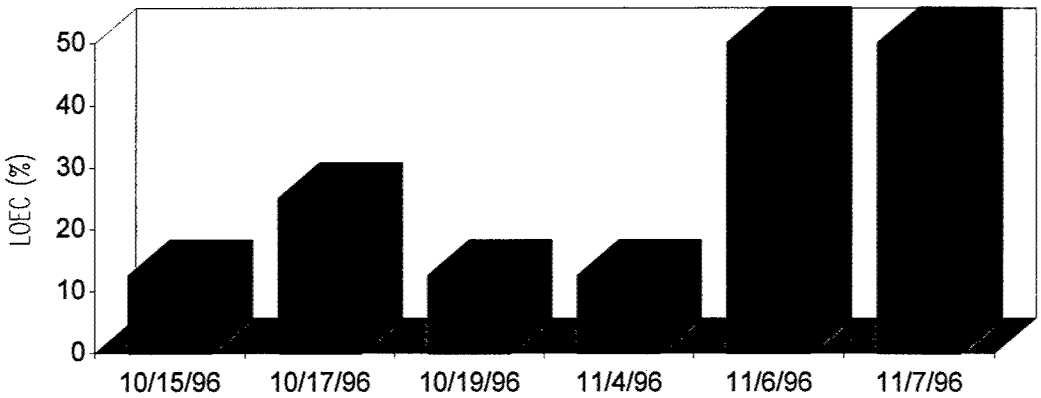


The Semipermeable membrane device (SPMD) is a bioaccumulator of environmental contaminants in aqueous media.

RESULTS

Previous results from the use of the Daphnid, Flathead Minnow Acute Lethality Test indicated toxicity of the system effluent consistently on quarterly samples for 2 years. Parallel sampling with the Microtox system for the fourth quarter of 1996 demonstrated toxicity at a concentration between 12.5 and 50 percent based on a Lowest Observable Effective Concentration (LOEC). Determination of the cause of the toxicity resulted in no significant findings in regard to metal contamination or SPMD bioaccumulated toxicity. Only when chlorine neutralization was utilized in the Microtox testing was toxicity eliminated. The simplest answer is sometimes the most elusive.

Microtox Analysis of DSN 001



The results of Microtox Chronic Testing indicate toxicity at a concentration between 12.5 and 50 percent based on a Lowest Observable Effective Concentration (LOEC).

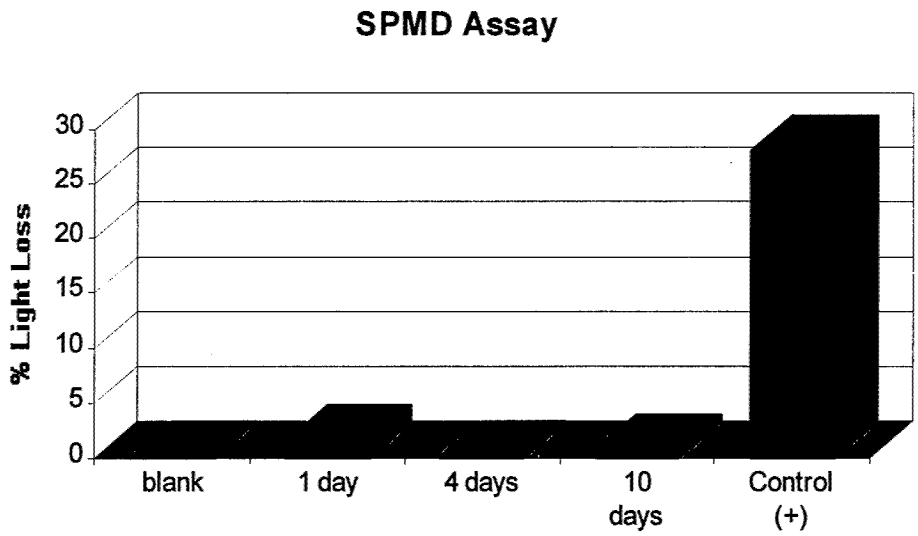
ICP-MS
Comprehensive Report

Sample ID: DSN-001
Sample Date/Time: October 11, 1996
Number of Replicates: 1
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55
Method c:\elandata\Method\totalquant1.mth
Dataset File: c:\elandata\Dataset\TotalQuant
Tuning File: default.tun
Optimization File: default.dac
Response File: c:\elandata\System\current.rsp

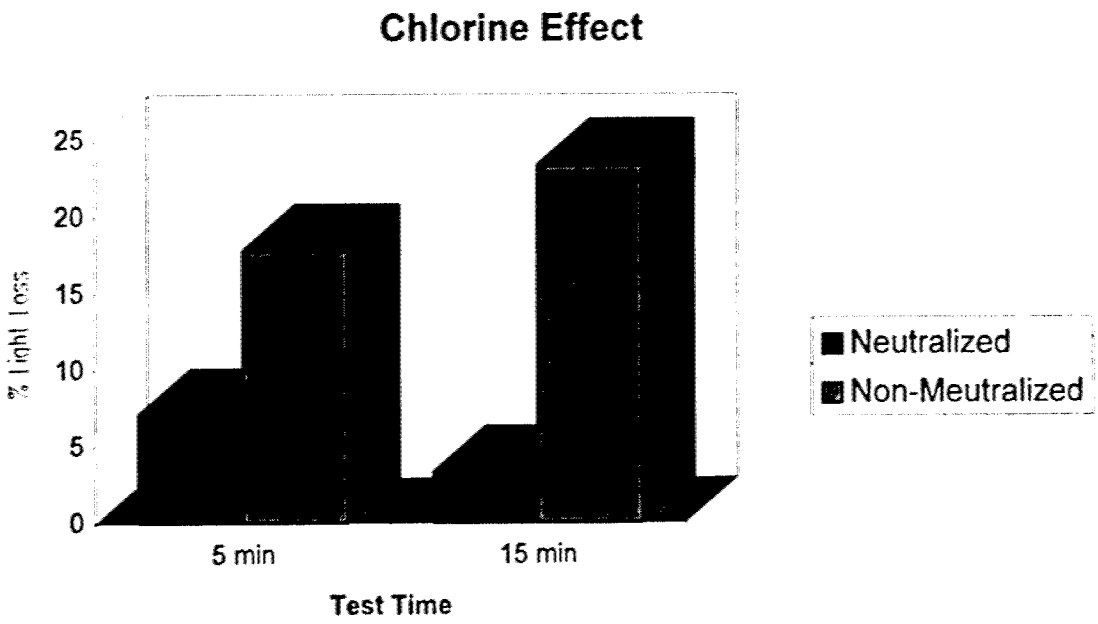
Analyte	Conc (mg/l)
H	Not Measured
He	Not Measured
Li	0.00000
Be	0.00000
B	0.00000
C	0.01728
N	76.38274
O	Not Measured
Na	0.02024
Mg	0.01638
Al	0.00022
Si	0.00214
P	0.00046
S	0.44642
Cl	0.04952
Ar	
K	0.00584
Ca	0.05783
Sc	0.00000
Ti	0.00017
V	0.00001
Cr	0.00001
Mn	0.00001
Fe	0.00067
Co	0.00000
Ni	0.00001
Cu	0.00001
Zn	0.00002
Ga	0.00000
Ge	0.00000
As	0.00000
Se	0.00001
Br	0.00110
Rb	0.00002
Sr	0.00082
Y	0.00000
Zr	0.00000
Nb	0.00000
Mo	0.00254
Ru	0.00000
Rh	0.00177
Pd	0.00000
Ag	0.00008
Cd	0.00007
In	0.00000
Sn	0.00001
Sb	0.00001
Te	0.00000
I	0.00007
Cs	0.00000
Ba	0.00094
La	0.00000
Ce	0.00000
Pr	0.00000
Nd	0.00000
Sm	0.00000
Eu	0.00000
Gd	0.00000
Tb	0.00000
Dy	0.00000
Ho	0.00000
Er	0.00000
Tm	0.00000
Yb	0.00000

Lu	0.00000	Au	0.00002
Hf	0.00010	Hg	0.00001
Ta	0.00000	Tl	0.00000
W	0.00005	Pb	0.00002
Re	0.00000	Bi	0.00000
Os	0.00000	Th	0.00000
Ir	0.00000	U	0.00000
Pt	0.00000		

ICP-MS analysis of the effluent showed no significant metal contamination.



Samples collected from SPMD's showed no significant toxicity using the Microtox system.



Neutralized samples using sodium thiosulfate showed no significant toxicity as compared to Non-Neutralized samples (neutralized samples showed an LOEC of >100%; non-neutralized samples showed an LOEC of 12.5-50%)

Total Residual Chlorine

Date (1997)	DSN001 Result (ppb)	Manhole 32 Result (ppb)	Time	Permit Limit (ppb)
15-Jan	400	NR	12:30	63.3
28-Jan	100	NR	1:01	63.3
12-Feb	200	NR	2:40	63.3
28-Feb	300	NR	1:20	63.3
4-Mar	100	NR	10:05	63.3
5-Mar	90	NR	9:42	63.3
6-Mar	130	NR	9:28	63.3
12-Mar	270	NR	12:19	63.3
26-Mar	200	NR	3:18	63.3
16-Apr	260	NR	2:08	63.3
29-Apr	320	NR	3:45	63.3
7-May	290	NR	2:25	63.3
21-May	220	NR	3:01	63.3
3-Jun	230	NR	2:20	63.3
20-Jun	290	NR	4:58	63.3
8-Jul	60*	60**	1:40	63.3
9-Jul	80*	50**	9:05	63.3
9-Jul	310*	NR	4:07	63.3
10-Jul	30*	90**	9:20	63.3
14-Jul	80*	240**	8:00	63.3
14-Jul	20*	50**	3:20	63.3
15-Jul	50*	200**	9:45	63.3
15-Jul	90*	NR	3:15	63.3
16-Jul	170*	NR	11:11	63.3
17-Jul	90*	NR	11:03	63.3
18-Jul	80*	NR	9:10	63.3
25-Jul	23*	NR	9:49	63.3
22-Aug	135*	NR	4:21	63.3
29-Aug	70*	NR	7:30	63.3
12-Sep	10*	NR	3:02	63.3
30-Sep	130	NR	2:48	63.3
9-Oct	70***	NR	9:48	63.3
24-Oct	30***	NR	2:59	63.3

* Aeration system installed at manhole upstream from discharge point
** Reading taken upstream from the aeration point
*** a second aeration system was activated at MH32

Total Residual Chlorine for site DSN-001

CONCLUSIONS

The Microtox System performed well in conjunction with the Daphnid, Flathead Minnow Acute Lethality Test. Each test demonstrated similar toxicity in duplicate samples.

Chlorine is most likely Toxic Substance in Samples from DSN001.

ADEM (Alabama Department of Environmental Management) will be Petitioned for Approval to begin a Comparative Study.

The Microtox Toxicity Assay has provided a significant cost savings to NASA, as a supplement and potential replacement for current methods.

Future Plans

AERATE INDUSTRIAL DISCHARGE

AJT & ASSOCIATES, INC.

AJT & ASSOCIATES, INC.
544-7976

DESIGN CRITERIA STATEMENT
January 29, 1998

GENERAL: The industrial wastewater discharge, near the intersection of Martin Road and Indian Creek, contains unacceptable amounts of chlorine. The chlorine can be removed from the water by aeration.

CIVIL\STRUCTURAL: Design a concrete basin to receive outflow at the discharge point. Install (2) two blower units and piping leading to air diffusers in the bottom of the new basin to aerate the wastewater. During construction, the existing discharge water will be pumped from behind the existing weir and discharged at a point downstream away from the construction.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 1999	Conference Publication

4. TITLE AND SUBTITLE

Third Aerospace Environmental Technology Conference

5. FUNDING NUMBERS

6. AUTHORS

A.F. Whitaker, D.R Cross, S.V. Caruso, M. Clark-Ingram, Editors

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

8. PERFORMING ORGANIZATION REPORT NUMBER

M–921

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautic and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA/CP—1999–209258

11. SUPPLEMENTARY NOTES

Prepared for Materials and Processes Laboratory, Science and Engineering Directorate
Proceedings of a conference held at Huntsville, AL, June 1–3, 1998

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified — Unlimited
Subject Category 23
Standard Distribution

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The elimination of CFC's, Halons, TCA, other ozone depleting chemicals, and specific hazardous materials is well underway. The phaseout of these chemicals has mandated changes and new developments in aerospace materials and processes. We are beyond discovery and initiation of these new developments and are now in the implementation phase. This conference provided a forum for materials and processes engineers, scientists, and managers to describe, review, and critically assess the evolving replacement and clean propulsion technologies from the standpoint of their significance, application, impact on aerospace systems, and utilization by the research and development community. The use of these new technologies, their selection and qualification, their implementation, and the needs and plans for further developments were presented.

14. SUBJECT TERMS

environment, technology and laws, replacement technology, solvents, non-CFC's, propulsion, replacement fire suppressants, precision cleaning, coating technology, aqueous process, lessons learned

15. NUMBER OF PAGES

726

16. PRICE CODE

A99

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

National Aeronautics and
Space Administration
AT01S
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama
35812