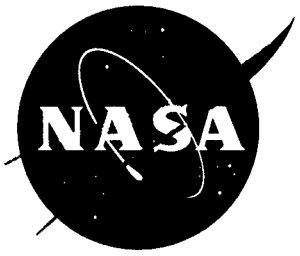
NASA Conference Publication 3298

Aerospace Environmental Technology Conference

A.F. Whitaker, Editor

Summary of a conference held in
Huntsville, Alabama
August 10–11, 1994

March 1995



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

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CHEMICAL PROPULSION AND THE ENVIRONMENT

ATMOSPHERIC ENVIRONMENTAL IMPLICATIONS OF PROPULSION SYSTEMS

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ABSTRACT

Three independent studies have been conducted for assessing the impact of rocket launches on the earth's environment.[1,2,3] These studies have addressed issues of acid rain in the troposphere, ozone depletion in the stratosphere, toxicity of chemical rocket exhaust products, and the potential impact on global warming from carbon dioxide emissions from rocket launches. Local, regional, and global impact assessments were examined and compared with both natural sources and anthropogenic sources of known atmospheric pollutants with the following conclusions:

- Neither solid nor liquid rocket launches have a significant impact on the earth's global environment, and there is no real significant difference between the two.
- Regional and local atmospheric impacts are more significant than global impacts, but quickly return to normal background conditions within a few hours after launch.
- Vastly increased space launch activities equivalent to 50 U.S. Space Shuttles or 50 Russian Energia launches per year would not significantly impact these conclusions.

However, these assessments, for the most part, are based upon homogeneous gas phase chemistry analysis; heterogeneous chemistry from exhaust particulates, such as aluminum oxide, ice contrails, soot, etc., and the influence of plume temperature and afterburning of fuel–rich exhaust products, need to be further addressed. It was the consensus of these studies that computer modeling of interactive plume chemistry with the atmosphere needs to be improved and computer models need to be verified with experimental data. Rocket exhaust plume chemistry can be modified with propellant reformulation and changes in operating conditions, but, based upon the current state of knowledge, it does not appear that significant environmental improvements from propellant formulation changes can be made or are warranted. Flight safety, reliability, and cost improvements are paramount for any new rocket system, and these important aspects cannot be compromised. A detailed environmental cost–benefit–risk analysis must be conducted before any new chemistry or changes in rocket operating conditions should be seriously considered for any future space or defense applications.

This paper presents a summary of the results of environmental assessments contained in these independent studies.

*Vice President and Senior Staff
**Scientist

INTRODUCTION

These studies were conducted to answer a basic question: As a result of increased space launch activities, will chemical rocket propulsion have a major impact on the earth's environment? This issue was first raised by environmentalists who were particularly concerned about the deposition of hydrogen chloride (HCl) from solid rockets into the atmosphere. HCl in the presence of water can form acid rain (hydrochloric acid) in the launch area as well as deposit a chlorine–containing gas directly into the ozone layer of the stratosphere. These issues were of sufficient concern that the original U.S. Air Force–NASA joint program office for the Advanced Launch System (ALS) would not consider solid rockets for that application unless the propellants were reformulated to produce less than one percent by weight of HCl in the exhaust plume, compared to the 21 percent for current propellants. As a result, several alternative propellants that were perceived to be more environmentally acceptable were formulated in the laboratory and tested in subscale motors under U.S. Air Force–sponsored "clean propellant" programs. Initially, existing solid propellant formulations were modified to reduce the HCl content in the exhaust plume; later formulations included totally new propellants that contained non–chlorine oxidizers (these propellants were referred to as "totally clean" propellants). All of these so–called "clean" propellants have some serious drawbacks in one or more important propellant characteristics: losses in performance (specific impulse or density); difficulties in processing and/or reduced physical properties and aging characteristics; humidity sensitivity; increased safety hazards during propellant processing or use; limited ballistic tailoring; and reduced bonding capability. Moreover, many have significant increases in costs over contemporary solid propellants using ammonium perchlorate (AP) as the oxidizer. The chemistry of solid rocket propellants is the single most important factor in determining the performance, safety, reproducibility, reliability, and cost of a solid rocket propulsion system. Departing from a well–established experience base, along with the lack of understanding of the real environmental impact of chemical rocket exhaust, dictated the need to fully examine this issue before changes in solid rocket propellant chemistry were warranted.

It was decided to examine the environmental impact of all rocket propellants, both solid and liquid. Table I lists the propellant combinations that were examined and the major exhaust products from these propellants. The first propellant in the table is the standard solid rocket propellant used in all space launch vehicles incorporating solid rocket boosters (SRBs) today; all current space launch solid propellants use a rubber binder containing aluminum as the primary fuel and AP as the oxidizer. The second formulation in the table is a "clean" propellant that replaces a portion of the AP oxidizer with sodium nitrate. As this propellant burns, most of the

Propellant System	Major Exhaust Products
Ammonium perchlorate . Aluminum	HCl, Al_2O_3, CO_2, CO*, N_2, H_2*, H_2O
Ammonium perchlorate . Sodium nitrate Aluminum	NaCl, Al_2O_3, CO_2, CO*, N_2, H_2*, H_2O
Ammonium perchlorate . Magnesium	MgO, $MgCl_2$, CO_2, CO*, N_2, H_2*, H_2O
Ammonium nitrate .... Magnesium or aluminum	Al_2O_3 or MgO, N_2, CO_2, CO*, H_2*, H_2O
Liquid oxygen ..... Liquid hydrogen	H_2O, H_2*
Liquid oxygen ..... Hydrocarbon	CO*, CO_2, hydrocarbons, H_2O
N_2O_4 ..... Dimethylhydrazine	N_2, NOx, CO*, CO_2, H_2O

*Mostly consumed during afterburning

Table I.
Chemical Propulsion Components
and Exhaust Species

HCl produced is scavenged inside the combustion chamber to form sodium chloride (NaCl), common table salt, as a combustion product rather than HCl. The third propellant is also a "clean" propellant and is sometimes referred to as the "Maalox rocket." This propellant replaces the aluminum fuel with magnesium to produce the oxide of magnesium metal (MgO) rather than aluminum oxide. Magnesium oxide in the presence of water forms magnesium hydroxide, which is a strong base. Magnesium hydroxide is the primary ingredient in Maalox for neutralizing stomach acid (which is also HCl). The magnesium oxide in the rocket exhaust neutralizes the HCl in the plume as it mixes with the water in the ambient air and the water that is produced as part of the combustion process, forming a magnesium chloride ($MgCl_2$) salt in place of HCl. The fourth propellant is referred to as a "totally clean" propellant because it replaces all of the AP oxidizer with an ammonium nitrate oxidizer to prevent any chlorine–containing compounds from being formed. There are several candidate nitrate oxidizers available, and many more energetic nitrate oxidizers are in laboratory development, but the exhaust gas chemistry produced is quite similar to the one shown in the table. The last three propellants are all–liquid rocket propellants used in various space launch vehicles; the simplest chemistry is produced from liquid hydrogen and liquid oxygen that forms water as the primary combustion product with considerable free hydrogen (H_2) present, as the engines are generally run fuel–rich for improved reliability and performance. It should be noted that all of the propellant combinations produce large quantities of water and most produce carbon monoxide (CO); carbon dioxide (CO_2), and free hydrogen (H_2) in the exhaust plume. The storable bipropellant system using nitrogen tetroxide (N_2O_4) and unsymmetrical dimethylhydrazine (UDMH) also produces free nitrogen and oxides of nitrogen. The environmental impact assessment that was made assumed that all of the hydrogen and carbon monoxide produced below an altitude of 25 kilometers was converted to water and carbon dioxide as a result of afterburning with the ambient air.

STRATOSPHERIC OZONE DEPLETION

Figure 1 depicts the various atmospheric zones surrounding the earth. The stratosphere located approximately 13 to 50 kilometers above the earth is particularly important to our environment because it contains a low concentration of ozone (O_3) that acts as a protective shield from damaging ultraviolet radiation from the sun.

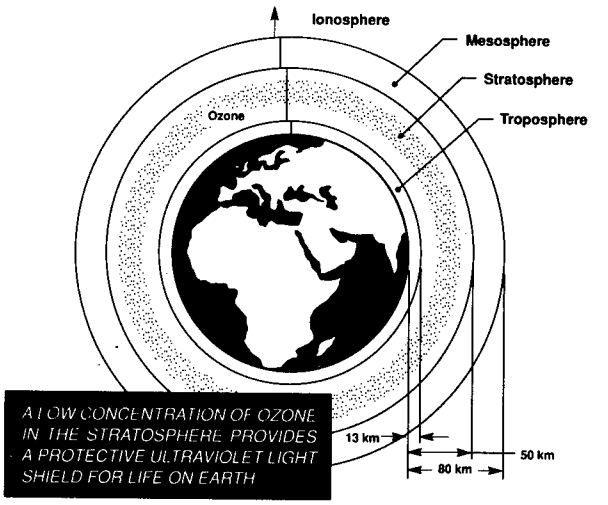


Fig. 1. Stratospheric Ozone Effects

Figure 2 presents the chemical and photochemical processes that are important in the formation of ozone from molecular oxygen in the stratosphere and the reactions associated with ozone destruction.[4] The process is very dynamic in that ozone is continuously being produced and destroyed by naturally occurring photochemical processes in the stratosphere.

Ozone Production

$$O_2 \xrightarrow{h\upsilon} 2O$$
$$O + O_2 + M \longrightarrow O_3 + M$$

Ozone Destruction

$$O_3 \xrightarrow{h\upsilon} O + O_2$$
$$O_3 + O \longrightarrow 2O_2$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$H + O_3 \longrightarrow HO + O_2$$
$$HO + O \longrightarrow H + O_2$$
$$OH + O_3 \longrightarrow HO_2 + O_2$$
$$O + HO_2 \longrightarrow OH + O_2$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$Br + O_3 \longrightarrow BrO + O_2$$
$$BrO + O \longrightarrow Br + O_2$$

Fig. 2. Natural Stratospheric Ozone Pathways

Figure 3 summarizes the naturally occurring ozone–depleting chemistries into nitrogen, hydrogen, oxygen and chlorine.[4] It is important to note that all are catalytic cycles in that the ozone–depleting species is regenerated such that it can re–enter the cycle to destroy additional ozone molecules. The asterisk on the chart reflects those ozone–depleting chemistries that are affected by rocket propulsion, i.e., nitrogen, hydrogen, and chlorine. It is interesting to note that chlorine chemistry is responsible for the least amount of ozone destruction. The reason chlorine chemistry has been of most concern is because it is the one that human activity has contributed to most.

	25 to 30 km Altitude (%)	Total Stratosphere (%)
Nitrogen*		
$NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + O \rightarrow NO + O_2$	70	32
Hydrogen*		
$OH + O_3 \rightarrow HO_2 + O_2$ $O + HO_2 \rightarrow OH + O_2$	10	26
$H + O_3 \rightarrow HO + O_2$ $HO + O \rightarrow H + O_2$		
Oxygen		
$O + O_3 \rightarrow 2O_2$	10	23
Chlorine*		
$Cl + O_3 \rightarrow ClO + O_2$ $ClO + O \rightarrow Cl + O_2$	10	19

* Relevant to chemical propulsion exhaust

Fig. 3. Relative Importance of Various Catalytic Stratospheric Ozone Depletion Cycles

Analysis of more recent data obtained from aircraft flying in the lower part of the stratosphere has cast some doubt on the predominance of nitrogen oxide reactions to ozone destruction in the lower stratosphere.[5] In the spring of 1993, for the first time, atmospheric researchers were able to obtain data from an instrument–laden aircraft that observed all the important families of radicals that affect ozone, i.e., chlorine, bromine, nitrogen, and hydrogen. A new instrument measured hydroxyl (OH) and hydroperoxyl (HO_2) radicals as the aircraft crisscrossed the stratosphere. The data obtained indicated that the hydrogen radical family may be a more important natural loss process for ozone than the nitrogen oxide cycles. These conclusions were also supported by more recent computer models that include heterogeneous chemistry; computer models used in the past based upon homogeneous chemistry alone predicted that nitrogen oxides were the predominant ozone destruction mechanism.

Figure 4 pictorially represents the differences between an all–liquid propulsion system and the Space Shuttle, which uses both solid rocket and liquid propulsion. The exhaust products of interest—HCl, H_2O, and H_2—deposited in the troposphere by either vehicle are of little concern because H_2 afterburns to H_2O, and both HCl and H_2O are quickly removed by raining out in the troposphere. Approximately two–thirds of the exhaust produced from the Space Shuttle SRBs is deposited in the troposphere, and the remainder is exhausted into the stratosphere where the boosters burn out. It is also important to note that the exhaust products produced—H_2O, H_2, and HCl—do not react directly with ozone;

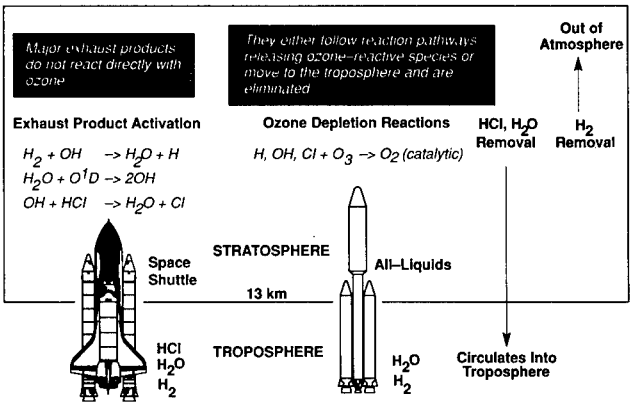


Fig. 4. Mechanisms of Potential Effect of Rocket Exhaust on Ozone

the ozone–reactive species (H, OH, Cl) must be released from the molecules in the plume before any ozone destruction can occur. Much of the HCl and water deposited into the lower portion of the stratosphere is removed by circulation into the troposphere, and considerable hydrogen deposited in the upper stratosphere is removed by escaping into the mesosphere.

Figure 5 depicts the molar concentration of important exhaust gases and where they are deposited from the Space Shuttle SRBs and the Space Shuttle main engines (SSMEs). Ozone–reaction chemistry is controlled by the molar concentration of the reacting species and the chemical reaction kinetics associated with releasing the reactive species and its subsequent reaction with ozone. It was assumed that all of the rocket exhaust produced in the stratosphere stayed there to react with ozone and none of it circulated into the troposphere or escaped into the mesosphere. It should be noted from Fig. 5 that, even though the SRBs do generate a considerable amount of HCl, from a molar basis, water and hydrogen are the major exhaust products. Even though the SSMEs produce only water and hydrogen, the SRBs, because of their much higher thrust level, deposit nearly as much water and hydrogen into the stratosphere as the SSMEs; most of the SSME exhaust is deposited above the stratosphere.

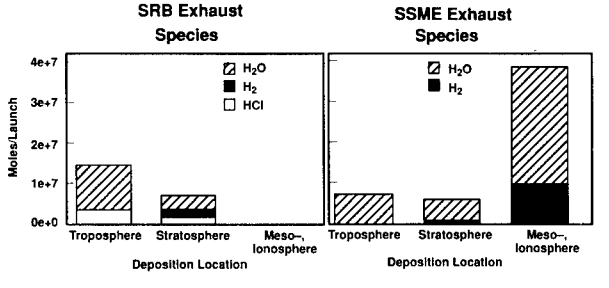


Fig. 5. Space Shuttle Exhaust Species

Much of the environmental concern with solid rocket motors was a by–product of associating solid rocket–produced HCl with chlorofluorocarbons (CFCs). Figure 6 presents a schematic representa-

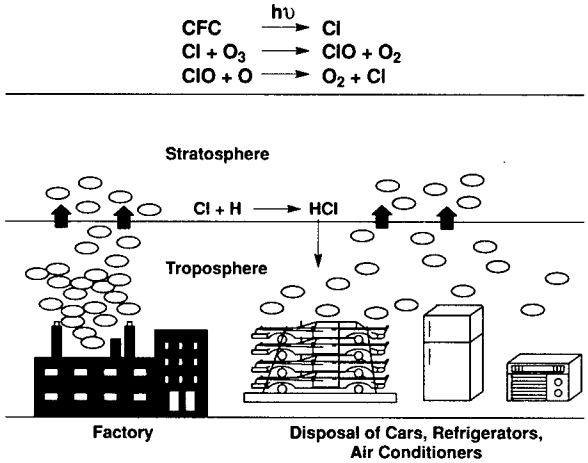


Fig. 6. Effects of CFCs on Ozone

tion of the CFC problem. CFCs are very chemically stable compounds used in refrigeration, air conditioning systems, aerosol products, and many cleaning solvents. These compounds are man-made chemicals that were designed to be chemically inert for the intended applications. As a result, there are no natural processes in the troposphere that will break down these chemicals until they reach the stratosphere, where photolysis by ultraviolet radiation releases chlorine atoms from the CFCs. The released chlorine then enters into a catalytic ozone destruction cycle. One of the major problems with CFCs is the long life and tremendous reservoir of these materials in discarded automobiles, refrigerators, air conditioners, etc., that provide a source of these chemicals to eventually enter the stratosphere for hundreds of years. Unlike HCl, which is washed out and removed as the stratospheric air circulates into the troposphere, CFCs are inert to most chemical processes in the troposphere. It is interesting to note from Fig. 6 that the chlorine released in the stratosphere from CFCs is eventually removed by the reaction of chlorine with stratospheric methane to form HCl, which can then circulate to the troposphere and be removed. As can be seen from Fig. 6, there is a significant difference between CFCs and HCl from solid rocket exhaust. In fact, *the formation of HCl* is the *primary removal process for chlorine atoms released from CFCs* in the stratosphere. Conventional wisdom indicates that all CFCs that are released to the atmosphere will eventually make it to the stratosphere, and will remain in the stratosphere until their chlorine is released by photodissociation from sunlight (a process that cannot be avoided) in the form of active chlorine (Cl) atoms; the released chlorine atoms will continue to catalytically destroy ozone until the chlorine is tied up in a reservoir specie or can be removed by forming HCl. However, HCl deposited directly into the stratosphere from rockets must undergo a chemical reaction before the ozone-destroying chlorine atoms can be released. HCl is not subject to photodissociation. As a result, some of the HCl deposited directly into the stratosphere may never release any chlorine before it has the opportunity to circulate back into the troposphere where it is readily rained out. Furthermore, HCl is a naturally occurring chemical in the earth's atmosphere, with a large natural reservoir of HCl in the troposphere and stratosphere in contrast to the unnatural molecules of CFCs that were engineered by man.

Figure 7 is a projection of the cumulative global stratospheric chlorine burden in parts per billion (ppb) over a 75-year time frame from 1979 to 2054, assuming that the Montreal Protocol ban on the production of Class 1 ozone depleting chemicals (ODCs) is effective by 1996 as planned.[6] Superimposed on this chart is the contribution to stratospheric chlorine in the form of hydrogen chloride from all rocket launches which represents a steady-state contribution of chlorine from HCl of approximately 0.003 ppb. This assumes a world launch rate of solid rockets equivalent to one Space Shuttle launch every month.[7] This launch rate represents a constant 40 percent increase in HCl deposited in the stratosphere from solid rocket launches over what was actually achieved in 1993.

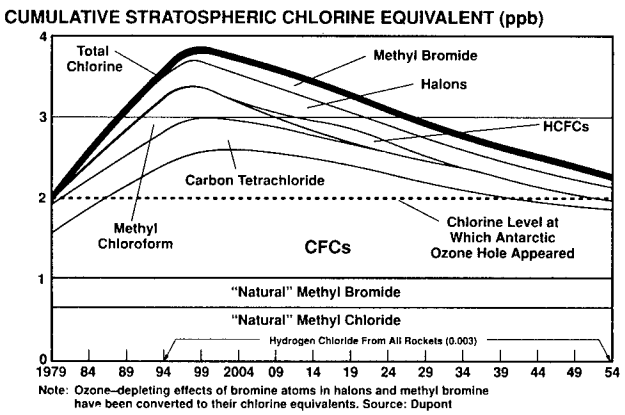


Fig. 7. Levels of Chlorine in Stratosphere Will Decrease Slowly Under Montreal Protocol

Figure 8 depicts the relative annual contributions from various sources to the stratospheric chlorine burden.[8] Industrial halocarbon-derived chemicals, primarily CFCs, producing 300 kilotons per year, are a major contributor to stratospheric chlorine and are the principle source of anthropogenic chlorine. Natural sources, primarily methyl chloride (CH_3Cl) from the oceans and burning vegetation, were estimated to add an additional 75 kilotons of chlorine to the stratosphere. Volcanoes can inject HCl directly into the stratosphere, and when major volcanic activity occurs, such as the 1991 Mount Pinatubo eruption in the Philippines, it tends to

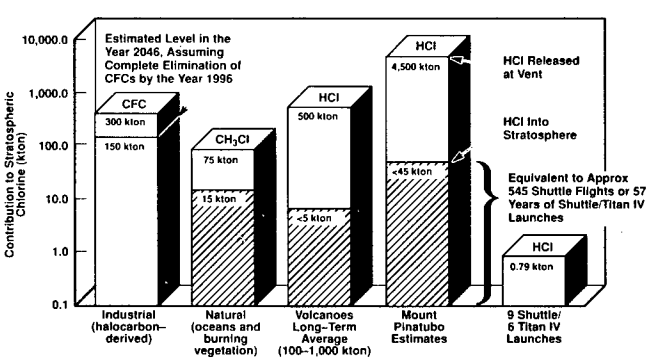


Fig. 8. Relative Annual Contributions to Stratospheric Chlorine

overshadow all other sources during the rather short period of time of volcanic activity. Volcanoes are very random and sporadic sources of chlorine, but it was estimated that on a long–term average, volcanoes could inject anywhere from 100 to 1,000 kilotons of chlorine in the form of HCl directly into the stratosphere on an annual basis.[9] The chlorine burden from SRBs producing HCl adds less than 1 kiloton of chlorine to the stratosphere per year based upon a flight rate of nine Space Shuttles and six Titan IV launches per year. It should also be noted from Fig. 8 that, if we are successful in eliminating all CFC production by 1996 as mandated by the Montreal Protocol, we will still be adding 150 kilotons of chlorine to the stratosphere some 50 years later as a result of the long life and huge reservoir of these chemicals.

It should be noted in Fig. 8 that more recent data (represented by the cross–hatched area) obtained from volcanic activity indicate that only a small fraction of the HCl emitted from a volcano ever reaches the stratosphere as hydrogen chloride gas.[10] Data obtained from Mount Pinatubo, along with detailed computer modeling studies, indicated that less than 1 percent of the HCl gas emitted from the vent of the volcano reached the stratosphere in that form; more than 99 percent of the HCl is rained out of the stratosphere by the huge quantities of steam and water contained in the volcanic cloud. The quantities of steam emitted from the volcano produce roughly 1,000 times as much water as HCl while the volcanic cloud rises and cools. Nevertheless, the Mount Pinatubo eruption in June 1991 is estimated to have released 4.5 million metric tons of HCl. Assuming only 1 percent of the HCl reached the stratosphere, it would still result in injecting 45 kilotons of chlorine into the stratosphere, which is equivalent to approximately 545 flights of the U.S. Space Shuttle.

More recent data obtained from measurements taken by stratospheric aircraft (represented by the cross–hatched area) have also indicated less methyl chloride in the stratosphere than was originally thought.[11] As shown in Fig. 8, more recent data would reduce the stratospheric loading of methyl chloride from oceans and biomass burning from 75 kilotons to approximately 15 kilotons per year. These more recent data would indicate that natural sources of chlorine are considerably lower than was originally believed. If chlorine contributions from CFCs are as high as predicted (300 kilotons per year), then these anthropogenic contributions to stratospheric chlorine would be the major source of chlorine in the stratosphere. In any event, the 0.79 kilotons per year of chlorine from rocket launches remains small compared to CFCs or natural sources of chlorine.

Figure 9 presents a Pareto chart of the stratospheric ozone–depleting chemistries and the portion that can be attributed to chemical rockets. As can be readily seen, rocket contribution to stratospheric ozone depletion is extremely small, representing approximately 0.03 percent of the ozone depletion from all other sources. Therefore, based upon the current state of knowledge, it certainly would not appear to be technically or financially responsible to spend large sums of money trying to reduce the contribution of chemical rockets to destruction of stratospheric ozone.

There have been several numbers published in the literature for the magnitude of stratospheric ozone depletion due to solid rockets over the past few years. These numbers are not inconsistent, but

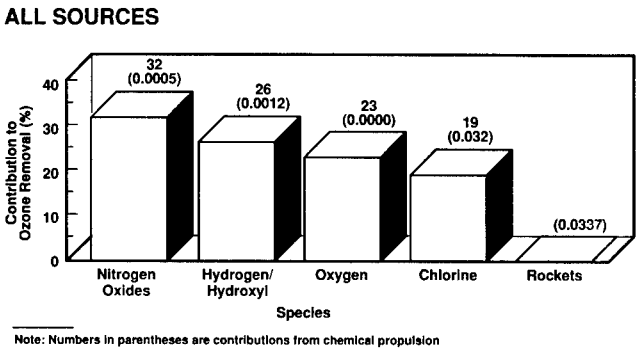


Fig. 9. Chemical Removal of Stratospheric Ozone

represent different sets of conditions as shown in Fig. 10.[12] Based on a two–dimensional (2–D) atmospheric computer model calculating local ozone depletion at a 40–kilometer altitude in the region (1,000 km by 1,000 km) above the launch site, long–term steady–state stratospheric ozone depletion approaching 0.25 percent would be calculated. This same analysis through the entire regional ozone column over the launch site reduces the ozone loss to less than 0.1 percent, which is further reduced to approximately 0.006 percent on a global scale. The global ozone depletion numbers presented in Fig. 9 are based upon first order approximations that are roughly five times more conservative than the 2–D models would predict, resulting in the 0.03 percent number shown. Since global stratospheric ozone depletion calculations based on these more sophisticated 2–D models (0.006 percent) have underpredicted ozone losses by a factor of two over the past few years, it is most probable that ozone depletion from rocket launches would not exceed a steady–state reduction of more than 0.012 percent based on the assumed yearly flight rate of nine Space Shuttles and six Titan IV vehicles.

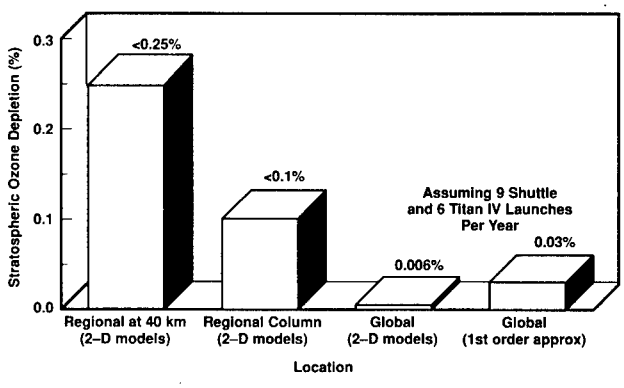


Fig. 10. Stratospheric Ozone Impact Due to Solid Rocket Motor Exhaust

There have been news media reports linking the ozone reduction in the stratosphere to rocket launches, and solid rocket motors in particular. It is clear that 0.006 to 0.012 percent reductions cannot be measured, especially when the natural annual variations in the northern hemisphere have varied over 20 percent, as shown in Fig. 11. Figure 11 covers a 33–year period from 1957 to 1991.[13]

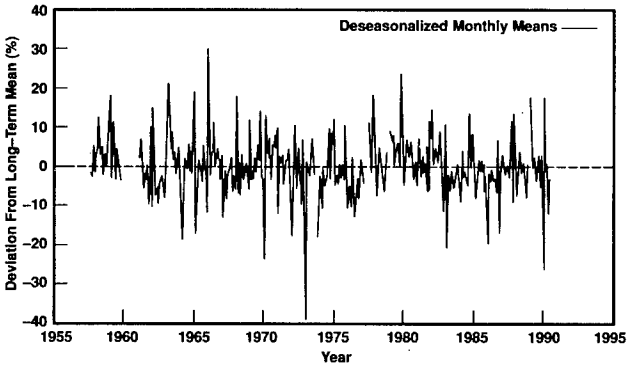


Fig. 11. Large Natural Variations in Stratospheric Ozone

Some people have been concerned that rockets may be creating an ozone hole directly over the launch site areas. As shown in Fig. 12, a typical Space Shuttle trajectory is not even close to being vertical, and, in fact, by the time the SRBs burn out near the top of the stratosphere, the Space Shuttle has as much down–range as vertical altitude.

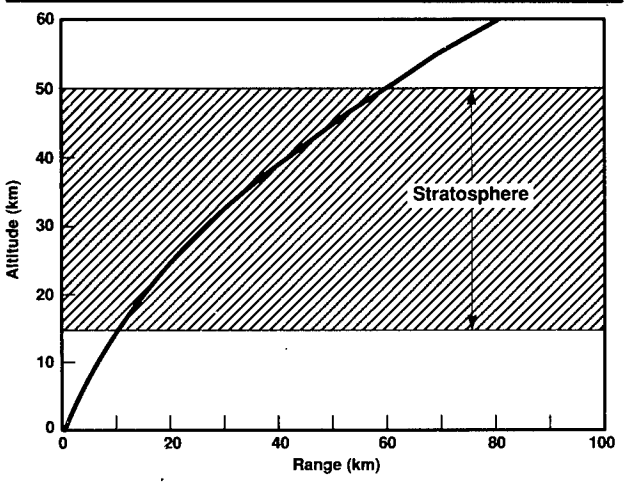


Fig. 12. Typical Space Shuttle Trajectory

Atmospheric scientists (Karol, Ozolin, and Rozanov[14]) from the Main Geophysical Observatory in Russia have examined the impact of rocket launches on local stratospheric ozone above the launch site. These Russian scientists concluded that 50 launches per year of either the U.S. Space Shuttle or Russian Energia would not significantly impact local or global ozone depletion in the stratosphere. Scaling the Russian data to an equivalent launch model consisting of nine Space Shuttles and six Titan IV launches per year results in good agreement with NASA's projection of 0.0065 percent global ozone depletion. Similar analysis conducted by the European Space Agency for the Ariane V,[3] when scaled to the same equivalent launch model, produced comparable results. The Russian scientists conducted time–dependent analytical calculations of local ozone depletion in the rocket plume as it mixes with the ambient air as the vehicle flies through the stratosphere. Calculations were conducted for both the U.S. Space Shuttle (S) and the Russian Energia (E) vehicle, as shown in Fig. 13. Figure 13 presents results at 40– and 16–kilometer altitudes for both vehicles up to one day after launch.[2] Ozone destruction in the near field of the rocket plume can be very severe (>90 percent) within just a few minutes after the launch vehicle enters the stratosphere; however, the ozone concentration is totally restored to background levels from natural mixing of the plume with surrounding air in this very localized area within a few hours after launch. It is also interesting to note that the magnitude of local ozone destruction is basically the same for the U.S. Space Shuttle with its SRBs and the all–liquid Russian Energia vehicle that does not produce any chlorine–containing compounds in the exhaust. The only difference noted between the two vehicles is that the non–chlorine Energia destroys ozone more quickly, but recovers faster, than the Space Shuttle; this recovery time difference is attributed to the HCl, as shown in Fig. 13.

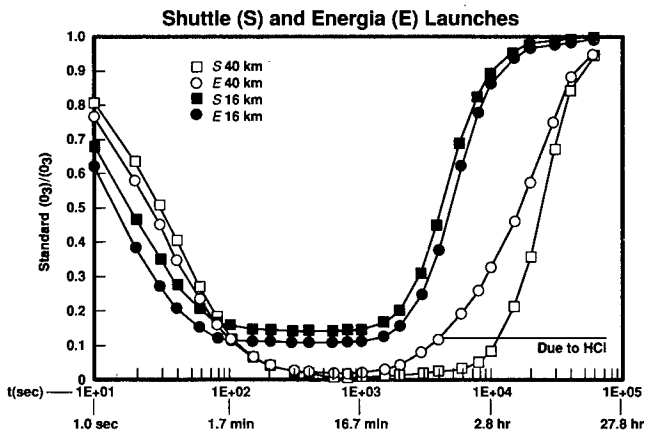


Fig. 13. Shuttle and Energia Impact on Local Ozone

The Russian atmospheric scientists Karol et al.[14] analyzed two sets of conditions to determine the local impact of NO_x and chlorine production from the Space Shuttle vehicle. Figure 14 presents the impact on local column ozone changes comparing the baseline calculations shown in Fig. 13 (Scenario A) assuming HCl and NO_x are the primary ozone–depleting chemistries in the plume with a second scenario (Scenario B) with decreased NO_x production and all chlorine from the SRBs in the form of chlorine gas (Cl_2) rather than HCl. As shown in Fig. 14, total column ozone destruction at any given time is less than 8 percent and is restored to normal background levels within a few hours after launch. The production of Cl_2 rather than HCl results in slightly more ozone destruction, but does not significantly affect the recovery time.

Computer modeling work conducted by Denison et al. at TRW[15] suggests that HCl from solid rocket plumes may be quickly converted to Cl_2 at high altitudes from afterburning. The TRW paper describes model calculations examining the local effects of solid rocket exhaust on stratospheric ozone at different altitudes. The afterburning calculations suggest that a significant fraction of the

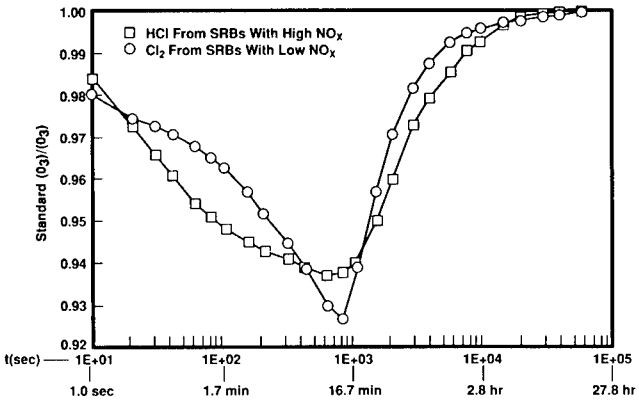


Fig. 14. Local Column Ozone Changes From Shuttle Launch

HCl is converted to Cl_2 in the hot plume—about 20 percent at an 18–kilometer altitude and as much as 80 percent at 30 kilometers. Ozone depletion is extensive during the first few minutes following a launch, but quickly recovers (within about one–half hour) to near background levels. It was found that the rate of plume dispersion has a very significant effect on local ozone loss. The differences in plume dispersion rates explains, at least in part, the differences between the Karol results[14] and the TRW results.[15] Both studies indicated local total column ozone depletion less than 10 percent; the major differences noted were in the time it took for recovery. The TRW results predicted much more rapid loss and recovery within seconds to minutes while the Karol results indicate somewhat similar impacts with total recovery occurring over a much longer period of time, i.e., a few hours.

Plume modeling work reported by Dr. R. B. Cohen of the Aerospace Corporation[16] has also indicated that high temperature afterburning reactions may rapidly convert the HCl to active Cl_2 and Cl in the plume in the stratosphere. More recent work done by German atmospheric research scientist, Dr. B. C. Kruger from the Institute for Geophysics and Meteorology at the University of Köln,[17] has examined the influence of chlorine production from solid–fuel rockets on local ozone depletion in the plume. Dr. Kruger's paper is a model study of the impact of the chlorine emissions from the Space Shuttle SRBs at various altitudes as a function of distance from the center of the plume as the plume evolves over time. Chlorine emissions were considered both in the form of HCl and Cl_2. The cases run were 100 percent HCl, 95 percent HCl and 5 percent Cl_2, and 50 percent HCl and 50 percent Cl_2. For the case of 100 percent HCl, Kruger predicts that ozone destruction will begin between 5 and 10 minutes after launch as the HCl reacts and begins to release its chlorine. The maximum depletion at 35 kilometers is about two percent at the center of the plume and lasts for more than 24 hours. At lower altitudes, the ozone depletion is much less—about 0.19 percent at 28.5 kilometers, and about 0.26 percent at 31.9 kilometers in altitude. Maximum column ozone depletion values given by Kruger are related to what an instrument with a given field of view (FOV) in orbit would see. In the case of 100 percent HCl, for a true vertical trajectory, the maximum column ozone decrease seen for a 1,664–km^2 (41 km x 41 km) FOV instrument like the NASA total ozone mapping spectrometer (TOMS) instrument would be about 0.5 percent. For the case of 50 percent chlorine and 50 percent HCl, the ozone is virtually depleted at high altitudes within 10 minutes of the launch. Maximum column ozone depletion which would be observed by an instrument with a 1,664–km^2 FOV is about 3 percent over the entire FOV. The predicted column values are somewhat lower than those calculated by Karol[14] and predict that the TOMS instrument would not have sufficient resolution to observe the impact on the local stratospheric ozone column from a Space Shuttle launch.

Thermochemical equilibrium calculations for Space Shuttle SRB propellant indicate HCl will be produced rather than Cl_2. Experimental sampling of solid rocket combustion gases at ground level has indicated that HCl is the major combustion product at a ratio of approximately 10:1 over Cl_2. There have not been any plume chemistry measurements made at stratospheric altitudes. There are very limited experimental data for determining the effects of rocket plumes on stratospheric ozone depletion; however, what data are available tend to support Russian scientific analysis. Ozone reductions greater than 40 percent were measured in the exhaust trail of a Titan III SRB at an altitude of 18 kilometers approximately 13 minutes after launch.[18] Considerable NO_x formation was also detected in the plume and the ozone depletion was attributed to NO_x at that time; chlorine measurements were not made. NASA has made several measurements of total column ozone concentration directly over Kennedy Space Center (KSC) after eight different Space Shuttle launches with the TOMS aboard the NIMBUS–7 satellite.[19] No evidence of ozone depletion was ever detected; however, the measurements that were taken were generally obtained several hours after launch. These data appear to be consistent with the Russian scientific calculations[14] and the Kruger analysis[17] which would predict that normal background levels of ozone are restored within a few hours of the launch and the ozone loss at any given time would be below the threshold of detectability within the FOV of the TOMS instrument.

Most of the local and global ozone depletion calculations to date have considered homogeneous gas phase chemical reactions only. Recent studies of the Antarctic ozone hole have identified the importance of heterogeneous chemistries on ice crystals in the polar stratospheric clouds. Decreases in mid–latitude ozone levels have also been attributed to catalytic activity on the surface of finely divided particulate matter injected directly into the stratosphere from volcanic eruptions. The question arises, "Can finely divided aluminum oxide (Al_2O_3) from SRBs, soot from liquid oxygen and hydrocarbon boosters, and ice contrails from all rockets also provide catalytic surfaces for ozone–destroying chemistries?"

There have been few published calculations for the potential impact of rockets in this area. The limited heterogeneous modeling of solid rocket plumes by several researchers has indicated that the effects on local plume chemistry are minor, and, therefore, the influence on local ozone depletion, if any, appears to be small.[15,17,20,21] The impact on global ozone depletion from rocket–produced aerosols is even less significant, i.e., could be responsible for about 1/1,000th of the current ozone depletion associated

with the unperturbed background heterogeneous chemistry in the absence of volcanic aerosols.[22]

Analysis of data from volcanoes can provide good qualitative insight as to the potential magnitude of particulate matter from solid rockets. Figure 15 shows the estimated total integrated surface area of finely divided particulate matter injected into the stratosphere by the El Chichon volcanic eruption in Mexico in 1982.[23] This figure also compares the natural background levels of stratospheric aerosols to the total quantities of aluminum oxide deposited by nine Space Shuttle and six Titan IV launches if all of the Al_2O_3 were deposited in the same region as the El Chichon cloud. The rocket contribution does not include any ice or soot particles from the launch vehicles.

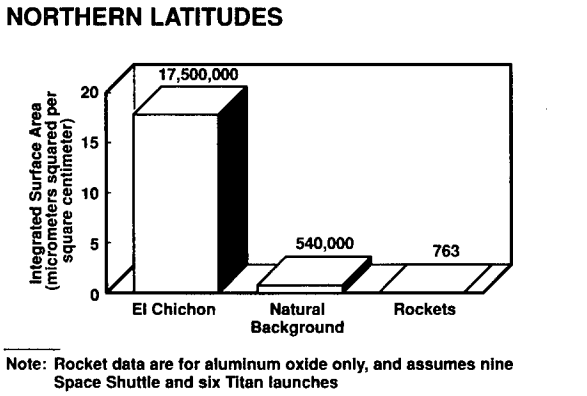


Fig. 15. Stratospheric Surface Area Available for Heterogeneous Chemistry

Figure 16 shows the maximum estimated ozone depletion in the region of the El Chichon–induced stratospheric cloud as compared to the estimated ozone depletion from natural aerosols and rockets producing Al_2O_3.[23,24] As can be seen from the figure, the ozone destruction within the cloud of El Chichon could be as high as 17 percent, as compared to the SRB contribution of less than 0.0007 percent on the same basis.

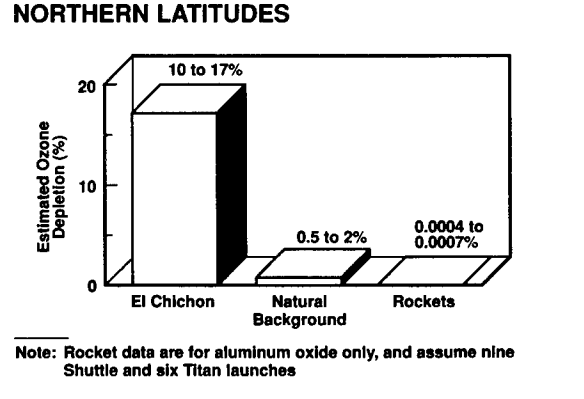


Fig. 16. Estimated Effects of Heterogeneous Chemistry on Stratospheric Ozone

The 1991 eruption of Mount Pinatubo in the Philippines was far more powerful than El Chichon. Atmospheric scientists believe that the aerosols from this volcano were probably responsible for the intensification of global ozone thinning noted since the eruption of Mount Pinatubo.[5]

ACID RAIN

Since SRBs produce hydrochloric acid in the exhaust plume, there has been considerable concern over the impact that this acid rain may have on the global environment, as well as local launch sites. All rockets produce some acid rain as a result of the formation of NO_x in the near field of the plume from afterburning that forms nitric acid in the presence of water. The studies presented here only consider HCl from solid rockets as a source of acid rain.

Figure 17 depicts the annual U.S. contribution to the global acid rain problem from various anthropogenic sources, including solid rockets.[25,26,27] As can be seen from the figure, other energy conversion processes such as heating and power production (33,000 kilotons), transportation (9,100 kilotons), and industrial processes (6,100 kilotons) clearly overshadow the acid production (3 kilotons) from solid rocket launches. Most of the acid produced from these industrial activities is in the form of sulfuric acid, with significant quantities of nitric and hydrochloric acid also produced. Without considering other countries in the world, rockets are responsible for less than 0.006 percent of acid rain produced by U.S. industries alone.

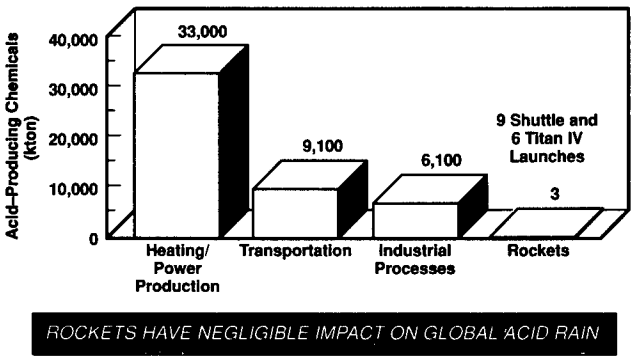


Fig. 17. Annual Contribution to Acid Rain (Continental U.S. Data)

Figure 18 reflects sources of hydrochloric acid other than rockets.[9] As can be seen in Fig. 18, natural sources of HCl from the oceans (330,000 kilotons), volcanoes (5,000 kilotons), and coal burning processes (1,980 kilotons) make solid rockets (3 kilotons) an insignificant contributor to global atmospheric HCl releases. It is estimated that launching nine Space Shuttles and six Titan IVs each year would deposit the same amount of HCl into the troposphere as is produced by the Atlantic ocean each year just east of the KSC launch site in an area of the ocean represented by a square less than 30 miles on each side. On a global scale, HCl produced by rocket launches is less than 0.001 percent of the total HCl production from the ocean alone and only 0.15 percent of anthropogenic sources, primarily coal burning power plants in the United States.

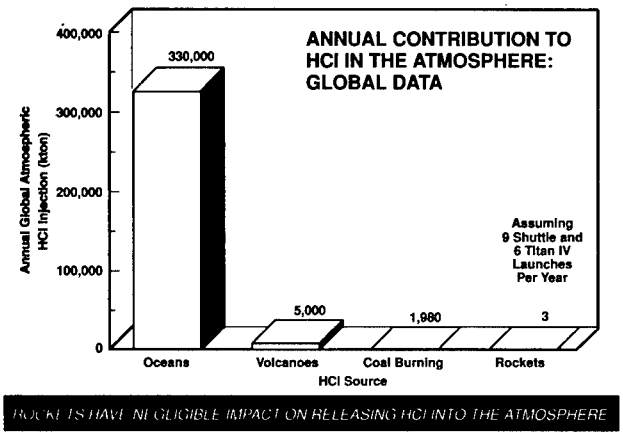


Fig. 18. Global HCl Releases

On a local scale, acid rain from SRBs is more significant and does have near–field acidification effects in the vicinity of the launch site.[28] These effects are limited to a very localized area within less than one–half mile from the launch pad directly in line with the SRB flame trenches, as shown in Fig. 19. Some plant and small fish (minnows) mortalities occur in the lagoon area just north of the launch pad, less than 0.1 square mile of area (which is much smaller than the launch pad itself). Catch basins for the sound suppression water is neutralized after each launch and the pre– and post–launch environmental conditions are documented on each Space Shuttle launch.

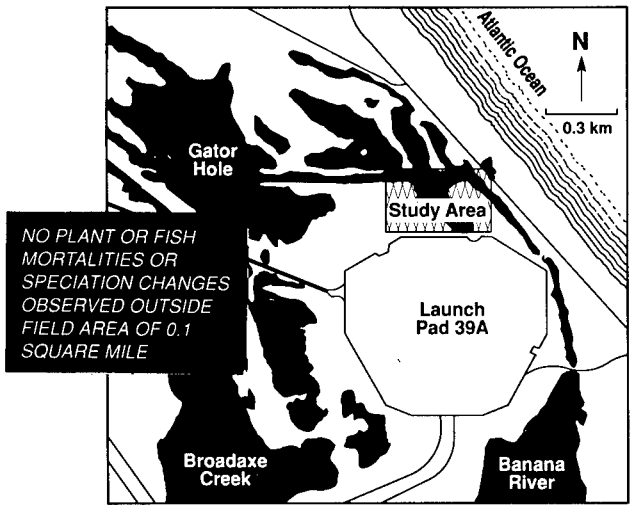


Fig. 19. Acid Rain: Near–Field Deposition Area

TOXICITY

Hydrochloric acid is the most toxic substance associated with cured solid propellants and it is only produced by combustion. Storable liquid bipropellants consisting of nitrogen tetroxide (N_2O_4) and hydrazine compounds are far more toxic, but have been safely and routinely handled at various launch sites for decades. As shown in Table II, even in very minute concentrations, these liquid bipropellants can be a significant health hazard while HCl in minute quantities is only considered a corrosive or irritant.[29]

- **Liquid rocket components—nitrogen tetroxide (N_2O_4), dimethylhydrazine, and hydrazine—are highly toxic, and handling is a local concern**
- **HCl is the most toxic of the common solid rocket exhaust species**

	Lethal Concentration, 50% (inhalation, rats)	Additional Concerns at Very Low Concentration Levels
N_2O_4	88 ppm/4 hr	Pulmonary edema
Dimethylhydrazine	242 ppm/4 hr	Suspected carcinogen
Hydrazine	570 ppm/4 hr	Suspected carcinogen
HCl	3,124 ppm/1 hr	Corrosive/irritant

Table II. Propellant and Exhaust Toxicity

Considerable concern has been raised relative to the toxicity and corrosiveness of the SRB ground cloud as it drifts away from the launch site. Figure 20 represents one of the rare Space Shuttle launch plume conditions that drifted inland rather than out over the ocean after the launch.[30] Bionetics Corporation has periodically monitored HCl concentrations for NASA and routinely conducts model calculations on HCl concentration in the far field of the Space Shuttle plume, as shown in Fig. 20. It should be noted that the maximum HCl concentration in the ground cloud of 0.9 parts per million is well below the American Conference of Governmental Industrial Hygienists' recommended threshold limit value (TLV) of 5 parts per million for long–term continuous exposure (8 hours per day—40 hours per week). HCl concentrations measured in the path of the Titan III SRB ground cloud as it drifted several kilometers from the launch site at Vandenberg AFB have also been well below the 5 ppm threshold limit values, i.e., 0.005 ppm to 0.5 ppm. Aircraft fly–throughs of the stabilized exhaust plumes of the Titan III and Space Shuttle at 1 to 2 kilometers above ground level have measured HCl concentrations at the TLV of 5 ppm for 10 to 60 minutes after launch.[31]

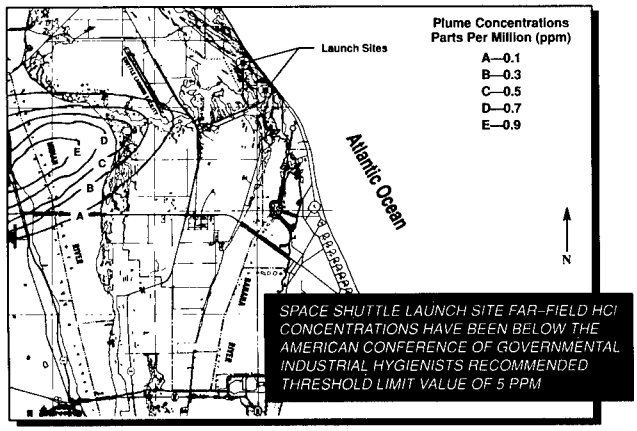


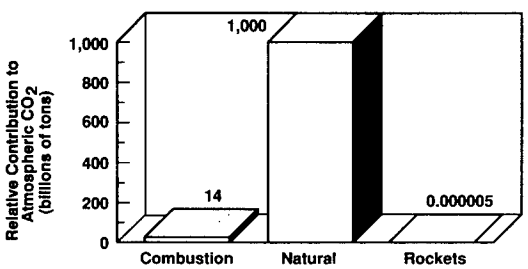
Fig. 20. Toxicity of Shuttle Exhaust Plume

There have been some published studies that have suggested an association of aluminum compounds with Alzheimer's disease. Solid rockets consume less than 0.01 percent of the 69 billion pounds of aluminum metal produced in the U.S. each year, and approximately 8 percent of the earth's crust consists of aluminum compounds, such as oxides, silicates, etc. Furthermore, many pharmaceuticals, food additives, and health care products (deodorants, for instance) contain aluminum compounds. To prevent people from throwing away their aluminum cookware and stop drinking from aluminum beverage cans, the U.S. Food and Drug Administration (FDA), the Alzheimer's Disease and Related Disorders Association, and the U.S. Environmental Protection Agency (EPA) released statements in 1989 that there was no evidence to support the hypothesis that aluminum contributed to Alzheimer's disease.

GLOBAL WARMING

It has been postulated by several scientists that production of certain gases, such as carbon dioxide (CO_2), from the continued burning of fossil fuels could eventually cause more of the sun's energy to be trapped in the earth's atmosphere, resulting in global warming or a greenhouse–type effect. As shown in Fig. 21, the amount of CO_2 produced from chemical rockets is extremely minute, representing less than 0.00004 percent of anthropogenic sources of CO_2.[27,32]

RELATIVE ANNUAL CONTRIBUTIONS TO ATMOSPHERIC CO_2



THE CONTRIBUTION OF ROCKET EXHAUST CO_2 TO THE GREENHOUSE EFFECT IS INSIGNIFICANT

Fig. 21. Greenhouse Effect Gases

It has also been suggested that particles from rocket launches could also contribute to global warming conditions or possibly global cooling. As indicated earlier, aluminum oxide deposited into the stratosphere by SRBs is so small that it would take nearly 300,000 Space Shuttle launches to equal a volcano the size of El Chichon.

CONCLUSIONS

Based upon our current state of understanding of the earth's atmosphere, the following conclusions can be drawn relative to the impact of chemical rocket launches:

1. The environmental impact of chemical rocket propulsion is extremely small, i.e., annual global stratospheric ozone depletion and tropospheric acid rain contributions are estimated to be less than 0.01 percent.
2. There is no significant difference in local stratospheric ozone depletion from the U.S. Space Shuttle with its solid rocket boosters and the all–liquid Russian Energia launch vehicle, and the impact is small even at launch rates as high as 50 flights per year of either vehicle.
3. Contrary to manmade CFCs, chemicals released from rockets are not foreign to the environment, but represent an extremely small fraction of large natural reservoirs of these materials in the atmosphere.
4. As a potential source of chlorine in the stratosphere, all rocket launches combined produce less than 0.25 percent of the chlorine introduced by CFCs on an annual basis. Enactment of the ban on the production of CFCs by 1996 will eliminate 99.75 percent of the current anthropogenic sources of new chlorine that could eventually find its way to the stratosphere.
5. The impact on the potential for global warming due to CO_2 from chemical rockets is minuscule (less than 0.00004 percent).
6. Local launch site area acidification is minor and manageable.
7. There is no rocket system that is totally "clean," and the environmental improvements available appear to be very limited. The amount of energy released to place objects into earth orbit will cause some minor damage to the earth's atmosphere independent of rocket chemistry.
8. The benefits of obtaining global weather and environmental data from satellites and space laboratories in earth orbit far outweigh the minor environmental impacts of placing these assets into space.

RECOMMENDATIONS

Recommendations for further work are primarily focused on improved atmospheric computer modeling, environmental data gathering, and establishing reasonable environmental criteria for future launch systems. These following recommendations are summarized:

1. More measured data need to be obtained to verify the minimal impacts that are being projected.
2. Atmospheric computer modeling, which includes both homogeneous and heterogeneous chemistry, needs to reflect actual measured conditions for improving confidence in future projections and assessing effectiveness of potential mitigating strategies. These models need to include afterburning, equilibrium and non–equilibrium plume chemistry and combined exhaust gas chemistry from mixed propulsion launch vehicles.
3. "Clean" solid propellant work should be renamed "alternative propellants" and continued on a laboratory scale until more atmospheric experimental data are available to verify the minimal environmental impact conclusions that have been drawn to date.

4. New launch system development should include criteria for assessment of the environmental impacts along with safety, performance, reliability, and cost requirements.

5. A detailed environmental–cost–benefit–risk analysis should be conducted for any new launch system, and any potential environmental benefits that are identified should be adequately demonstrated and verified prior to incorporation into the launch vehicle.

Based upon the environmental impact studies conducted to date, there is no reason to modify any launch vehicles or change any propellant chemistry at this time.

REFERENCES

1. American Institute of Aeronautics and Astronautics Report, *Atmospheric Effects of Chemical Rocket Propulsion* (1 October 1991).

2. R. S. Harwood, C. H. Jackman, I. L. Karol, L. X. Qiu, M. J. Prather, and J. A. Pyle, World Meteorological Organization Ozone Report No. 25, *Scientific Assessment of Ozone Depletion,* 1991, Chapter 10: "Predicted Rocket and Shuttle Effects on Stratospheric Ozone," Sponsored by the World Meteorological Organization and the United Nations Environment Program, National Aeronautics and Space Administration, National Oceanic and Atmospheric Administration, and the United Kingdom Department of Environment (Spring 1992).

3. A. E. Jones, S. Bekki, and J. A. Pyle, "Modelling Assessment of the Atmospheric Impact of Exhaust Products (chlorine, H_2O, Al_2O_3) From Ariane 5 Rocket Launches," Report to the European Space Agency, University of Cambridge, United Kingdom (June 1993).

4. M. McElroy and R. Salawitch, "Changing Composition of the Global Stratosphere," *Science*, 243, 763 (1989).

5. P. S. Zurer, "Ozone Depletion's Recurring Surprises Challenge Atmospheric Scientists," *Chemical and Engineering News* (24 May 1993).

6. P. S. Zurer, "Looming Ban on Production of CFCs, Halons Spurs Switch to Substitutes," *Chemical and Engineering News* (15 November 1993).

7. M. K. W. Ko, N. D. Sze, and M. J. Prather, "Better Protection of the Ozone Layer," *Nature*, 367, 505 (10 February 1994).

8. R. Cicerone, "Halogens in the Atmosphere," *Rev. Geophys. Space Phys.* 19, 732 (1981).

9. R. Symonds, W. Rose, and M. Reed, "Contributions of Cl– and F–Bearing Gases to the Atmosphere by Volcanoes," *Nature* 334, 415 (1988).

10. A. Tabazadeh and R. P. Turco, "Stratospheric Chlorine Injection by Volcanic Eruptions: HCl Scavenging and Implications for Ozone," *Science*, Vol. 260, p. 1,085 (21 May 1993).

11. G. Taubes, "The Ozone Backlash," *Science*, 260, p. 1,582 (11 June 1993).

12. M. Prather, M. M. Garcia, A. R. Douglass, C. H. Jackman, M. Ko, and N. D. Sze, "The Space Shuttle's Impact on the Stratosphere," *J. Geophys. Res.* 95 (D11), 18583 (1990).

13. G. G. Bjarnason, O. E. Rognvaldsson, T. I. Sigfusson, T. Jakobsson, and B. Thorkelsson, *Analysis of Total Ozone Data From Reykjavik for the Period 1957–1991*, Science Institute, University of Iceland, Report RH92–3 (April 1992).

14. I. L. Karol, Y.E. Ozolin, and E. Y. Rozanov, "Effect of Space Rocket Launches on Ozone and Other Atmospheric Gases," Presented at the European Geophysical Association Conference, Wiesbaden, Germany (1991).

15. M. R. Denison, J. J. Lamb, W. D. Bjorndahl, E. Y. Wong, and P. D. Lohn, "Solid Rocket Exhaust in the Stratosphere: Plume Diffusion and Chemical Reactions," AIAA Paper No. 92–3399, AIAA 28th Joint Propulsion Conference, Nashville, Tennessee (July 1992).

16. R. B. Cohen, "Learning About Potential Effects of Solid Propellants Exhaust on the Stratosphere," Presented at the Air Force Phillips Laboratory Solid Propellant Environmental Issues Technical Interchange Meeting and Conference, Ogden, Utah (24–25 March 1994).

17. B. C. Kruger, "Ozone Depletion in the Plume of a Solid–Fueled Rocket," To Be Published in the *Annales Geophysicae* (Summer 1994).

18. R. B. Stewart and R. I. Gomberg, "The Production of Nitric Oxide in the Troposphere as a Result of Solid–Rocket Motor Afterburning," NASA TN D–8137 (1976).

19. R. McPeters, M. Prather, and S. Doiron, Reply to Comment on "The Space Shuttle's Impact on the Stratosphere," by M. J. Prather, et al., *Journal of Geophysical Research*, 96 (D9), 17379 (1991).

20. M. Y. Danilin, "Local Stratospheric Effects of Solid–Fueled Rocket Emissions," *Annales Geophysicae*, 11, 828–836 (1993).

21. G. F. Carrier, F. E. Fendell, and R. S. Dahbura, "Chlorine Production by Particle–Catalyzed Reaction Between Rocket Exhaust and Ambient Stratospheric Reservoir Species," AIAA Paper No. 92–3505, AIAA 28th Joint Propulsion Conference, Nashville, Tennessee (July 1992).

22. C. H. Jackman, "The Impact of Emissions from Space Transport Systems on the State of the Atmosphere," International Scientific Colloquium on the Impact of Emissions from Aircraft and Spacecraft Upon the Atmosphere, Cologne, Germany (18–20 April 1994).

23. D. J. Hofmann and S. Solomon, "Ozone Destruction Through Heterogeneous Chemistry Following the Eruption of El Chichon," *J. Geophys. Res.* 94 (D4), 5029 (1989).

24. G. P. Brasseur, C. Granier, and S. Walters, "Future Changes in Stratospheric Ozone and the Role of Heterogeneous Chemistry," *Nature* 348, 626 (1990).

25. National Acid Precipitation Assessment Program, *Interim Assessment: The Causes and Effects of Acidic Deposition,* Government Printing Office, Washington, D.C. (1987).

26. S. E. Schwartz, "Acid Deposition: Unraveling a Regional Phenomenon," *Science* 243, 753 (1989).

27. E. Robinson and R. C. Robbins, *Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants*, Stanford Research Institute, Report SRI Project PR–6755 (February 1968), Supplemental Report (June 1969).

28. Bionetics Corporation, "STS–32 Launch Effects Summary Report," Contract No. NAS10–11624, BIO–EN4–007 (March 1990).

29. N. L. Sax and R. Lewis, Jr., *Dangerous Properties of Industrial Materials*, 7th Edition, Van Nostrand Reinhold, New York (1989).

30. Bionetics Corporation, *STS–5 Launch Effects Summary Report*, Kennedy Space Center, Florida, KSC–STS–Effects–STS 5 (July 1983).

31. B. Lundblad, Aerospace Corporation presentation "Environmental Characteristics and Potential Impacts of Solid Rocket Motor Exhaust Ground Clouds" (May 1994).

32. H. Schneider, "The Greenhouse Effect: Science and Policy," *Science*, 243, 771 (1989).

MANUFACTURING WASTE DISPOSAL PRACTICES OF THE CHEMICAL PROPULSION INDUSTRY

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ABSTRACT

The waste production, mitigation and disposal practices of the United States chemical propulsion industry have been investigated, delineated, and comparatively assessed to the U.S. industrial base. Special emphasis has been placed on examination of ozone depleting chemicals (ODCs). The research examines present and anticipated future practices and problems encountered in the manufacture of solid and liquid propulsion systems. Information collected includes current environmental laws and regulations that guide the industry practices, processes in which ODCs are or have been used, quantities of waste produced, funding required to maintain environmentally compliant practices, and preventive efforts.

COMPARATIVE SIZE OF THE INDUSTRY

The U.S. gross national product (GNP) for 1994 has been estimated at approximately 6.7 trillion dollars. (1) The Aerospace industry accounts for approximately 92 billion dollars of manufactured goods, or 1.3% of the GNP. (1) It also accounts for a disproportionately high (approximate) 25% of the research and development "technology" expenditures in any given year. (1) Space propulsion units and parts, which equates in this paper to the chemical propulsion (CP) industry, accounts for approximately 3.7 billion dollars of the Aerospace total (~4%); this is approximately 0.06% of the GNP. (1) The research and development expenditures for space propulsion are similarly disproportionate within the total Aerospace expenditures. The resultant is that the chemical propulsion industry may account for 3% of the nation's research and development "technology" expenditures (calculated assuming a 10-15% fraction of Aerospace dollars, and based on approximately $1,000,000 of the CP industry's total dollars). The following delineation is instructive in revealing the comparative size of the CP industry to other U.S. manufacturing areas: (1)

Aerospace:	$	92,300,000,000
Aircraft		36,000,000,000
Aircraft engines and parts		13,300,000,000
Aircraft parts and equipment		12,500,000,000
Guided missiles/space vehicles		24,000,000,000
Space propulsion units and parts		3,700,000,000
Space vehicle equipment		1,980,000,000
Motor vehicles and parts (estimated for 1994)	$	175,800,000,000
Net sales and revenue (GM, Ford, Chrysler-1992)		236,400,000,000
Profit (GM, Ford, Chrysler - 1992)		27,100,000,000
Petroleum products (1990) - U.S	$	237,681,000,000

This paper presents specific issues related to the aerospace industry and samples of its advances in meeting pending legislation. The samples are taken from manufacturing waste practices of the four major United States space launch vehicles. These four vehicles are the Atlas, Delta, Titan, and Space Shuttle. A significant portion of the research, development, and technology insertion dollars from the chemical

propulsion industry are currently targeted at environmental issues associated with pending and existent legislation. The federal government has passed, and continues to pass, laws regulating hazardous waste generation. Figure 1 graphically depicts the increase in environmental laws in recent years. (2)

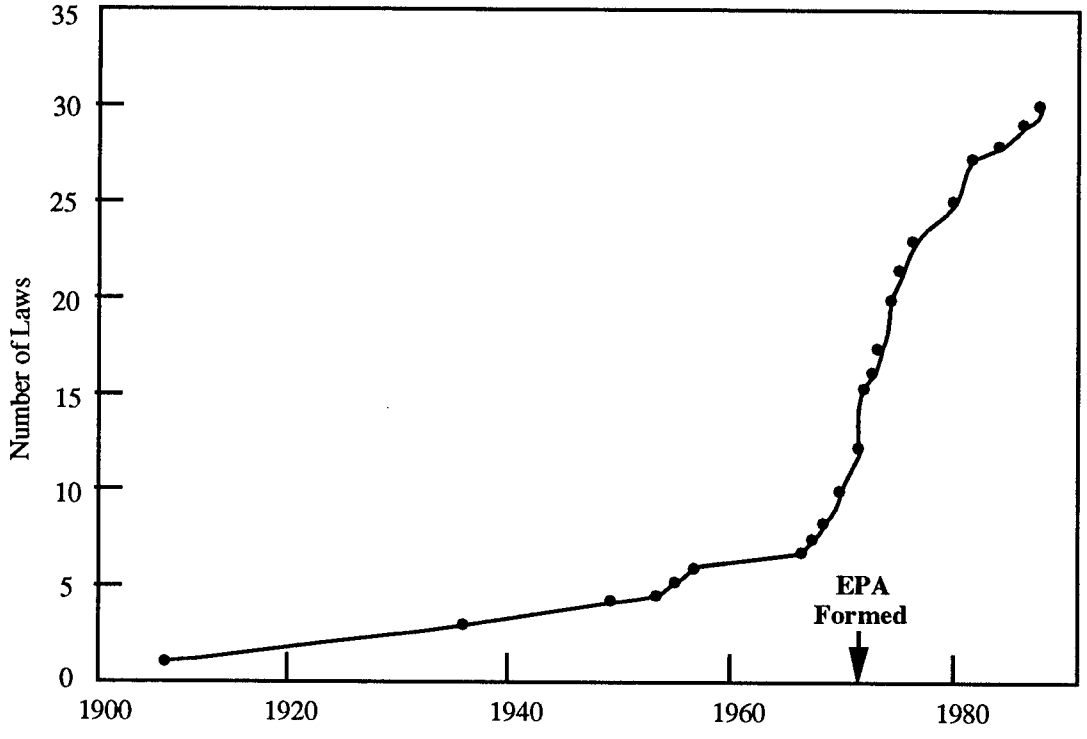

Figure 1. Major U.S. Legislation:1906-1988

Much of the environmental legislation applicable to aerospace manufacturing processes is at the federal government level. The major federal laws and regulations affecting all aerospace manufacturers are listed as follows:

- Clean Water Act (CWA)
- Clean Air Act (CAA)
- Clean Air Act Amendments (CAAA)
- Resource Conservation and Recovery Act (RCRA)
- Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)
- Superfund Amendments and Reauthorization Act of 1986 (SARA)
- Federal Insecticide, Fungicide, & Rodenticide Acts (FIFRA)
- Hazardous Material Transportation Act (HMTA)
- Endangered Species Act (ESA)
- Toxic Substances Control Act (TSCA)
- National Environmental Policy Act (NEPA)
- Pollution Prevention Act (PPA)
- Occupational Safety and Health Act (OSHA)
- Oil Pollution Act (OPA)
- National Emission Standards for Hazardous Air Pollutants (NESHAPS)

The CAAAs have particular impact on the industry's use of ODCs. Title VI of the CAAAs divides the ODCs into two classes. Class I chemicals are CFCs, halons, carbon tetrachloride and methylchloroform. This group will be phased out by January 1, 1996. Class II chemicals are hydrochlorofluorocarbons (HCFCs) and will be completely phased out by January 1, 2030. (3)

The trend toward legislative controls is anticipated to continue. Currently, there are 159 NESHAPS planned for promulgation by the year 2000. The chemical propulsion industry appears to have significant impacts from approximately 34 of these at this time. Each industrial group will have 18 months (from promulgation) to get their reporting processes in place and three years for complete implementation and compliance. Following these impacts, legislation covering additional water resource concerns is anticipated.

ISSUES SPECIFIC TO THE INDUSTRY

While the manufacturers of the chemical propulsion vehicles face the elimination or reduction of Chlorofluorocarbons (CFCs), hazardous air pollutants (HAPs), volatile organic chemicals (VOCs) and accompanying legislation and Acts governing U.S. manufacturing, there is one substantive difference between this industry and many others. The chemical propulsion industry has critical, and precariously non-robust, technologies that govern the utilization of large liquid and solid propulsion systems.

Manufacturing aerospace components and assembly systems is a highly specialized process and demands an extraordinary degree of perfection. Specifications require that, after cleaning, parts are left with less than one milligram per square foot of contamination. Anything less than absolute cleanliness may have dramatic consequences. For example, unpredicted outgassing -- an accidental introduction of particles into the space environment -- can have an extreme consequence. Even the slightest residue can interfere with tiny valves; a single unwanted particle can clog a small bearing. Chlorinated hydrocarbons and CFCs, long the solvents of choice in aerospace and other precision manufacturing operations, are typically used to clean hardware in preparation for further manufacturing (e.g., machining, welding, coating, bonding) or final assembly. (4) The above legislated changes affect the chemistry involved in the cleaning, bonding, measurement and chemical constituents of the empirically derived databases that govern chemical propulsion system design and usage.

The replacement technologies required for the liquid and solid propulsion industries and the consequent technological challenges to the reliability and safety of the chemical propulsion systems are specific to the propulsion moiety. The solid industry has two current, significant, major challenges: pending elimination of 1,1,1 trichloroethane (TCA) and the disposal of waste propellants from current and past manufacture. Additional (and significant) funding is being targeted at ancillary vehicle systems (thrust vector control, avionics and paint/coatings) that, potentially, have other manufacturing industries addressing similar issues. The liquid propulsion industry's most significant problems are associated with the elimination of CFCs, and specifically CFC-113.

As before, it is instructive to provide comparative utilization values for those chemicals cited for elimination by the CP industry and the total U.S. manufacturing citations: (5,6,7,8)

Solid industry specific chemicals:

U.S. production of 1,1,1 trichloroethane (1992)		691,630,000 lbs
NASA utilization of TCA		1,000,000 lbs
CP industry utilization of TCA (estimated)		4,000,000 lbs

Liquid industry chemicals:

U.S. production of CFCs (1993)		257,000,000 lbs
NASA utilization of CFCs (1992)		644,904 lbs
CP industry utilization of CFCs (estimated)		2,000,000 lbs
U.S. production of CFC-113 (1991)	allowed	80,000,000 lbs
U.S. production of CFC-113 (1992)	allowed	60,000,000 lbs
U.S. production of CFC-113 (1993)	allowed	40,000,000 lbs
U.S. production of CFC-113 (1994)	allowed	15,000,000 lbs
NASA utilization of CFC-113 (1992)		404,251 lbs
CP industry utilization of CFC-113	estimated	1,200,000 lbs

Note: The estimated values for total chemical propulsion industry usage of TCA, CFCs and CFC-113 are taken by scaling the accurate NASA numbers to their relative portion of the thrust capability and materials to be cleaned within the industry. It has also been estimated that the current production is approximately three-fourths of allowed capacity.

These values may be conservative by up to 30%. It is readily evident that the solid industry represents approximately 0.5% of the TCA usage in the U.S. Similarly, the liquid propulsion industry represents approximately 0.8% of the total U.S. CFC usage and approximately 2% of the total CFC-113 usage. However, the chemical propulsion industry is providing a very significant portion of the research funding required for its specific needs in replacement technologies for TCA and CFC-113. NASA's portion alone may well exceed $5 - $10,000,000 exclusive of technology insertion and system (and new facility) development, test and qualification. (5)

To make a chemical propulsion system viable, the propellants must account for upwards of 85% of the mass of the system. Although the manufacture of these propellants (for liquids) is produced by subtier venders to the propulsion industry, and for solids is a complex mixture of materials provided by subtier vendors, the significant proportion of these materials in a chemical propulsion system requires investigation for appropriately detailing the manufacturing impacts of the industry to the environment. Solid systems use approximately 20 million pounds per year whereas the liquid industry uses approximately 70 million pounds per year of propellants. Three propellants make up the majority of the U.S. liquid propulsion system usage: (1,9,10,11)

North American production capacity for hydrogen	225 short tons/day = 164,250,000 lbs/yr
NASA hydrogen utilization (1992)	11,000,000 lbs
CP industry hydrogen utilization (estimated)	20,000,000 lbs
U.S. production capacity for oxygen	6,750,020,000 lbs
CP industry utilization (FY93)	50,000,000 lbs
U.S. production of jet fuel	$17,784,000,000
U.S. production of residual fuels	$ 8,715,000,000
U.S. use of RP-1 (kerosene rocket fuel)	$ 572,250

So the industry usage is approximately 12% of hydrogen production capacity, 0.75% of the manufactured oxygen capacity and 0.0065% of the fuels similar to rocket fuel manufactured yearly in the U.S. These values are again a small percentage of the total production.

Cleaning of cryogenic oxygen processing and propulsion equipment is critical to ensure product purity and safe operating conditions. The oxygen compatibility of materials is a function of local energy density and energy density rates, making the performance of materials in these environments a statistically predictable issue. Significant testing and data is required to adequately develop the statistical predictions. Higher energy density and rates (functions of purity, flow velocities, temperature and pressure) increase the likelihood of the occurrence of a combustion event. But it also increases the likelihood that the areas of significant concern reside further into the tails of the population. This results in significant issues solely relevant to the chemical propulsion industry, and the correspondingly high research and development expenditures.

The prime constituents in the manufacture of solid propulsion systems are ammonium perchlorate, rubber (binder) and aluminum. Twenty to 30 million pounds of ammonium perchlorate per year may be used. The primary constituents for this material are table salt (NaCl) and ammonium chloride. (10) This material usage represents a very small fraction of the salt and ammonia markets. The aluminum usage is covered below and the rubber material usage is minimal.

The solid propulsion manufacturing industry uses TCA as a vapor degreaser to clean adequately the large steel pressure vessels in preparation for bonding the insulation and propellant materials. These bondlines are one of the most critical feature of a solid rocket motor, inspection may be difficult and

debonds may be catastrophic. Again the margin for failure is limited and the requirements for cleanliness somewhat unique to this industry. Substantive progress has been made toward reduction of TCA usage in the majority usage processes (e.g., the vapor degreasing systems) but some critical processes, using less than 10% of the industry total usage, require significantly more research to qualify. Qualification for end product certification is also a substantive issue within the solid propulsion industry. Labscale testing, which is of relatively minor cost, often can not simulate the kinetic and thermodynamic effects present in large (or full scale) systems. Statistical testing of large systems is rarely possible; the shuttle redesigned solid rocket motor tests may cost upwards of $15,000,000 apiece.

The solid industry also has an issue with disposal of scrap propellant and of the obsolete systems requiring destruction under existing arms control treaties. It has been estimated that approximately 140 million lbs of solid rocket propellants will require disposal between 1993 and 2005. (12) The Air Force, as the largest customer in this area, prepared a Statement of Operational Need (SON AFLC 003-90) in April of 1991 for "Solid Rocket Propellant Disposal". Compounding this issue, the number of disposal sites was reduced from approximately 1200 in 1980 to less than 200 in 1987. (12) Current data is unavailable, but open pit burning of propellants clearly has a limited useful lifetime.

It is instructive to compare the production of hazardous waste (per year) from the solid industry to that of the U.S. and chemical manufacturing industries: (1,2,12)

U.S. Hazardous Waste	~300,000,000 tons
Chemical Manufacturing Industry Hazardous Waste	~213,000,000 tons
Department of Defense Hazardous Waste	~650,000 tons
Solid Propulsion Industry	~6,500 tons

The solid industry's waste is divided as follows: (12)

Propellant - Residue	7,270,000	4,701,000
Propellant Testing	5,380,000	3,574,000
Other (inert, lab, etc....)	2,040,000	3,456,000
Solvents	979,000	1,143,000

These data reveal approximately a 20% reduction in the industry's waste streams and clearly define the largest issues to be propellant disposal. Overall however, the industry represents approximately 0.02% of the U.S. hazardous waste totals.

Compliance costs have also risen considerably. The Air Force has estimated that equivalent man-years associated with environmental compliance rose by approximately a factor of 10 between 1980 and 1990. (2,12) Substantive research in these areas is ongoing. Full implementation may cost in the hundreds of millions to low billions of dollars with anticipated recovery estimated in the low hundreds of millions of dollars. (2,12)

The use and manufacture of nitrogen tetroxide and hydrazines will not be explored within this paper. Their environmental constraints are among the most mature of the chemical propulsion manufacturing community due to their inherently hazardous nature.

The other major components of liquid and solid propulsion systems are the pressure vessels, which are either steel or aluminum. The industry uses on the order of 10 million pounds of steel per year versus the steel industry's U.S. consumption of 185 billion lbs, or 0.0054%. The chemical propulsion industry uses approximately 5 million pounds of aluminum versus the aluminum industry's 17.162 billion lbs (total shipment), or 0.03%. (1,11)

The total poundage of HAPs, VOCs and ODCs used by the chemical propulsion industry has been shown to be minimal, and the industry's contribution to the development of replacement technologies quite substantive. It is revealing to note an Environmental Protection Agency assessment that estimates that three years after promulgation of the Hazardous Organic Emissions Standard for Hazardous Air Pollutants the emissions at chemical plants should reduce by up to 1 billion pounds (or about 80%). (1) Usage by the

chemical propulsion industry of such chemicals clearly pales in comparison. This follows a reduction of 35%, by U.S. chemical producers, of toxic releases to the environment between 1987 and 1991. (1)

INDUSTRY ADVANCES IN MEETING PENDING LEGISLATION

The following information relates specific environmental advances in the manufacture of the Atlas, Delta, Titan and Space Shuttle, and relies solely on information shared by the vehicle contractors. It is not intended to be an exhaustive research of each aerospace company's use of ODCs, but rather a sample of ODC usage and the concerted efforts to reduce or eliminate their use.

Atlas

The Atlas II is a medium-lift commercial launch vehicle developed by General Dynamics Space Systems Division (GDSS) and manufactured in San Diego, California. This vehicle is primarily used by commercial interests. [Note: GDSS was recently purchased by the Martin Marietta Corporation (MMC) who also owns the Titan launch vehicle; however, the research for this document relies on data obtained while the Atlas was owned by GDSS].

The Atlas program has produced several significant environmental achievements in the production of the vehicle since 1990. TCA emissions have been cut 86% from 1990 to 1993 to save over 640 tons of TCA while production rates for precision cleaned hardware have been increasing. (13) For the period of July 1990 to May 1994, Atlas has eliminated historically derived use of 1,775,670 lbs of TCA. (14) The Atlas program cut both their division ozone-depleting emissions and their Form R-reported emissions 79% and achieved virtually zero air toxic health risk at their Kearny Mesa plant. (13) They have eliminated CFCs from precision cleaning and from nearly all other processes. "Industrial toxics" emissions have been reduced 57% from their 1988 baseline. These achievements have earned the Atlas Program environmental awards which include a 1992 Environmental Protection Agency (EPA) Stratospheric Ozone Protection Award and a 1993 San Diego Industrial Environmental Association "Environmental Responsibility Award." (13)

The Atlas Program has several initiatives planned for its Environmental Resources Management (ERM) program. Plans are to eliminate ozone-depleting emissions, reduce EPA "industrial toxics" emissions 90%, implement a comprehensive hazardous materials management program, eliminate air toxic-related health risks at the Kearny Mesa plant, develop and implement a "world class" ERM program, and implement a state-of-the-art alkaline precision cleaning process. (13)

Some of the program's ERM goals for 1994 include establishing a hazardous materials management program, eliminating TCA, TCE and CFCs from all processes, continue building a "world class" pollution prevention program, continue building a "world class" energy conservation program, and continue building "world class" regulatory compliance programs. (13)

Delta

The Delta II is a medium-lift commercial launch vehicle developed by McDonnell Douglas Aerospace (MDA) and manufactured in Pueblo, Colorado. Primary users are the Department of Defense (DoD), NASA, and commercial interests.

MDA is proceeding with its plan to replace ODCs currently being used in the manufacture of the Delta vehicle. MDA is working to select and implement substitute materials and processes to assure uninterrupted manufacture of their product. A schedule has been established to accomplish these goals in three phases: Phase 1 - define the problem; Phase 2 - define the solutions; and Phase 3 - implement the solutions by the end of 1996. (15)

The Phase 1 search of vapor degreasing requirements is almost complete. TCA is currently used for vapor degreasing operations. Isopropyl alcohol has been chosen as a replacement handwipe cleaner. (16)

Titan

The Titan launch vehicle was developed by Martin Marietta Corporation (MMC) and is manufactured at their plant in Denver, Colorado. MMC offers the Titan III for commercial and NASA uses, while the Titan IV is used primarily by DoD.

MMC has an environmental program actively in place to eliminate or significantly reduce hazardous wastes in the manufacture of the Titan vehicle. MMC has defined objectives to reach their environmental goals. They intend to drastically reduce the use of solvents and other toxic chemicals by identifying and implementing suitable alternative cleaning technologies and/or material substitutes. They will also work to reduce the company's exposure to existing regulations and future liabilities. (4)

These objectives are apparently already being met. MMC's pollution prevention projects have resulted in a combined reduction of 90% of toxic releases (base year of 1987). Total hazardous waste generation has been reduced from 1,100 tons in 1987 to 175 tons in 1992. (4)

TCA has been the favored solvent for Titan manufacturing operations involving first stage degreasing, a process which removes shop dirt as well as the fish-oil-like substance that coats and protects aluminum panels from corrosion. After an exhaustive search for a replacement, MMC chose a nontoxic aqueous cleaner called Daraclean 282 as an acceptable alternative to TCA vapor degreasing. MMC has now virtually eliminated its use of TCA, reducing annual consumption by 98% in 1991 compared to 1988. Daraclean 282 is biodegradable, easily recyclable, and has no known harmful environmental effects. There is no known employee health risk and it cleans surfaces better than the TCA it replaced. (4)

CFC-113 is generally used as the principal cleaner in the second stage of cleaning. The replacement search for this cleaner ended with isopropyl alcohol (IPA). IPA had been used successfully in other operations for over twenty-five years and met all performance requirements. Also, alcohol evaporates readily, leaving less residue than the other compounds tested. The new IPA cleaning system eliminates the use and release of approximately 55,000 pounds of CFC-113 a year. Distillation and volatile organic compound (VOC) treatment have also been added to the system, facilitating IPA recycling and reducing VOC releases to nearly zero. (4)

Space Shuttle

The Space Shuttle is manufactured by NASA in association with prime contractors Rockwell International, Rocketdyne, Martin Marietta, and Thiokol. Users thus far have been NASA, DoD, industry academia and international partners. The Space Shuttle is comprised of several major elements including the orbiter, external tank (ET), solid rocket boosters (SRBs) and Space Shuttle main engines (SSMEs). The focus of waste disposal for the Space Shuttle is on the ET, SRB, and SSME since new orbiters are no longer being manufactured.

External Tank. MMC is the primary contractor for the ET, which is manufactured at the Michoud Assembly Facility (MAF) in New Orleans, Louisiana. Several pollution sources originate from various ET production operations including aluminum barrel panel and propellant tanks cleaning, primer coating, sprayed-on foam insulation, liquid oxygen tank proof test and cleanliness verification. They are carefully monitored and handled to ensure safety and environmental compliance. Control systems designed to manage the sources and abate pollution include carbon adsorption, thermal oxidizers, air strippers, a hazardous waste storage facility, incinerators, and a solvent recovery system. (17)

In their pollution prevention effort, MMC has targeted chemicals in response to ODC phase-out, the EPA 33/50 commitment, and Louisiana Air Toxic maximum emission rates. The goals are to maintain methyl ethyl ketone emissions below 20,000 lbs (minor source), maintain chromium emissions less than 25 lbs and eliminate where possible, apply maximum available control technology (MACT) to dichloral methane emissions by 1996, eliminate CFC usage, and apply MACT to trichloroethylene (TCE) emissions by 1996. (17)

Space Shuttle Main Engine. Rocketdyne is the primary SSME contractor and is located at Canoga Park, California. Rocketdyne established a Hazardous Materials Elimination Team (HMET) in 1989. (18) HMET is actively pursuing methods to eliminate use of chrome, CFCs, TCA, VOCs, and other hazardous

chemicals from their manufacturing processes. Chrome is currently used in the following processes: chromic acid anodizing, chrome plating, zinc-chromated primers, and dry film lube containing chrome. CFCs are used for circuit board defluxing, hydraulic fluid particle counts, freon blown foam, cooling systems, and cleaning. TCA is used primarily for fine cleaning of parts. VOCs are used as solvent handwipes. All of these materials are scheduled for elimination. (19)

One of HMET's primary tasks is the elimination of ODCs. The group has been instrumental in the elimination of CFC-113, traditionally used as a solvent to clean electrical assemblies and rocket engine hardware. This was accomplished by modifying equipment and replacing the CFC solvent with other materials. The team has overseen an 85% reduction in Rocketdyne's use of TCA, which they use primarily in vapor degreasers for cleaning hardware. (18) They have deactivated 11 of 14 TCA vapor degreasers and made improvements to the remaining large units. In 1995, when TCA is totally eliminated from Rocketdyne's manufacturing processes, the facility will be converted to a water-based cleaning process. Rocketdyne is also eliminating Freon-11, another ozone-depleter that is used to apply insulation on the SSMEs. They have evaluated an alternative foam that uses carbon dioxide instead of Freon as the blowing agent. This new foam is being incorporated into the cryogenic insulation system of the SSMEs. (20)

Solid Rocket Boosters. Thiokol Corporation is the prime contractor for the Shuttle's SRBs. Their manufacturing facility is located near Brigham City, Utah, with refurbishment facilities near Ogden, Utah. A variety of ODCs are used in the manufacture of SRBs, most of which are undergoing replacement technology efforts. TCA is used for degreasing during refurbishment and manufacturing, tool cleaning, diluent, sling liner cleaning, floor usage, mixer bowl/blades cleaning, and critical hand cleaning, seal surface preparation, and rubber insulation activation. There has been a 50% reduction in TCA usage since 1989. Thiokol projects an 87% reduction by 1996 with total elimination by 2002. (21)

In their efforts to eliminate ODCs from the manufacturing process, Thiokol has developed a master schedule for replacement of all ODCs currently used. Thiokol plans a 90% ODC reduction for manufacturing processes by February 1996. The final 10% ODC reduction should be accomplished by 1999. (21) The company is in the midst of a five year, $31 million program to eliminate ODCs from the solvents used for cleaning the solid rocket motors. The substitutes should be cost effective as well as environmentally safe. (22) Efforts have already begun paying off in the form of a 1993 EPA Ozone Protection Award. (23)

Efforts are focusing on new technologies such as ultrahigh-pressure water wash, spray-in-air cleaners, low emission vapor degreasing, surface cleanliness measurements, surface chemistry analyses, advanced vapor degreasing, and carbon dioxide pellet blasting. To further their efforts, Thiokol has formed partnerships with the NASA Operation Environment Team (NOET), NASA: Assured Shuttle Availability (ASA), NASA Headquarters - Environmental Engineering, the United Nations Solvents, Coatings, and Adhesives Technical Options Committee, the Aerospace Industries Association - Environmental Committee, Brigham Young University, and the University of Alabama in Huntsville. (21)

CONCLUSION

In summary, the chemical propulsion manufacturing industry is conducting a significant effort to pursue environmental replacement technologies for ODCs to assure compliance with federal laws and regulations. Efforts to date appear to concentrate on replacement of CFCs and TCA since the production and use of these chemicals are scheduled to be banned in the near future. The chemical propulsion industry represents a minute fraction of the production and production waste in the U.S., typically below 0.1% but is indicated at approximately 3% of the solution. The chemical propulsion industry's environmental issues are comparatively small but the industry has recognized those issues and is proactively addressing them in a manner that provides for technology transfer for the rest of the national industrial base.

REFERENCES

1. U.S. Department of Commerce, U.S. Industrial Outlook: 1994 (35th Edition) Washington, DC, January 1994.

2. Hawkins, T.W., and Wilkerson, B.E., "Environmental Propellant: Current Issues and Assessment", 1992 JANNAF Propulsion Meeting, Indianapolis, IN, 1992.

3. McCaleb, R.C., Chief of MSFC's Environmental Engineering and Management Office; presentation entitled "MSFC Environmental Council Meeting," dated July 24, 1992.

4. Dykema, K.J., and G.R. Larsen, "Case Study: The Greening of Corporate Culture: Shifting the Environmental Paradigm at Martin Marietta Astronautics Group," *Pollution Prevention Review,* Spring 1993.

5. Clarke-Ingram, M., of Marshall Space Flight Center, Alabama, from NASA's Environmental Resource Requirements Call, 1994. Personal communication.

6. Dunn, D., of Dupont Fluoroproducts, Wilmington Delaware. Personal communication, May 1994.

7. Industry Profile (monthly), Chemical Manufacturers Association, 2501 M St. NW, Washington, DC 20037.

8. Ozone Depleter Compliance Guide, Thompson Publishing Group Inc., March 1993.

9. Air Products and Chemicals, Inc., Government Systems Department, from Information collected by SRI International, 1993. Personal communication.

10. Shackelford, B., of Marshall Space Flight Center, Alabama. Personal communication.

11. U.S. Bureau of the Census, Statistical Abstract of the United States: 1993 (113th Edition.), Washington, DC, 1993.

12. Rising, S., of Armstrong Laboratory, Environics Directorate; also referencing: Hawkins, T.W., "Environmentally Enhanced Propulsion - Solution Propellant Research", 1994 JANNAF Propulsion Meeting, 1994. Personal Communication.

13. Kropp, C., of General Dynamics. GDSS Program Brief entitled, "Environmental Resources Management (ERM)," dated December 9, 1993; brief was provided on May 27, 1994.

14. Kropp, C., of General Dynamics. Personal communication and data. May 25, 1994.

15. Fahrner, R.L, of McDonnell Douglas Aerospace - West; presentation entitled "Ozone Layer Depleting Substance (OLDS) Elimination Status Update to Ken Francis' Excon," dated May 27, 1994.

16. Philyaw, P., of McDonnell Douglas Aerospace, Huntsville; supplied data sheets entitled, "MDA ODC Applications/Materials."

17. Wallo, M., of Martin Marietta. Personal communication and data. May 19, 1994.

18. Bodemeijer, R., of Rocketdyne. Personal communication, July 7, 1994.

19. Shoemaker, M., of Rocketdyne. Personal communication and data. May 1994.

20. "Environmental Report," Rockwell International, 1992. Supplied by Phil Krotz of RI, May 1994.

21. Bowman, R., of Thiokol Corporation. Supplied presentation entitled "Environmentally Sound Manufacturing," presented May 10-11, 1994, at the 10th Annual Technical Business Exhibition and Symposium in Huntsville, Alabama.

22. LeSueur, S.C., "Rocket Motors Tagged for Cleanup," *Space News*, Volume 5, No. 16, April 18-24.

23. Saderholm, C.A., of Thiokol Corporation; provided data package dated July 6, 1994.

CFD ASSESSMENT OF THE POLLUTANT ENVIRONMENT FROM RD-170 PROPULSION SYSTEM TESTING

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ABSTRACT

Computational Fluid Dynamics (CFD) technology has been used to assess the exhaust plume pollutant environment of the RD-170 engine hot-firing on the F1 Test Stand at Marshall Space Flight Center. Researchers know that rocket engine hot-firing has the potential for forming thermal nitric oxides (NO_x), as well as producing carbon monoxide (CO) when hydrocarbon fuels are used. Because of the complicated physics involved, however, little attempt has been made to predict the pollutant emissions from ground-based engine testing, except for simplified methods which can grossly underpredict and/or overpredict the pollutant formations in a test environment. The objective of this work, therefore, has been to develop a technology using CFD to describe the underlying pollutant emission physics from ground-based rocket engine testing. This resultant technology is based on a three-dimensional (3D), viscous flow, pressure-based CFD formulation, where wet CO and thermal NO finite-rate chemistry mechanisms are solved with a Penalty Function method. A nominal hot-firing of a RD-170 engine on the F1 stand has been computed. Pertinent test stand flow physics such as the multiple-nozzle clustered engine plume interaction, air aspiration from base and aspirator, plume mixing with entrained air that resulted in contaminant dilution and afterburning, counter-afterburning due to flame bucket water-quenching, plume impingement on the flame bucket, and restricted multiple-plume expansion and turning have been captured. The predicted total emission rates compared reasonably well with those of the existing hydrocarbon engine hot-firing test data.

INTRODUCTION

Russian-built kerosene fueled engines such as RD-170 or its likeness have been identified as potential candidates to fly the Single-Stage-to-Orbit Rockets. The potential of forming thermal nitric oxides (NO_x) and of producing carbon monoxide (CO) has been a concern for ground-based engine testing using hydrocarbon fuels. The release of these criteria pollutants into the atmosphere not only contributes to acid rain and ozone depletion (NO_x), but also poses as a potential threat (CO) to living organisms. It is therefore important to predict accurately those criteria pollutant emissions from engine testing for the environmental impact assessment. Several simplified analyses have been used in the past for first principle estimates. For example, thermochemical analysis using chemical equilibrium computer (CEC) code[1] can provide CO concentration at nozzle exit plane. However, it over-predicts CO concentration due to the omission of its subsequent after-burning with air. In addition, it can not predict NO formation unless gross assumption on the amount of air mixing can be made; A perfectly-stirred reactor analysis has been reported to treat the plume-air mixing[2]. Albeit simple, the condition of perfect mixing between the plume and entrained air is not justified. Besides, there is an inherent difficulty in estimating the residence time; Other methods such as steady two-dimensioal analysis of a free exhaust plume can be performed, However, the physics depicted is far from that occurring on a test stand and the evolution of the plume is a transient process.

The rapid gains made in CFD and computer technologies have made possible the development of a computational methodology that can describe the pollutant emission physics from ground-based rocket engine testing: 3D air entrainment, 3D multiple-nozzle plume interaction and mixing with air, finite-rate afterburning reaction, plume impingement with flame bucket and plume quenching through deluge water, and 3D restricted multiple plume expansion. In this study, a pressure-based CFD method heavily benchmarked for nozzle, plume, and combustion driven flows was used for this development. The hot-firing of a RD-170 engine on the F1 Stand was simulated. For the purpose of this study, an 11-species, 18-reaction finite-rate chemistry set described the after-burning. A nominal hot-firing with water-quenching (homogeneous two-phase formulation) was computed, along with two cases including the frozen chemistry and finite-rate chemistry (both without water-quenching) for comparison. The emission rates of the pollutants and the exhaust plume properties were computed and the effects of after-burning and water-quenching on the pollutant formation were compared. This resultant technology has potential applications in actual rocket launches and in the development of air-breathing engines.

GOVERNING EQUATIONS

The present flow solver, Finite Difference Navier-Stokes (FDNS) code[3,4,5] is used to provide multi-component, steady-state and unsteady viscous flowfield solutions by solving the Reynolds-averaged transport equations such as mass conservation equation, Navier-Stokes equations, energy equation and other scalar transport equations. The general form of these conservation equations can be written as:

$$\frac{\partial \rho q}{\partial t} + \frac{\partial}{\partial x_j}\left\{\rho\left(u - u_g\right)_j q - \mu_e \frac{\partial q}{\partial x_j}\right\} = S_q \qquad (1)$$

where ρ and q = (1, u, v, w, h, k, ε and α_i) stand for the fluid density and the flow primitive variables for the continuity, momentum, energy, turbulence model and species mass-fraction equations, respectively. u_g stands for the grid moving speed. $\mu_e = (\mu_l + \mu_t)/\sigma$ represents the effective viscosity which is a sum of the laminar viscosity and the turbulence eddy viscosity divided by a turbulence modelling constant[5], σ. The source terms S_q, for the governing equations in 3D space x_i can be written in fully conservative form as:

$$S_q = \begin{Bmatrix} 0 \\ -\dfrac{\partial P}{\partial x_i} + \dfrac{\partial}{\partial x_j}\left(\mu_e \dfrac{\partial u_j}{\partial x_i}\right) - \dfrac{2}{3}\dfrac{\partial}{\partial x_i}\left(\mu_e \dfrac{\partial u_j}{\partial x_j}\right) \\ \dfrac{DP}{Dt} + \Phi + Q_t \\ \rho(G - \varepsilon) \\ \rho\dfrac{\varepsilon}{k}\left[\left(C_1 + C_3\dfrac{G}{\varepsilon}\right)G - C_2\varepsilon\right] \\ \omega_i,\ i = 1,\ldots\ldots n \end{Bmatrix} \qquad (2)$$

where Φ, Q_t and ω_i stand for the energy dissipation function, heat source and species source terms, respectively. G stands for the turbulence kinetic energy production rate which is written as:

$$G = \frac{\mu_t}{\rho}\left\{\frac{1}{2}\left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j}\right)^2 - \frac{2}{3}\left(\frac{\partial u_k}{\partial x_k}\right)^2\right\} \qquad (3)$$

The turbulence modeling constants C_1, C_2 and C_3 are given as 1.15, 1.92 and 0.25 respectively in the extended k-ε turbulence model[6]. The extended k-ε model is superior than the standard k-ε model[7] in that a second time scale of the production range of turbulence kinetic energy spectrum is added to the dissipation rate equation. This extra time scale enables the energy transfer mechanism of the turbulence model to respond to the mean strain more effectively. This extended

k-ε turbulence model was rigorously benchmarked with fully developed turbulent channel and pipe flows, turbulent free-shear flows, flat plate turbulent boundary layer flow, turbulent flow over a backward-facing step, a confined turbulent swirling flow, and dump combustor flows. The compressibility effect on the turbulence is taken into account by using the method of Mach number correction[8,9].

SOLUTION ALGORITHM

To solve the system of nonlinear partial differential equations, it uses finite-difference approximations to establish a system of linearized algebraic equations on non-staggered grid mesh systems. A pressure-based predictor plus multi-corrector time-marching scheme is employed so that flow over all-speed range can be analyzed. The time-marching scheme, total variation diminishing variation (TVD) discretization, and penalty function tretament of the reaction source terms are pertient to this work and are depicted in the following.

Time-Marching Scheme

The time-marching scheme is described below. For convenience, transformed equation (from x_i to ξ_i system with J as the Jacobian of coordinate transformation) of Eq. (1) is written as:

$$\frac{1}{J}\frac{\partial \rho q}{\partial t} = -\frac{\partial F_i}{\partial \xi_i} + S_q = R_q \qquad (4)$$

where F_i represents convection and diffusion fluxes in i-direction. First, Eq. (4) is discretized in finite difference form,

$$\frac{1}{J\Delta t}\left\{(\rho q)^{n+1} - (\rho q)^n\right\} = \theta R_q^{n+1} + (1-\theta) R_q^n \qquad (5)$$

where superscripts n and n+1 represent old and new time levels respectively. θ is a time marching control parameter and, θ = 1.0 and θ = 0.5 are for an implicit Euler and a time-centered time marching schemes, respectively. The following linearization is then incorporated.

$$(\rho q)^{n+1} = (\rho q)^n + \rho^n \Delta q^n \qquad (6)$$

$$R_q^{n+1} = \left(\frac{\partial Rq}{\partial q}\right)^n \Delta q^n + R_q^n \tag{7}$$

With the above approximations, the final form of the time-marching scheme can be written as:

$$\left\{\frac{\rho^n}{J\Delta t} - \theta\left(\frac{\partial R_q}{\partial q}\right)^n\right\}\Delta q^n = R_q^n \tag{8}$$

The pressure-based multi-corrector solution method is formulated using simplified perturbed momentum and continuity equations[3,4,5]. The simplified velocity correction equation can be written as:

$$\frac{\partial \rho U_i}{\partial t} \approx -\nabla P' \tag{9}$$

or, in discrete form,

$$u_i' \approx -\beta\frac{\Delta t}{\rho}\nabla P' \tag{10}$$

$$P^{n+1} = P^n + P' \tag{11}$$

where β represents a pressure relaxation parameter (typical value of 1.0). The velocity and density fields in the continuity equation are then perturbed to form a correction equation. Neglecting higher order terms, the continuity equation can be written as,

$$\frac{\partial \rho'}{\partial t} + \nabla(U_i\rho') + \nabla(\rho U_i') = -\left(\frac{\partial \rho}{\partial t}\right)^n - \nabla(\rho U_i)^n \tag{12}$$

Substituting Eq. (10) into (11) and letting $\rho' = P'/RT$, the following all-speed pressure correction equation is obtained,

$$\frac{Mw}{RT}\frac{\partial P'}{\partial t} + \nabla\left(U_i\frac{Mw}{RT}P'\right) - \nabla(\beta\Delta t\ \nabla P') = -\left(\frac{\partial \rho}{\partial t}\right)^n - \nabla(\rho U_i)^n \tag{13}$$

To reduce potential oscillations in the pressure field, an upwind TVD adaptive dissipation term based on the density field, which is described in the next section, is added to the right hand side of Eq. (13). Once solution of Eq. (13) is obtained, the velocity and pressure fields are updated using Eqs. (10) and (11). The density field is then updated through the equation of state. The temperature field can also be modified by using a perturbed temperature correction equation. The entire corrector step is repeated 3 or 4 times such that the mass conservation condition is

enforced before marching to the next time level. For steady-state flow solutions, however, only one corrector step is used for computational efficiency.

Total Variation Diminishing Discretization

Second-order central differencing schemes are employed to model the diffusion fluxes and the source terms of the governing equations. High-order upwind schemes are used for the nonlinear terms, convection fluxes, to maintain solution accuracy and to enhance numerical stability. A third-order upwind TVD scheme[4] is employed in the present flow solver. Only the convection terms are modeled using the TVD flux limiters. The convection terms of the governing equations can be expressed by finite difference approximation as:

$$\frac{\partial F}{\partial \xi} = f_{i+1/2} - f_{i-1/2} + h_{i+1/2} - h_{i-1/2} \tag{14}$$

where f and h represent first-order fluxes and TVD flux limiters respectively. The TVD flux limiters are functioned as anti-diffusion terms to recover the scheme to high-order accuracy. The first-order fluxes and the TVD flux limiters are given below.

$$f_{i+1/2} = \max\left\{0,(\rho U)_{i+1/2}\right\}\phi_i + \max\left\{0,-(\rho U)_{i+1/2}\right\}\phi_{i+1}$$

$$h_{i+1/2} = \begin{cases} \frac{1}{4}|\rho U|_{i+1/2}\left\{d\phi^+_{i+1/2} + d\phi^-_{i-1/2} + \alpha\left(d\phi^+_{i+1/2} - d\phi^-_{i-1/2}\right)\right\}, U > 0 \\ \frac{1}{4}|\rho U|_{i+1/2}\left\{d\phi^-_{i+1/2} + d\phi^+_{i+3/2} + \alpha\left(d\phi^-_{i+1/2} - d\phi^+_{i+3/2}\right)\right\}, U < 0 \end{cases}$$

where the minmod functions in the TVD flux limiters are written as:

$$d\phi^{\pm}_{i+1/2} = sign\left(\Delta\phi_{i+1/2}\right)\max\left\{0,\min\left[\left|\Delta\phi_{i+1/2}\right|,\beta\ sign\left(\Delta\phi_{i+1/2}\right)\Delta\phi_{i+1/2\mp1}\right]\right\}$$

The order of accuracy of this scheme is determined by the parameters α and β. Only the second-order and third-order upwind schemes were used in this study. That is,

$$\alpha = \begin{cases} -1, & 2nd-order\ upwind \\ +\frac{1}{3}, & 3rd-order\ upwind \end{cases}$$

$$\beta = \frac{3-\alpha}{1-\alpha}$$

The compression factor, β, is used to sharpen the contact discontinuities and slip streams for better wave tracking resolution. Other schemes such as second-order and third-order upwind schemes and a second-order central plus fourth-order dissipation scheme are also available, through input data selection, in the present flow solver. The option using central-difference scheme with artifical dissipation has been heavily benchmarked with practical rocket engine nozzle, plume, and combustion driven flow tests and applications such as the Space Shuttle Main Engine (SSME) performance and nozzle/plume flowfields (compared with JANNAF standard codes and hot-fire test data)[5], SSME start-up and shut-down transients[10], transient SSME fuel preburner flow[11], Ramjet dump combustor flows[12], integrated combustion chamber (SSME, Space Transportation Main Engine, 40k) flow and heat transfer[13], and base flow characteristics for a four-engine clustered nozzle configuration[14].

Penalty Function Treatment of the Reaction Source Terms

For the gas-phase chemical reaction modeling, a general system of chemical reactions can be written in terms of its stoichiometric coefficients (ν_{ij} and ν_{ij}') and the i-th chemical species name (M_i) of the j-th reaction as

$$\sum_i \upsilon_{ij} M_i = \sum_i \upsilon_{ij}' M_i \tag{15}$$

If we define the Arrhenius reaction rate for forward (R_{fj}) and backward (R_{bj}),

$$R_{fj} = K_{fj} \prod_k \left(\frac{\rho \alpha_k}{Mw_k}\right)^{\upsilon_{kj}} \tag{16}$$

$$R_{bj} = K_{bj} \prod_k \left(\frac{\rho \alpha_k}{Mw_k}\right)^{\upsilon_{kj}} \tag{17}$$

the net rate of change in the molar concentration of species i due to reactions j, R_{ij}, can be written as:

$$R_{ij} = Mw_i (\upsilon_{ij}' - \upsilon_{ij}) \left(R_{fj} - R_{bj}\right) \tag{18}$$

and the species production rate ω_i (in terms of mass fraction), is calculated by summing over all reactions,

$$\omega_i = \sum_j R_{ij} \tag{19}$$

The forward reaction rate for each of the reactions is given by the modified Arrhenius law

$$Kf_j = A_j T^{B_j} \exp(-\frac{E_j}{RT}) \tag{20}$$

and the corresponding backward reaction rate is obtained using

$$Kb_j = \frac{Kf_j}{Ke_j} \tag{21}$$

where Ke_j is the equilibrium coefficient

$$Ke_j = (RT)^{-\sum_{i=1}^{n}(\nu'_{ij}-\nu_{ij})} \exp\left[-\frac{\sum_{i=1}^{n}(g_i\nu'_{ij}-g_i\nu_{ij})}{RT}\right] \tag{22}$$

To solve the chemistry system equations numerically, an efficient penalty function method[15] is employed in the present study. In the penalty function method, the system of species equations are solved by employing a small time step size based on the assigned tolerance (0.01 used in this study) for species mass fraction equation, that is

$$\Delta t_s = \min\left[\frac{\rho\,(\Delta\alpha)_{assigned}}{\omega_i}, i=1,n\right] \tag{23}$$

To ensure species conservation and element balance conditions, the species solutions are subject to the following constraints:

$$\sum_i \alpha_i = 1.0 \tag{24}$$

and

$$0.0 \le \alpha_i \le 1.0 \tag{25}$$

A penalty function is therefore devised to ensure the above constraints are met after every time marching step. This function is defined as

$$PF_i = \frac{1.0-\alpha_i^k}{\alpha_i^* - \alpha_i^k} \quad for \quad \alpha_i^* - \alpha_i^k > 0.0 \tag{26}$$

$$PF_i = \frac{-\alpha_i^k}{\alpha_i^* - \alpha_i^k} \quad for \quad \alpha_i^* - \alpha_i^k < 0.0 \tag{27}$$

The allowable changes in species mass fractions, which are the solutions of the species continuity equations, are calculated by the following expression such that the second constraint, Eq. (25), is satisfied,

$$\alpha_i^{k+1} = \alpha_i^k + (\alpha_i^* - \alpha_i^k) \cdot PF \tag{28}$$

where PF = min (PF_i), i=1, 2, · · · · n. This procedure is a crucial requirement for the numerical stability and accuracy of a the present model. The resulting limited changes are adjusted so that they are proportional to the species source terms from which the first constraint, Eq. (24), is satisfied. For transient reacting flow calculations, multiple steps of the penalty function procedures are used to reach the flow time step size based on the operator-splitting point implicit approach.

BOUNDARY CONDITIONS

The present flow solver supports various types of boundary conditions for the inlet, exit, symmetry, wall, cyclic/zonal boundaries and singularity lines, etc. For subsonic inlets, fixed total pressure or fixed mass conditions can be specified. For supersonic inlets, all flow variables are fixed unless transient inlet boundary conditions are required. In case of incompressible flow applications, only pressure field is extrapolated at the inlet boundaries. In the present application, the free stream boundary around the nozzles is a modified subsonic inlet with fixed total pressure boundary condition to allow air entrainment. This is accomplished by making two assumptions: 1) air entrainment boundaries are sufficiently far from the nozzles such that the flow is isentropic and irrotational; 2) flow is allowed to entering through the air entrainment bounadries only. Based on assumption 1), Bernoulli's equation is used to solve for the total velocity

$$q = [2(P_o - P_e)/\rho_e]^{0.5} \tag{29}$$

where subscript e indicating quantities extrapolated form the interior and P_o is the ambient stagnation pressure. Obtaining a total extrapolated velocity from the interior q_e, we can compute a total velocity at the air entrainemnt boundary as

$$q^{n+1} = q_e + \omega(q - q_e) \tag{30}$$

where ω is defined as a relaxation parameter. The flow directions are then extrapolated from the interior. In order not to violate assumption 2), the total velocity is set to zero if the flow directions indicating an outflow condition and the pressure is set to its ambient value.

RD-170 is a regeneratively cooled, four-nozzle clustered engine which burns Kerosene fuel with liquid oxygen and was used to thrust Energia launch vehicles. Thermochemical analysis[1] was performed for the thrust chamber at a nominal operating condition and the equilibrium products at the nozzle exit were used as the input to the propulsion system. Table 1 shows the computed flow properties at the chamber, throat and nozzle exit. $CH_{1.9423}$[1] was used as the chemical formula for Kerosene fuel.

Table 1. RD-170 thrust chamber equilibrium flow properties

	Chamber	Throat	Nozzle Exit
P, atm.	241.96	139.45	0.6337
T, deg. K	3877	3667	1818
Mach Number	0.000	1.000	3.972
Species Mole Fractions			
CO	0.30671	0.30035	0.24569
CO_2	0.16619	0.17879	0.26158
H	0.02245	0.01936	0.00016
HCO	0.00006	0.00004	0.00000
HO_2	0.00010	0.00006	0.00000
H_2	0.07551	0.07349	0.09662
H_2O	0.34357	0.35801	0.39591
H_2O_2	0.00004	0.00002	0.00000
O	0.00988	0.00741	0.00000
OH	0.05779	0.04820	0.00004
O_2	0.01768	0.01427	0.00000

It can be seen that a significant amount of CO (24.569%) existed at the nozzle exit. This is the amount that could be dumped into the environemnt and can only be chemically reduced through afterburning. It can also be seen that there is no soot nor polycyclic aromatic hydrocarbon fragments produced throughout the thrust chamber, although graphite carbon and polycyclic aromatics were considered. This is to be expected under the nominal RD-170 operating condition at a near stoichiometric equivalence of 1.2939. Regenerative cooling is another factor since there is no need for turbine exhaust dump inside the thrust chamber.

The inlet condition to the flame trench is supersonic and fixed water mass flow rates are specified along the deflector wall and other wall boundaries in the flame trench. The free stream

around the plume downstream of the trench outlet is frozen at see-level condition with a wind speed of 10 ft/sec. At exit boundaries, direct extrapolation (for supersonic outlet only), fixed mass or fixed pressure at a point boundary conditions can be specified. The fixed pressure boundary condition was used in this study for the downstream plume outlet boundary. For symmetry planes, which are the center planes of the computational domain, zero gradient boundary conditions are applied for all scalars and tangency conditions are imposed for the velocity vectors. Non-slip boundary conditions are employed for the momentum equations at solid wall boundaries. Wall-normal zero gradient pressure boundary conditions are used in the code. Isothermal or adiabatic wall boundary conditions can be specified separately for each wall segment. In the case of turbulent flow computations using high-Reynolds number turbulence models, wall function approaches[7,8] are employed, which is the case in the present study.

FINITE-RATE AFTERBURNING KINETICS

To accurately predict the contaminant concentrations of the exhaust plume, finite-rate chemical kinetics are included in the numerical modeling. The plume chemistry occurring in the flame-bucket/Test-stand flow physics includes the afterburning of CO to CO_2, thermal NO_x formation and decomposition, counter-afterburning effect on CO conversion due to water quenching and its reduction effect on NO_x formation. These are described with a wet CO (12 reactions) and a thermal NO (6 reactions) finite-rate mechanisms, as shown in Table 2. The well-known Zeldovich mehcanism is included in the thermal NO chemistry. For computational efficiency, only NO is considered in this work since other species of the No_x family such as NO_2 is converted from NO and usually exists in trace amount. Their existence is hence included in the NO as "equivalent NO". The wet CO and thermal NO mechanisms are sub-sets of a combustion kinetics model for complex hydrocarbon (coal derived) fuels developed for Department of Energy[16,17,18]. Their reaction rates, in Arrhenius law form, have been validated with Jet-stirred combustor data, including blow-out limits, shock-tube measurements of ignition delay times[17,18], and turbulent diffusion flames and flat flames data[19]. In addition, the thermal NO_x reactions have also been benchmarked with an industrial burner data[20].

The formation of thermal NO is significantly influenced by flame temperature than other types of NO, e.g., the fuel NO resulting from nitrogen compounds contained in the fuel. Its strong dependence on temperature results from both the temperature dependence of the forward rate constant of reaction $O + N_2 = N + NO$ and the sensitivity of O atom equilibrium concentration to temperature. Production of thermal NO is generally negligible at low temperatures. It is therefore expected that most of the thermal NO will be formed in the flame front, .i.e., the plume mixing layer near the exit plane of the nozzles.

Table 2. Afterburning chemical kinetics

Reaction	A	B	E/R
Wet CO Mechanism			
$H_2 + O_2 = OH + OH$	1.7000E13	0	2.4070E4
$OH + H_2 = H_2O + H$	2.1900E13	0	2.5900E3
$OH + OH + O + H_2O$	6.0230E12	0	5.5000E2
$O + H_2 = H + OH$	1.8000E10	1.0	4.4800E3
$H + O_2 = O + OH$	1.2200E17	-0.91	8.3690E3
$M + O + H = OH + M$	1.0000E16	0	0
$M + O + O = O_2 + M$	2.5500E18	-1.0	5.9390E4
$M + H + H = H_2 + M$	5.0000E15	0	0
$M + H + OH = H_2O + M$	8.4000E21	-2.0	0
$CO + OH = H + CO_2$	4.0000E12	0	4.0300E3
$CO + O_2 = CO_2 + O$	3.0000E12	0	2.5000E4
$CO + O + M = CO_2 + M$	6.0000E13	0	0
Thermal NO Mechanism			
$O + N_2 = N + NO$	1.3600E14	0	3.7750E4
$N_2 + O_2 + NO + NO$	9.1000E24	-2.5	6.4600E4
$NO + O = O_2 + N$	1.5500E9	1.0	1.9450E4
$M + NO = O + N + M$	2.2700E17	-0.5	7.4900E4
$N + OH = NO + H$	4.0000E13	0	0
$CO_2 + N = CO + NO$	2.0000E11	-0.5	4.0000E3

* M stands for third-body collision partner

COMPUTATIONAL GRID GENERATION

The grid generation for the nozzles and test stand was performed using an EZSURF code[21]. It was used to interactively create the edge curves of the nozzle exits, aspirator, flame deflector and multi-zone block edges. The initial surfaces were then generated using transfinite interpolation in EZSURF. The flame deflector and nozzle exit surfaces were then elliptically smoothed. Further work was done on the nozzle exit surfaces using Bezier curve and local redistribution in EZSURF. The volume grid for the first block (Zone 1) was created using two linear stackings; one from the top of the block to the nozzle exit plane and then another form the

nozzle exit plane to the bottom of the aspirator. The flame deflector block (Zone 2) and subsequent external ambience (Zone 3) volume grids were created using transfinite interpolation.

The F1 Test Stand, standing 230 feet tall with a flame bucket (deflector) attached to the aspirator, was used to test F1 engines with which Saturn launch vehicles were propelled. Not only does the flame bucket quenches the rocket exhaust plume with deluge water, but also turns the vertical flowing exhaust plume to that of a horizontal direction, after which the plume expands and dissipates into the atmosphere. Fig. 1 shows the computational domian for the F-1 Stand. The RD-170 engine is mounted vertically, firing down into the flame bucket. Due to symmetry, only half of the domain was actually computed. The four RD-170 nozzles (mounted beneath the platform that is not modeled) and the aspirator are described by Zone 1 which contains 63,360 grid points (72x40x22). The aspirator itself is mounted on top of the flame bucket such that the air entrainment can be promoted and the plumes are centered while impinging at a predetermined area in the flame bucket (approximately 45-degree elbow at the bottom). Ambient air is allowed to be entrained through the top and four side boundaries of Zone 1. The flame bucket is modeled by Zone 2 which composes of 72,000 grid points (72x40x25). The plumes are then quenched through water deluge injecting from all four walls inside the bucket. The water injection pattern is designed as such that most of the water injects at the plume impingement area.

After passing through the flame bucket (Zone 2), the quenched plumes expand into the vast surrounding atmosphere (Zone 3) which is described by 156,975 grid points (91x69x25). The relative sizes and loactions of all three zone are shown in Fig. 2. Total number of grid points used in this study was 292,335.

RESULTS AND DISCUSSION

A frozen chemistry analysis was performed at first for a small period of elapsed time in order to establish an initial plume in the system. This not only prepared for the initial flowfields for the computation of subsequent parallel finite-rate chemistry and finite-rate chemistry with water-quenching cases, but also served as an excellent check of mass conservation using carbon balance. This procedure is allowed since the total pollutant emission rates during a nominal steady RD-170 hot-firing are desired and not those of an actual start-up sequence. The goals are therefore to compute the growth rate of NO and the disappearance rate of CO until they achieve asymptotic states.

Fig. 3 shows the computed velocity vectors colored by Mach number contours to represent the entrained air surrounding the bulk rocket plumes. Entrained from surroundings close to the open platform, the air accelerated and mixed with the plume bounadry layer and

entered the opening of the aspirator, where it continuously mixed with the advancing plume bounadry layer. In addition to cooling and dilution of the contaminant, the entrained air also provides the source of reactants for afterburning and thermal NO formation. Due to a backward-facing step geometry between the aspirator and the flame bucket, flow recirculation patterns formed underneath the aspirator.

Fig. 4 shows the computed temperature contours for the water-quenching case. Water jet vectors are shown for the top and bottom walls. The water jets at the back wall are mostly blocked out by the center temperature contours, whereas the water jets from the front wall are not shown for clarity. Most of the thermal NO is formed near the aspirator level where it has the most mixing and the hottest temperature. This is in agreement with the characteristics of the Zeldovich mechanism. It can also be seen that the plumes impinge on the 45-degree bend section of the flame bucket where it encounters the most water-quenching, that agrees with the original design. The quenched plumes then turn and partially hit the outer wall, where it moves horizontaly out, following the direction of the flame bucket.

Fig. 5 shows the comparisons of averaged mass fraction in the system for species CO, CO2, NO and OH, with respect to elapsed time. The averaged mass fraction for CO in the add water-quenching case is more than that of the purely finite-rate chemistry case due to the counter after-burning effect of deluge water, and vice versa for that of CO2. The higher level of OH in the finite-rate case shows a higher degree of after-burning reaction, due to higher overall plume temperature without water-quenching. Total NO production drops significantly in the add water-quenching case. The concentraion of NO in the add water-quenching case is almost two orders of magnitude lower than that in the finite-rate chemistry only case. This is not surprising since the extent of thermal NO formation depends heavily on the local temperature. The effect of water deluge on the formation of NO is the reduction in peak temperature caused by the heat capacity of water.

The computed growth of plume volumes is shown in Fig. 6. It can be seen that the growth rates of the plumes have reached their approximate asymptotic states. Obviously, the plume energy of the finite-rate chemistry is higher than that of the add water-quenching case. Correspondingly, the plume volume growth rate of the finite-rate case is larger than that of the add water-quenching case. It is anticipated that the characteristics of computed growth of plume energies would be similar to those of plume volumes. These CFD results ultimately serve as the basis (input) for the subsequent meteorological cloud dispersion calculation, where the plume volume growth rate helps determining the eventual plume size and the plume energy growth rate helps determining the magnitude the plume buoyancy force.

A comparison of the calculated criteria pollutant total emission rates for RD-170 with those measured for other Kerosene-fueled engines[22] is shown in Table 3. Since thrust levels are quite different, the measured emission rates were extrapolated to a RD-170 level by thrust ratios. Although the operations of the engines and test stands are vastly different, and there is a question on whether the point sampling technique used in the measurement representative of the whole

plume. The agreement in terms of order-of-magnitude for these engines is reasonable and encouraging. Among RD-170 CFD computations, the emission rate of CO is maximum and that of NO is zero for the frozen chemistry case, since afterburning reactions are not turned on, whereas the effect of water deluge has reduced the CO conversion rate from 83% of the finite-rate chemistry case to that of 67%. This is of interest since the effect of water deluge also has reduced the NO_x production by 95%.

Table 3. Total emission rates

Engine	Thrust, lbf	NO_x, lb/sec	CO, lb/sec
MA5B/hot-firing	370,000	5.4/25.9*	133/641*
MA3S/hot-firing	165,000	2.7/29.1*	210/2,266*
MA3B/hot-firing	60,000	1.5/45.6*	138/4,111*
RS27/hot-firing	205,000	1.2/10.6*	94/820*
RD-170/CFD			
Frozen	1,777,000	-	1,382
Finite-Rate	1,777,000	8.0	232
Add Water	1,777,000	0.4	463

* based on extrapolation of measured emission rate to a RD-170 by thrust ratio

CONCLUSION

A 3D viscous flow, pressure based CFD technology has been developed to predict the contaminant emissions from ground-based rocket engine RD-170 propulsion testing. Pertinent test stand flow physics such as the multiple-nozzle clustered engine plume interaction, aspiration from base and aspirator, plume mixing with entrained air that resulted in contaminant dilution and afterburning, counter-afterburning due to flame bucket water-quenching, plume impingement on the flame bucket, and restricted multiple-plume expansion and turning, have been predicted. The predicted criteria pollutant total emission rates agreed reasonably well with those of the existing hydrocarbon engine hot-firing test data. This resultant technology has potential applications in actual rocket launches and in the development of air-breathing engines.

ACKNOWLEDGEMENT

The authors thank the support from Robert Schwinghamer of NASA Operational Environment Team. The discussions with Rebecca McCaleb and Clay Horan of Environmental and Engineering Office were also appreciated. We would also like to thank Catherine Dumas of Sverdrup for making the iso-value graphics and flowfield animation.

REFERENCES

[1] Svehla, R.A., and McBride, B.J., "FORTRAN IV Computer Program for Calculation of Thermodynamic and Transport Properties of Complex Chemical Systems," NASA TN D-7056, 1973.

[2] Leone, D.M., and S.R. Turns, "Active Chlorine and Nitric Oxide Formation From Chemical Rocket Plume Afterburning," AIAA Paper 94-0788, January 1994.

[3] Chen, Y.-S., "Compressible and Incompressible Flow Computations with a Pressure Based Method," AIAA Paper 89-0286, January 1989.

[4] Chen, Y.-S., Liaw, P., Shang, H.-M., and Chen, C.-P., "Numerical Analysis of Complex Internal and External Viscous Flows with a Second-Order Pressure-Based Method," AIAA Paper 93-2966, July 1993.

[5] Wang, T.-S. and Chen Y.-S., "Unified Navier-Stokes Flowfield and Performance Analysis of Liquid Rocket Engines," Journal of Propulsion and Power, Vol. 9, No. 5, 1993, pp.678-685.

[6] Chen, Y.-S., and Kim, S.W., "Computation of Turbulent Flows Using an Extended k-ε Turbulence Closure Model," NASA CR-179204, Oct. 1987.

[7] Launder, B.E., and D.B. Spalding, "The Numerical Computation of Turbulent Flows," Computer Methods in Applied Mechanics and Engineering, Vol. 3, No. 2, 1974, pp.269-289.

[8] Chen, Y.-S., Cheng, G.-C., and Farmer, R.C., "Reacting and Non-Reacting Flow Simulation for Film Cooling in 2-D Supersonic Flows," AIAA Paper 93-3602, July 1992.

[9] Cheng, G.-C., Farmer, R.C., and Chen, Y.-S., "Numerical Study of Turbulent Flows with Compressibility Effects and Chemical Reactions," AIAA Paper 94-2026, June 1994.

[10] Wang, T.-S., "Numerical Study of the Transient Nozzle Flow Separation of Liquid Rocket Engines," Computational Fluid Dynamics Journal, Vol.1, No.3, Oct. 1992, pp. 319-328.

[11] Wang, T.-S., Chen, Y.-S., Farmer, R. C., and Tucker, P. K., "Numerical Investigation of the Transient SSME Fuel Preburner Combustor Flowfield," AIAA Paper 90-0646, January 1990.

[12] Wang, T.-S., Chen, Y.-S., and Farmer, R. C., "Numerical Study of Reactive Ramjet Dump Combustor Flowfield with a Pressure Based CFD Method", AIAA Paper 89-2798, July 1989.

[13] Wang, T.-S., and Luong, V., "Hot-Gas-Side and Coolant-Side Heat Transfer in Liquid Rocket Engine Combustors," Journal of Thermophysics and Heat Transfer, Vol. 8, No. 3, 1994, pp. 524-530.

[14] Wang, T.-S., "Numerical Analysis of Base Flowfield at High Altitude for a Four-Engine Clustered Nozzle Configuration," AIAA Paper 93-1923, June 1993.

[15] Chen, Y.-S., and Farmer, R.C., "Computations of Premixed and Diffusion Flames with a Fast Chemistry Integration Scheme," 4th International Symposium on CFD, U.C. Davis, 1991, pp.172-177.

[16] Edelman, R.B., R.C. Farmer, and T.-S. Wang, "Combustion and Emissions of Synthetic Fuel Components - Analysis and Modeling," Combustion of Synthetic Fuels, American Chemical Society Symposium Series 217, 1983, pp. 29-48.

[17] Wang, T.-S., Farmer, R. C., and Tucker, P. K., "Turbulent Hydrocarbon Combustion Kinetics - Stochastic Modeling and Verification," AIAA Paper 89-0486, January 1989.

[18] Wang, T.-S., Farmer, R. C., and Edelman, R. B., "Turbulent Combustion Kinetics for Complex Hydrocarbon Fuels," AIAA Paper 88-0733, January 1988.

[19] Edelman, R.B., and P.T. Harsha, "Some Observations on Turbulent Mixing with Chemical Reactions," Turbulent Combustion, Progress in Astronautics and Aeronautics, Vol. 58, pp.55-101, 1978.

[20] Harsha, P. T., Edelman, R. B., Wang, T.-S., and Farmer, R. C., "Performance Modeling of Advanced Gas Burner Systems," GRI-82/0016, SAI 82-041-CHA, June 1982.

[21] Warsi, S., "Algebraic Surface Grid Generation in Three-Dimensional Space," NASA CP-3143, April 1992.

[22] Anon, "Estimation of Pollutants in Rocket Exhuast," Final Report, Rockwell International, May 1984.

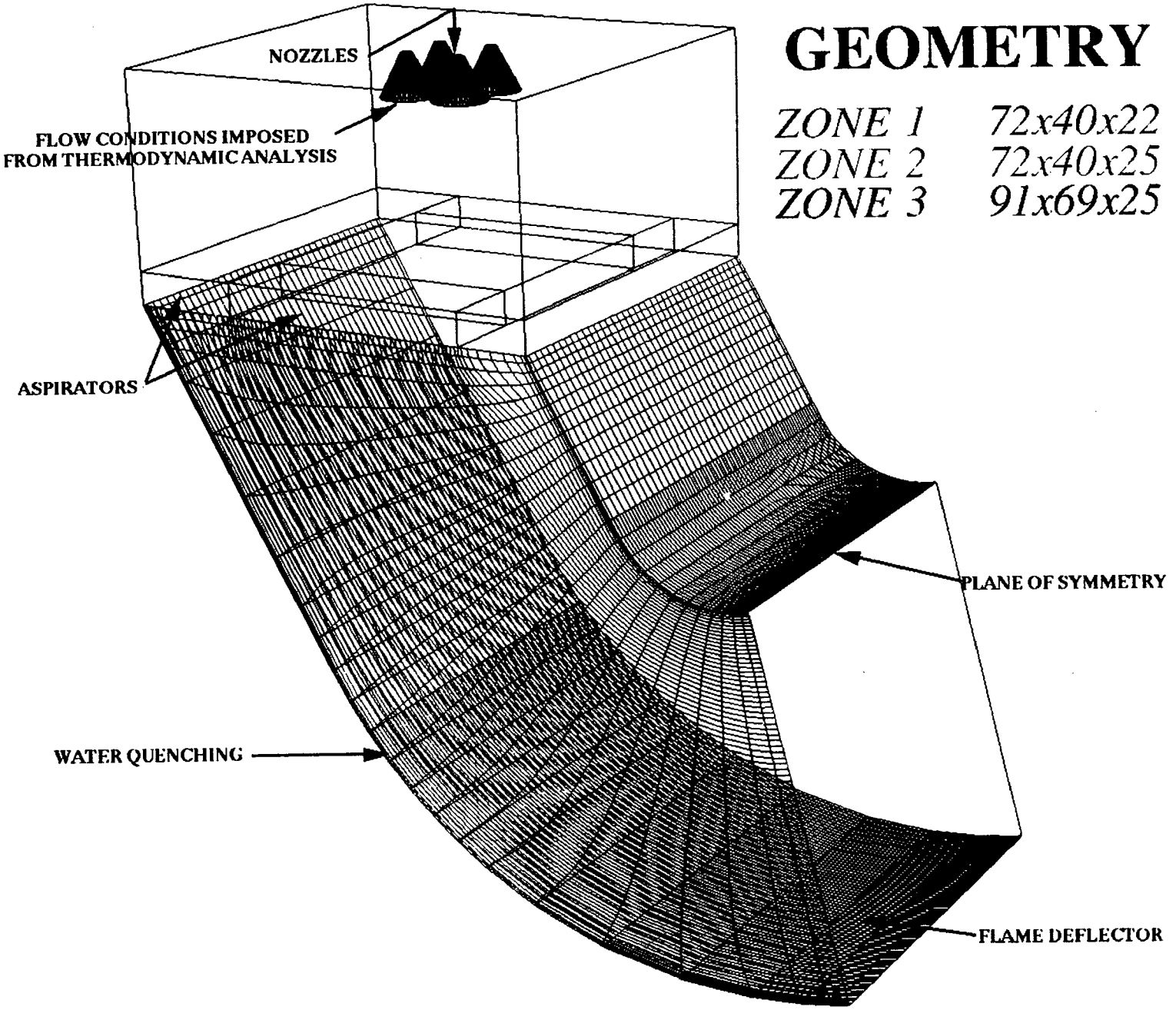

Fig. 1 Computational domain for the RD-170 nozzles and F-1 Test Stand.

GEOMETRY

ZONE 1 *72x40x22*
ZONE 2 *72x40x25*
ZONE 3 *91x69x25*

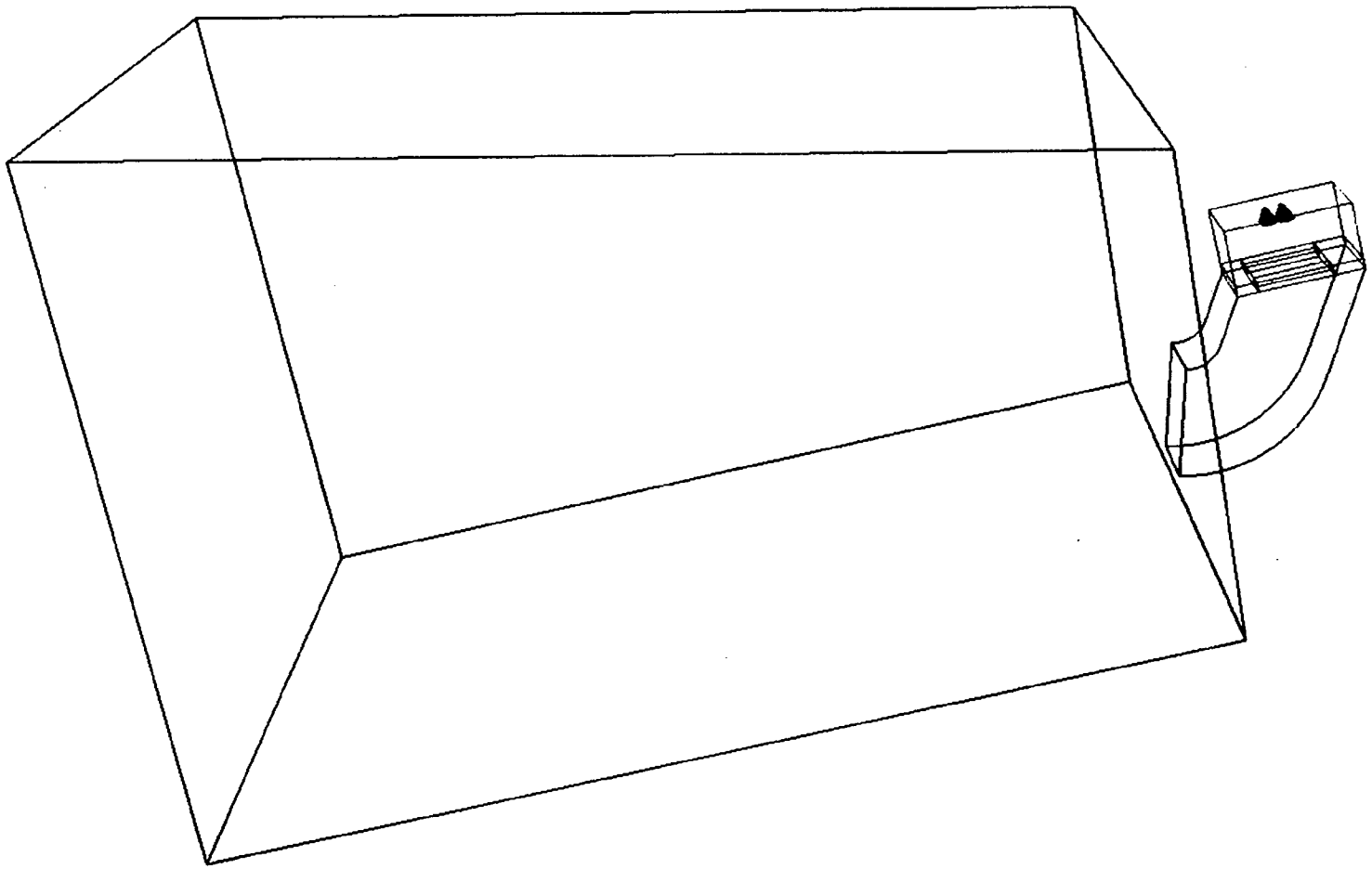

Fig. 2 Computational domain for all three zones.

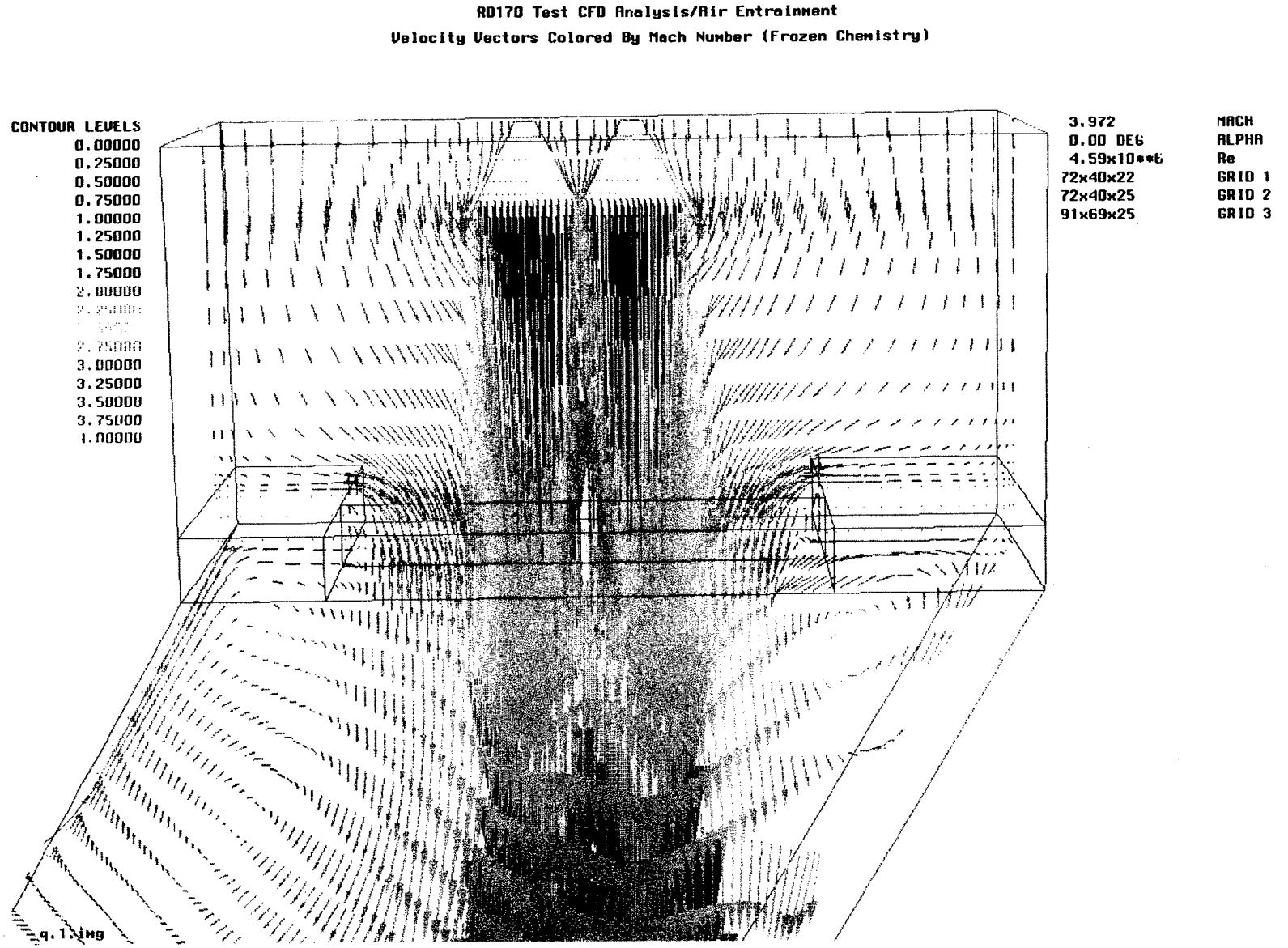

Fig. 3 Velocity vectors colored by Mach number for the air entrainment.

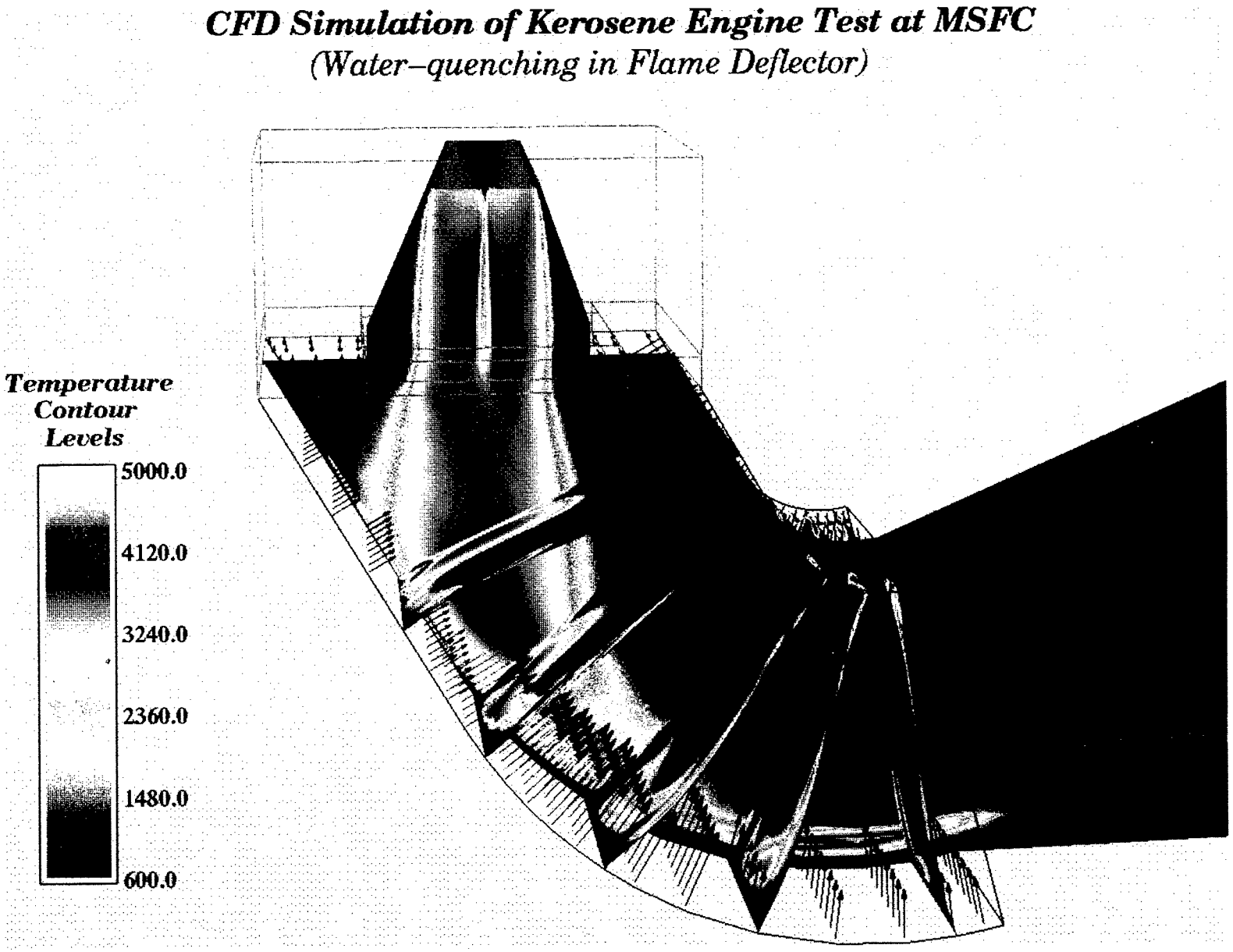

Fig. 4 Computed temperature contours for the water-quenching case.

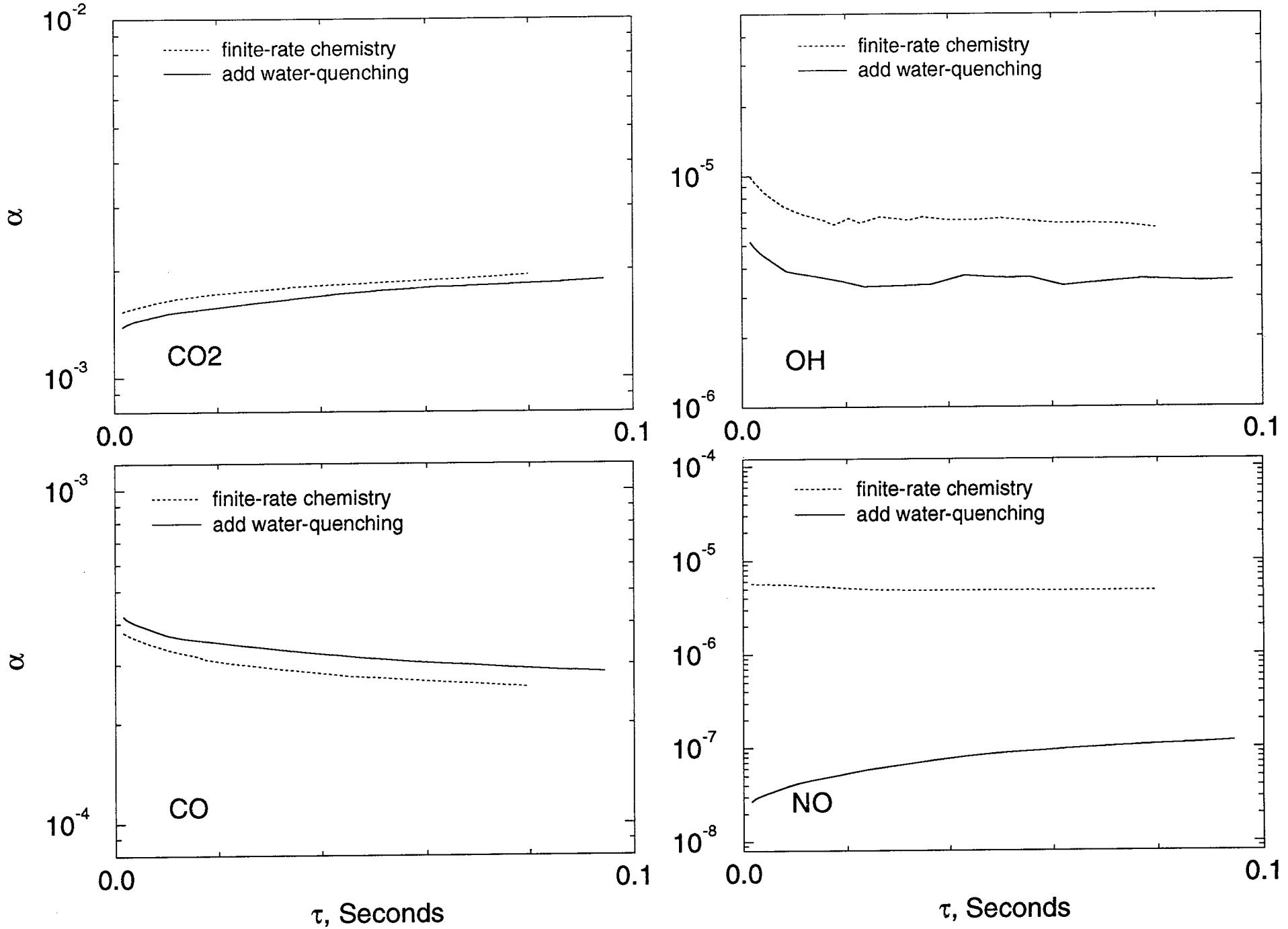

Fig. 5 Comparisons of averaged mass fraction in the system for species CO, CO2, NO and OH.

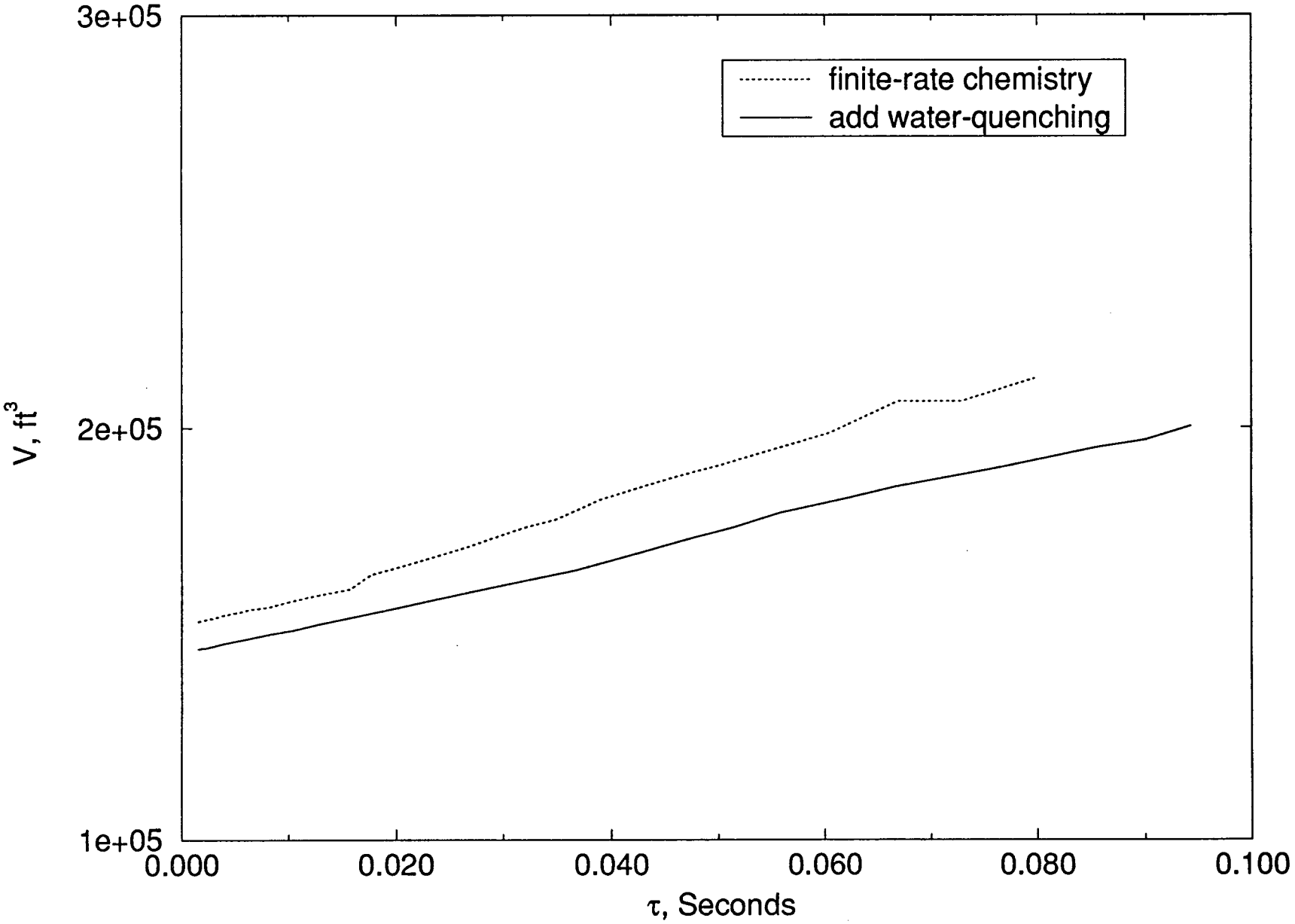

Fig. 6 Comparison of plume volume growth.

ENVIRONMENTAL BENEFITS OF CHEMICAL PROPULSION

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Huntsville, Alabama

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The benefits of chemical propulsion are tightly linked to the measurement and understanding of global climate change and Earth Observation. Anthropogenic and natural influences affecting the Earth system are recognized internationally as having potentially adverse, global consequences over the long term, threatening the current standards for quality of life. Measurement of fossil fuel resources, fish, wildlife, metals and minerals, once performed with dousing rods and exploration parties may now be accomplished via satellite on a global scale. Thus, the availability of chemical propulsion allows a measured, sustainable utilization of Earth's renewable resources, and an informed utilization of the non-renewable ones. The state-of-the-art technology available, enables a quality of life to exist that has never before been possible. The consequent human impacts to the environment are also at previously unseen levels. It is only through effective stewardship of the global resources, which mandates comprehensive measurement capabilities, that we can understand and guide makind's occupation of the Earth.

It is important to comprehend, in context, the issues associated with our current understanding of global change phenomenon. While the implications of any shift in climate are far reaching and without regard for international boundaries, myopic decisions, based on incomplete knowledge of our Earth system, can ultimately do more harm than good to our environment and economy. Given the current economic realities, significant climate shifts, if they do occur, will have global consequences and not be limited to the specific, climate affected regions. In response to these identified global change issues, a number of research and coordinating bodies for Earth science disciplines have emerged throughout the world.[1,2,3,4] The nature of these issues is quite complex, as are the scopes of the international efforts. Figure 1 represents, in summary form, the international organizations involved and their associated prime purposes.

The NASA publication, "Earth System Science, A Closer View," provides a comprehensive and concise picture of the environmental interactions which occur on time scales ranging from decades to centuries.[5] This conceptual model, shown in Figure 2, attempts to identify relationships between extrinsic variables and the predominant chemical reactions which control our environment. It also serves to portray the organized structure required for assessment of these interactions by the scientific community. The two largest rectangles represent the Physical Climate System and the Biogeochemical Cycles. Within these two broad categories are smaller rectangles representing the major subsystems. The arrows denote pathways and information flows necessary to integrate the subsystems and characterize the complete

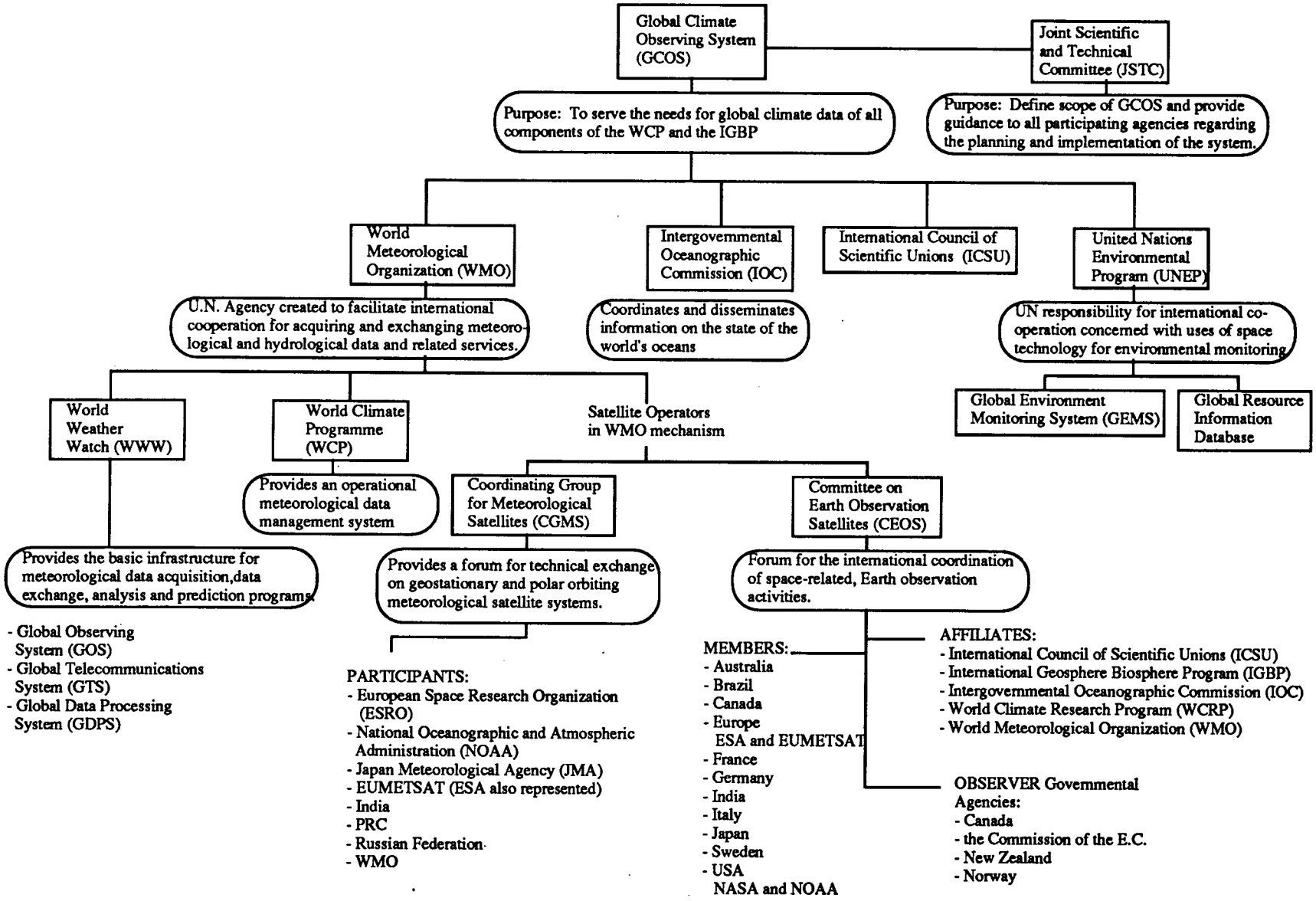
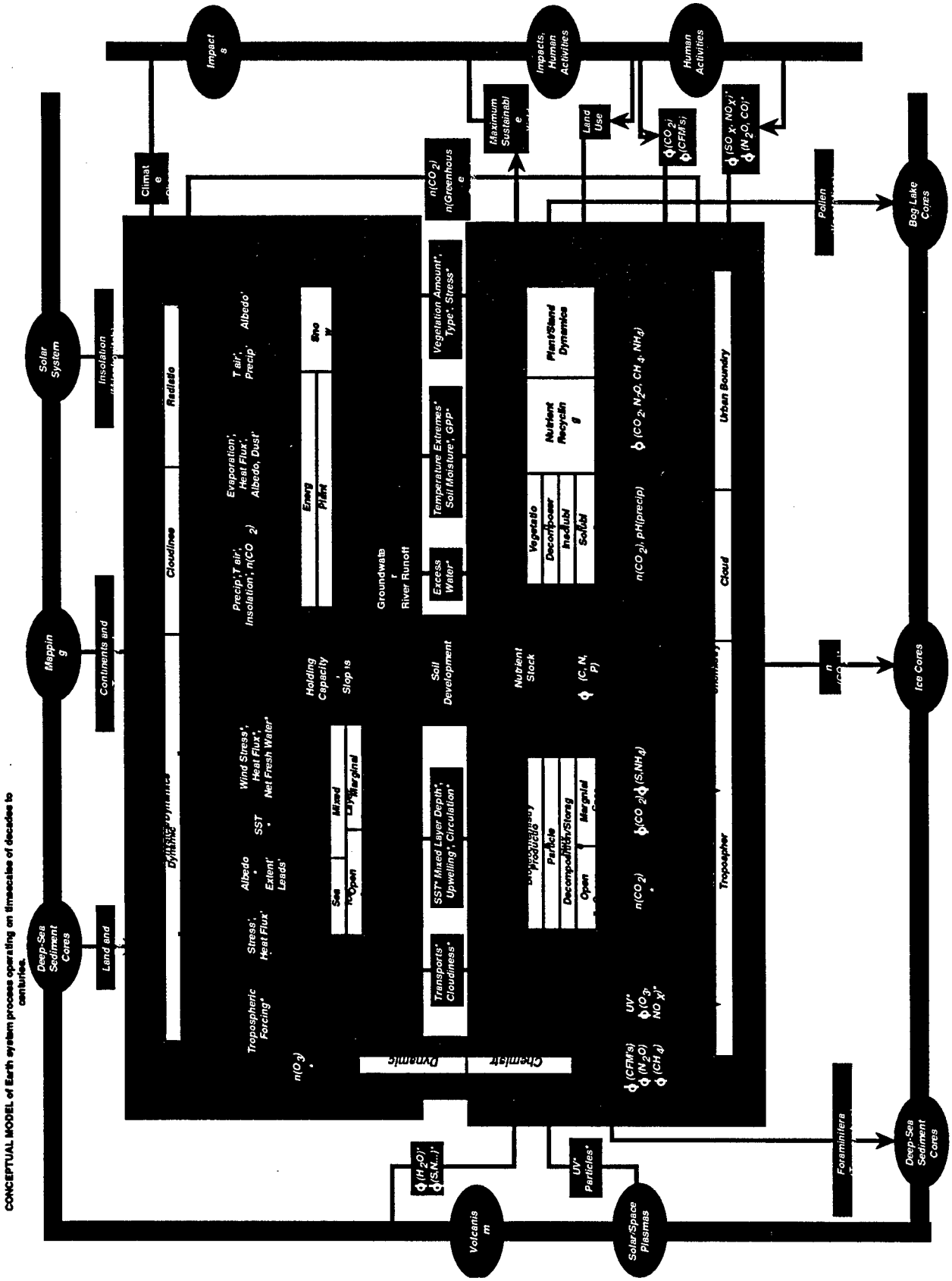


Figure 1: International Global Research and Monitoring Organizations

Figure 2: NASA's Conceptual Model of the Earth System on Timescales of Decades to Centuries



Earth system. The ovals represent system inputs and outputs, including both naturally and anthropogenically induced sources. Each subsystem comprises a focused scientific discipline area. These scientific areas are represented by subroutines within an integrated Global Climate Change Model (GCM) to allow predictive analysis of multi-variant scenarios associated with global change.

GCMs analytically model the natural and induced forces within the atmosphere, their resultant consequences and, ideally, their interactions with the Earth's land, oceans and solar boundaries.[6] These models predict probable outcomes and responses of the Earth system due to perturbations. For instance, sensitivity analysis, potential anthropogenic impacts and natural disaster scenarios may be assessed, and the resultant data evaluated for use in policy and legislative decisions.

The practice of utilizing computer models to study complex systems is widespread throughout the engineering and scientific communities. However, it is a commonly accepted fact that the performance of a model is dependent not only on the completeness, accuracy and precision of the representation and mathematically modeled interactions, but also on the data which specifies the variables. An engineering standard requires that models be verified prior to their accepted usage. Unverified model data is not typically considered acceptable information. However, if potential consequences are so dire as to preclude time for model verification and validation, the data can be treated as preliminary information, but only with the acceptance of a high level of risk.

Although they represent the best available technology, the current models inadequately account for all of the variables and interactions required to accurately predict the environment of the future.[7] This inadequacy is due to several factors: the tremendously complex nature of the Earth system, a lack of appropriate data, and the general state of the science. Furthermore, only a select few portions of the GCMs remain verified, and then only in the non-interactive portions. For example, one relevant measure of the model verification status is evident daily in the short- and long-term weather forecasts. However, the effects that weather has on the ocean currents and the Earth's overall energy and moisture balance are neither understood completely nor incorporated into the models.

Those who espouse elimination of satellite monitoring systems in favor of ground- or air-based systems do not have a clear understanding of the complexities of these issues. Some representative usages and requirements for satellite usage will serve, for the purposes of this document, to illustrate these complexities.

Chemical propulsion has had a tremendous impact in the meteorological field. The ability to launch satellites, afforded by the existence of chemical propulsion, has enabled the meteorological community to develop a global meteorological satellite network. This network, consisting of polar and geostationary orbiting satellites, complemented by a ground-based network of sensors, is operated by the WMO.[8] When combined with developments in satellite remote sensing technology, this network provides continuous, worldwide monitoring of the atmosphere. The data generated by this network is responsible for the present validation of this segment of Global Climate Models. It further enables meteorologists to identify, accurately predict and track atmospheric conditions. This ability to forecast and track weather conditions translates directly into economic savings and/or gains for many industries.

These economic gains are evident within the shipping industry. An ocean liner transporting cars from Japan to the United States, for instance, has advanced knowledge of the weather ahead on its course. If a typhoon forms in the Pacific Ocean, the company, because of satellite technology, knows the predicted course and intensity of the storm. If the ship is threatened by the storm, it can alter its planned course to avoid the weather or return to port, without jeopardizing the crew or cargo. The aviation industry has also realized significant economic benefits due to satellite technology. As in the case of the shipping industry, scheduling and routing of commercial flights are largely contingent upon the weather. Thus, human lives and millions of dollars of freight are saved from potential damage or destruction because of our ability to forecast the weather accurately.

The complexity of the Earth system processes presents perhaps the largest challenge to scientists modeling the system. Scientists are aware of some modeling unknowns, for example: How does vegetation affect the local and global climate, and vice versa? How sensitive is the climate to changes in "radiatively important trace species?" How does the ocean circulation respond to atmospheric forcing? How will changes in ocean circulation affect surface temperature distribution? How will the uptake of heat by the oceans affect the alleged global warming? How much is climate sensitivity affected by sea ice and cloud?[9] In order to answer these questions, and many others, pertinent information is necessary. For instance, accurate measurements of the absorption of long-wavelength radiation emitted from the Earth's surface by various trace gases, the distribution of water vapor in the atmosphere, associated circulation and temperatures are some variables needed to characterize the physical-climate system. Further information, including sea-surface temperature and the resulting wind patterns, radiation measurements and cloudiness data all contribute to a

more complete identification of the complex land-sea interaction processes. Until the gaps in existing knowledge are filled, investigators must make numerous assumptions in Global Climate Models regarding the variables' influence on the processes and their interactive roles.

The modeling unknowns can be treated in sensitivity analysis to allow resource prioritization for keying in on the critical areas, as noted above. These areas must then be assessed with proper validation techniques. This, requires the gathering of significant quantities of relevant data in order to improve our knowledge of the Earth system. The use of satellites is critical to acquiring this data. Satellites afford us the unique opportunity to monitor large areas of the earth at one time, while simultaneously collecting and transmitting the real-time data. From the vantage point of space, we can study the synoptic atmospheric dynamics. This information allows scientists to update, validate or change the fundamental assumptions made in the global climate routines. Thus, we will push the outer limits of scientific knowledge in the field of atmospheric and environmental sciences in order to gain understanding of the world on which we live.

No one single orbit can provide a complete mapping of the Earth.[10,11] Therefore, a coherent selection of satellite missions and placement, combined with polar platforms and Space Shuttle flights is necessary to achieve the defined scientific objectives via remote-sensing techniques. Current and planned space programs, particularly within NASA's Mission to Planet Earth, are designed to address some of these issues.

However, satellite data alone is not enough to ensure accurate measurement of Earth system variables. It is necessary to monitor and record environmental data in conjunction with in situ and low altitude observations in order to completely characterize a system parameter. In situ observations are useful for identifying and characterizing process variables which are more efficiently measured from space. Unfortunately, in situ measurements are often constrained by local effects. Humidity factors, precipitation, physical location (whether the sensor is near a grove of trees on next to asphalt), albedo, and so forth, all affect the in situ measurement. This site variability is difficult to account for in large scale measurement efforts extending over multiple geographical regions. Moreover, in situ observations are crucial for remote-sensing calibration and validation. Typically, sensing devices require periodic maintenance and calibration. A blend of space-based and in situ sensors ensures that sensor drift and malfunctions will be identified and corrected in a timely manner -- without resulting in excessive data loss. Low altitude data collection is also useful for

characterizing complex Earth processes.[12] It provides intermediate information on the atmospheric processes, as well as performing the calibration and validation functions for space-based remote-sensors. Both in situ and low altitude observations provide discrete data points, and therefore do not furnish a concise, dynamic picture of the global climate and interactions. The use of satellites is then critical to the measurement and validation of the GCMs. Chemical propulsion is the only efficient and cost-effective mechanism we have to utilize satellites.

Satellites have a multitude of uses in commercial ventures as well. The advent of the Global Positioning System (GPS) is a good example of the commercial use of satellites, particularly in the aviation industry. The GPS uses a series of satellites to triangulate the position of an object or location, in this case, of an aircraft, equipped with an encoding receiver, and outputs the global coordinates of its position. This revolutionary aircraft tracking system eliminates the reliance on the present system of radar and tracking stations. Because of GPS, transoceanic airline flights can now follow a great circle route rather than flying within suboptimal tracking zones. It is estimated that this will save millions of dollars per year in fuel costs for transoceanic flights alone!

The total impact of the GPS will not be fully realized for many years. Its potential, however, is extraordinary. In addition to the aviation industry, the GPS has beneficial applications in diverse fields ranging from agriculture, environmental management, mining, and surveying to maritime and military operations. To operate, the GPS requires the unique perspective and range of observation that is possible only from the Earth's orbit.

In conjunction with this new technology, entire industries are being created. A similar phenomenon occurred two decades ago, during the initial development of satellite technology. The demand for commercial products such as cable television and satellite dependent cellular telephones was spawned by the availability of affordable vehicles to launch the necessary satellites. Industries which did not exist fifteen years ago now employ thousands of people and are valued in the billions of dollars. This use of satellites is achievable only through the safe, cost effective, commercial availability of chemical propulsion. Advocates who envision non-chemical, non-polluting methods for placing satellites in orbit do not have an understanding of the salient issues.

Propulsion may be thought of as the process of changing the motion of an object. Balloons, planes and rockets all serve to change the motion of their payloads, placing it either higher in (the case of balloons and planes) of outside of (in the case of rockets) the Earth's atmosphere. The atmosphere is generally broken up into four zones: the

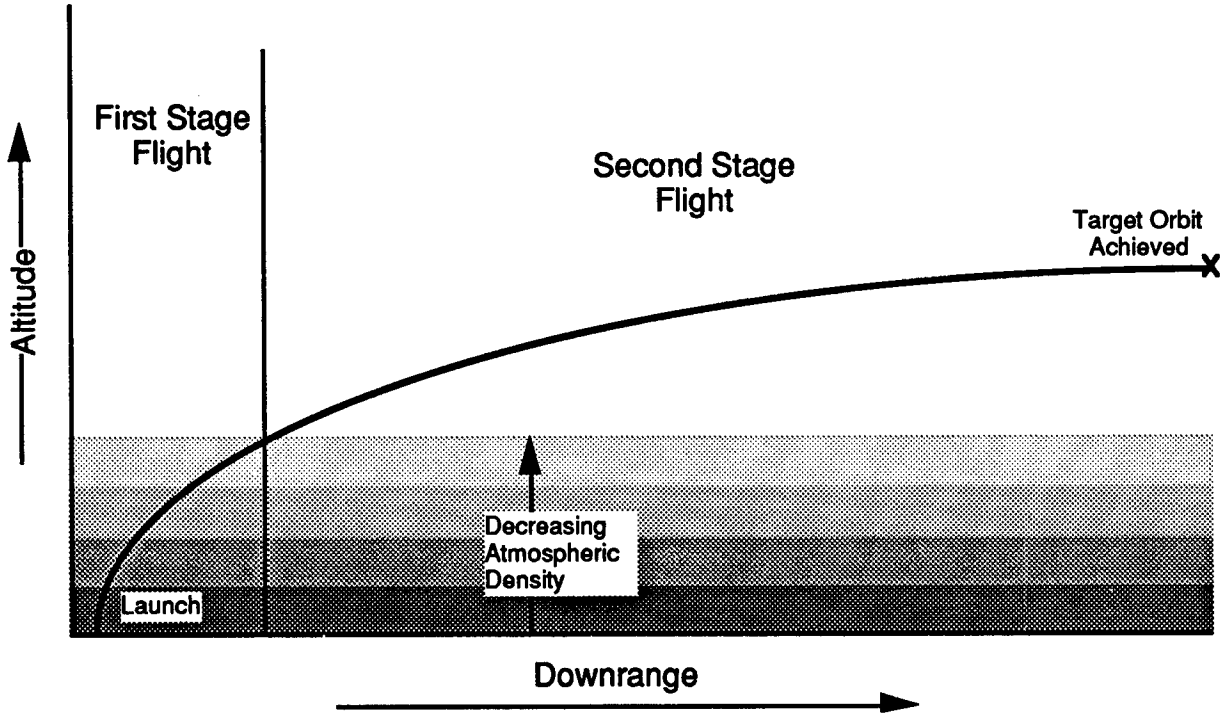
Troposphere (0 - 20 Km above sea level), the Stratosphere (20 - 50 Km above sea level), the Mesosphere (50 - 80 Km above sea level) and the Thermosphere (80 - 300 Km above sea level).[13] Only rockets can raise payloads into the thermosphere; the highest of high altitude balloons can raise payloads into the mesosphere. For the most part, jet planes are limited to the stratosphere; although, the lower levels of the mesosphere are attainable for limited systems.

The reasons that only rocket propulsion is viable for lifting payloads into the thermosphere are directly related to both the characteristics of the thermosphere and the velocities required to enter Earth orbit. The flight of a launch vehicle or space booster into orbit involves complex interactions of thrust, drag, gravity, atmosphere, winds, vehicle and payload weights, and vehicle efficiency and performance. The ascent flight profile is more analogous to a road trip by a delivery truck or the cross country flight of an airliner than the flight of a golf ball driven down a fairway or a projectile fired from a cannon. It is not only the total energy available to the vehicle in the form of propellants, but the judicious application of that energy which makes flight into orbit and deep space possible at all. Performance efficiency, or the rocket equivalent of gas mileage is called specific impulse (Isp). Specific impulse is calculated by dividing the total vehicle thrust by the total propellant flowrate.

Consider that a satellite in low earth orbit has a constant force (gravity) pulling it towards earth; the force of gravity is then balanced out by the centrifugal force of the vehicle. At the earth's surface, the required velocity to escape is 11,179 m/sec; at roughly 300 miles from the surface, the orbital velocity is approximately 7400 m/sec.[14] Today's technology precludes flight through the lower atmosphere at these velocities -- aerothermal heating alone would melt leading edges or nose cap materials. The following arguments reveal why no systems other than chemical propulsion seem feasible for placing satellites into earth orbit.

High thrust is required for a booster to rise from its launch pad, which is also when the vehicle weight is at its peak. These high thrust levels, however, are not necessary after the vehicle has passed through the dense lower atmosphere. Intermittently, thrust must be reduced during the flight, particularly during the highest aerodynamic loading, "max q," and at required points to control the acceleration loads, "g limits." A liquid engine can be throttled, and a solid motor can be designed to reduce thrust levels during portions of its burn. A typical rocket flight profile, such as the one shown in figure 3, is analogous to the operation of a truck stopped at a traffic light, then traveling up an entrance ramp onto a freeway. As the light changes to green, the driver begins to accelerate by using lower gears and pushing the accelerator to

Figure 3: A Typical Rocket Flight Profile



increase the engine output. As the truck gains speed, the need to run the engine at the high power levels diminishes, and the driver shifts into higher gears. By the time the truck reaches highway cruising speed, the engine is running at a power level which produces about 20 - 25% of its maximum horsepower.

Propulsion systems alternative to chemical propulsion have been and are being studied, but none have demonstrated the versatility that chemical propulsion exhibits. Energy can be supplied by both electromagnetic radiation and nuclear reaction. Force fields, gravitational or magnetic, have been utilized for limited types of propulsion. Nuclear energy sources inject heat to a working fluid, typically hydrogen, which then transfers kinetic energy in the form of ejecta out of a nozzle to provide propulsion. Nuclear propulsion is a special case of liquid propulsion. The high mass of the reactor and the low density of the hydrogen gas penalize its thrust capability, making it unsuitable for earth-to-orbit applications. However, nuclear propulsion provides a very high specific impulse and consistent, long duration energy source; thus it is suitable for interplanetary missions where total impulse, not thrust, is a prominent discriminator. Similarly, electric propulsion provides low thrust, long duration propulsion capability.

Electrostatic and ion propulsion do not involve the expansion of gas in a nozzle. They provide electrostatic field acceleration of ions, typically xenon, that results in vehicle thrust. Solar energy is useful in space, but also provides a low thrust, high Isp type system. The Sun is the source for a solar sail, which is external to the vehicle. These type systems are useful for attitude control, but following the rationale cited above, they are not credible for use in earth-to-orbit applications.

Earth-based accelerators, such as cannons and railguns, are also alternative sources for small payloads to reach orbital velocities. The energy, however, is applied at extremely high levels for very short intervals. The method produces severe acceleration loads, or g- forces, on the payload. Furthermore, the high initial velocities attained cause extreme aerodynamic heating and loads. Additionally, unless the payload has its own rocket motor, the variety of attainable orbits with a cannon or railgun is very restrictive. The laws of physics dictate that these orbits cannot have a perigee higher than the elevation of the launch site.

Advanced concepts, such as ion, solar, or photon propulsion exhibit the opposite problem: extremely high efficiencies, but prohibitively low thrust levels. These propulsion sources cannot produce the thrust necessary to lift off, and their physical configurations are anything but aerodynamic. There are potential applications for these systems in interplanetary flight and beyond, but they are unsuitable for the journey from a planetary surface to orbit. It is entirely possible that no scheme will ever

supplant chemical propulsion in boosting a vehicle on its initial escape from the earth's surface into space.

This paper has thus far identified the necessity of chemical propulsion to satellite usage and some of the benefits we accrue through our ability to monitor global resources and patterns. The remainder identifies, in summary fashion, how the information gathered via satellite is utilized to affect national and international policies.

Undeniably, science has already forced extensive political action in response to its theories on global climate change. While NASA is not a policy setting agency, we do play a major role in the creation of legislation. NASA conducts science missions and generates much of the data necessary for inputs to Global Climate Models. It is understood within the scientific community that these rudimentary GCMs produce results which are only as accurate and complete as the information which goes into them.

The data and output from these models are utilized by policy-makers to develop and establish environmental laws and regulations. Environmental legislation is initiated in the Congress. Through its Office of Legislative Affairs, NASA will review proposed legislation, when requested, for its technical content and merit.[15,16] Again, NASA does not set environmental policy, it does, however, attempt to provide the most accurate information available to the appropriate lawmakers. It is the responsibility of the scientific community to ensure that policy-makers are aware of the fidelity of these climate models and the resulting limitations of global climate analysis and prediction. Policy-makers, in turn, must make prudent and judicious decisions based upon information available today; with the understanding that as the state of the science matures, so will our understanding of the earth's environment.

The scientific community has identified and acknowledged shortfalls in our knowledge base and in climatic model inputs. In order to remedy these shortcoming, we require large-scale and long-term monitoring of the environment. The information required is dependent upon the continued utilization of chemical propulsion to launch satellites and experiments to gather relevant data. Since models are the basis for setting environmental policies, it is both logical and imperative that we continue to support NASA's proposed course of action.

Chemical propulsion, like all environmentally conscious industries, does provide limited, controlled pollutant sources through its manufacture and usage. However, chemical propulsion is the sole source which enables mankind to launch spacecraft and monitor the Earth. The information provided by remote sensing directly affects national and international policies designed to protect the environment and

enhance the overall quality of life on Earth. The resultant of chemical propulsion is the capability to reduce overall pollutant emissions to the benefit of mankind.

References

1. Committee on Earth Observation Satellites (CEOS): The Reference of Satellite Missions to the Study of Global Environment; UNCED Conference, Rio de Janeiro, 1992, British National Space Centre, London, UK, 1992.

2. Obasi, G.O.P.: Programmes and Strategy for the World Meteorological Organization with Respect to Earth Observation from Space. Proceedings of the Central Symposium of the International Space Year Conference, Munich, Germany, 1992.

3. Smith, B. et.al.: New Developments in the Coordination of Earth Observation from Space Activities: The Committee on Earth Observation Satellites (CEOS). Proceedings of the Central Symposium of the International Space Year Conference, Munich, Germany, 1992.

4. Jasentullyana, N. and R. Chipman: Space Activities and Environmental Protection: Role of the United Nations. Proceedings of the Central Symposium of the International Space Year Conference, Munich, Germany, 1992.

5. Earth Systems Sciences Committee, NASA Advisory Council: Earth System Science: A Closer View. National Aeronautics and Space Administration, Washington, D.C., January 1988.

6. Committee on Earth and Environmental Sciences: Our Changing Planet: The FY 94 US Global Change Research program. Washington, D.C., A Supplement to the President's Fiscal year 1994 Budget.

7. Earth Systems Sciences Committee, NASA Advisory Council: Earth System Science: A Closer View. National Aeronautics and Space Administration, Washington, D.C., January 1988.

8. Obasi, G.O.P.: Programmes and Strategy for the World Meteorological Organization with Respect to Earth Observation from Space. Proceedings of the Central Symposium of the International Space Year Conference, Munich, Germany, 1992.

9. Earth Systems Sciences Committee, NASA Advisory Council: Earth System Science: A Closer View. National Aeronautics and Space Administration, Washington, D.C., January 1988.

10. Report to Congress on the Restructuring of the Earth Observing System. National Aeronautics and Space Administration, March 9, 1992.

11. Wilson, G.S. and W. T. Huntress: Mission to Planet Earth. Palaeogeography, Palaeoclimatology, Palaeoecology, 90, Elsevier Science Publishers B.V., Amsterdam, 1991.

12. National Aeronautics and Space Administration: UARS Upper Atmosphere Research Satellite, A Program to Study Global Ozone Change. 1989.

13. ibid.

14. Sutton, George P., Rocket Propulsion Elements. 6th Ed. John Wiley & Sons, Inc. New York, 1992.

15. Intergovernmental Panel on Climate Change: 1992 IPCC Supplement: Scientific Assessment of Climate Change. UNEP and WMO, 1997.

16. Office of Mission to Planet Earth: Conversation with Mr. Mark Pine. National Aeronautics and Space Administration, May 17, 1994.

EMERGING TECHNOLOGIES FOR THE PROPULSION INDUSTRY

AP RECLAMATION AND REUSE IN RSRM PROPELLANT

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ABSTRACT

A solid propellant ingredient reclamation pilot plant has been evaluated at the Strategic Operations of Thiokol Corporation, located in Brigham City, Utah. The plant produces AP wet cake (95 percent AP, 5 percent water) for recycling at AP vendors. AP has been obtained from two standard propellant binder systems (PBAN and HTPB). Analytical work conducted at Thiokol indicates that the vendor-recrystallized AP meets Space Shuttle propellant specification requirements. Thiokol has processed 1-, 5-, and 600-gallon propellant mixes with the recrystallized AP. Processing, cast, cure, ballistic, mechanical, and safety properties have been evaluated. Phillips Laboratory static-test-fired 70-pound and 800-pound BATES motors. The data indicate that propellant processed with reclaimed AP has nominal properties.

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INTRODUCTION

In today's environment, recovery and beneficial reuse of hazardous waste materials is favored over destruction. Propellant and explosive manufacturers must treat day-to-day waste streams, and the government must treat overage and obsolete rocket motors. Thiokol has completed a two-phase cost sharing contract with the Joint Ordnance Commanders Group to reclaim ammonium perchlorate from composite Class 1.3 propellants, reprocess the material at AP vendors, and verify its reuse in rocket propellant. The first phase of the program, which has been reported previously,[1] involved recrystallizing the material through the

[1]Kathryn F. Miks, Thiokol Corporation, "Solid Propellant Ingredient Reclamation and Reuse," 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, Las Cruces, New Mexico.

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Western Electrochemical Company's batch process and manufacturing subscale-size propellant mixes and test articles. The second phase of the program, which is reported herein, involved recrystallizing the material through the Kerr-McGee Chemical Corporation's continuous process and manufacturing a production-scale propellant mix and larger test articles.

OBJECTIVE

The objective of this program was to compare reclaimed AP with virgin AP in a baseline rocket propellant formulation.

SUMMARY

One hundred and fifty thousand pounds of AP wet cake were reclaimed from two standard propellant binder systems (PBAN and HTPB). The AP was recrystallized at the Kerr-McGee Chemical Company in order to obtain material of a specific particle size. Laboratory acceptance analyses and standard safety tests were performed on the recrystallized/reclaimed material. Twenty-one 1-gallon, ten 5-gallon, and one 600-gallon Space Shuttle propellant (TP-H1148) mixes were processed with the recrystallized/reclaimed AP. Rheological, cure, mechanical, ballistic, and safety properties were evaluated at Thiokol. Phillips Laboratory static-test-fired three 70-pound BATES motors and one 800-pound BATES motor.

CONCLUSIONS

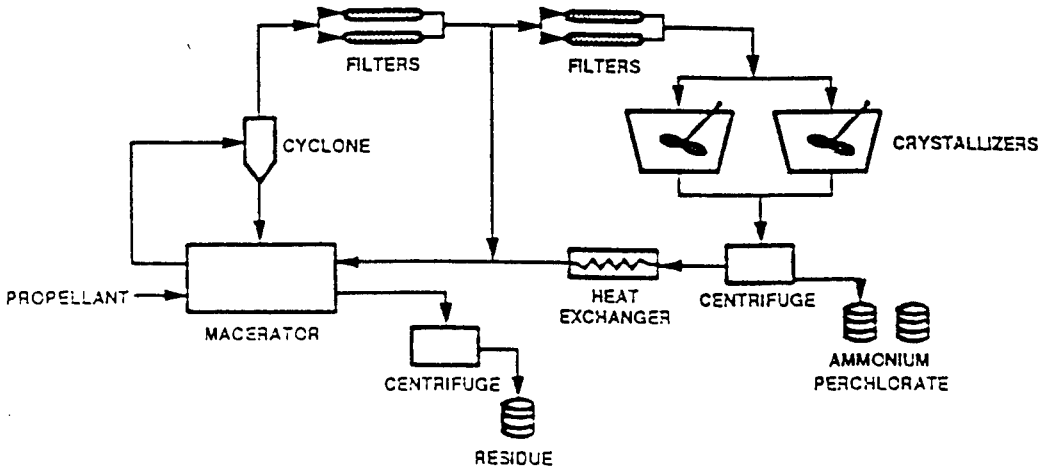
Reclaimed AP recrystallized at Kerr-McGee has nominal chemical, safety, friability, and grinding properties. Propellant processed with recrystallized/reclaimed AP has nominal rheological, mechanical, ballistic, and safety properties.

TECHNICAL DISCUSSION

DESCRIPTION OF PROCESS

A schematic of the reclamation process is presented below. A hydraulic macerator provides propellant size reduction and countercurrent extraction of the ammonium perchlorate at 160°F. The extract solution from the hydraulic macerator is passed through a liquid cyclone and an in-line filter to remove suspended solids before it is recirculated through the macerator. After the extract reaches a nominal 30 percent concentration, it passes through a second in-line filter and is cooled in two-stage batch crystallizers to precipitate the dissolved ammonium perchlorate. The recovered ammonium perchlorate crystals and the depleted propellant binder residue are dewatered in a basket centrifuge. The cold dilute filtrate from the crystallizers passes through a heat exchanger to pre-cool the next crystallizer batch before it is returned to the macerator for reuse.

AP Reclamation Process



AP RECOVERY

One hundred and fifty thousand pounds of AP wet cake were reclaimed over a 6-month period under a contract with Hill Air Force Base. Space Shuttle propellant (PBAN) comprised approximately two-thirds of the propellant feedstock, and Peacekeeper propellant (HTPB) comprised approximately one-third. The AP was integrated into the Kerr-McGee continuous process. Approximately 145,500 pounds of 50 percent reclaimed/50 percent virgin material were produced in a 4-day process run in 6 3/4 blend transient (BT) lots. One 21,000-pound BT lot, No. 99, was used in the subsequent evaluations.

AP ANALYSES

Space Shuttle specification acceptance analyses were performed on the recrystallized material and the results are presented in Table I. Specification requirements and nominal values for virgin Kerr-McGee material are also presented for comparison. Except for particle size, all of the recrystallized/reclaimed material values are within the specification requirements. The particle size data indicate that slightly smaller-than-nominal particles were obtained; a slightly lower-than-nominal percent of material is retained on the 70, 100, and 140 sieves. However, only the 100 and 140 sieves are below the specification requirement. BT Lot 99 was originally selected because analyses performed at Kerr-McGee showed that Lot 99 had a nominal particle size. The same analyses showed the remaining lots to be slightly large. Apparently, there was a bias between the Thiokol and Kerr-McGee analyses. Had a different lot been selected, it would have likely had a nominal particle size per Thiokol test methods.

In addition to the acceptance analyses, ion chromatography, inductively coupled plasma, gas chromatography/mass spectroscopy, nonvolatile organic, and Microtrac particle size analyses were performed. For comparison, the same analyses were run on virgin Kerr-McGee material. The results, presented in Table II, concur with the acceptance analyses that the reclaimed material is comparable chemically to virgin material, but the reclaimed AP has a slightly smaller particle size.

A friability evaluation was performed on two samples of reclaimed AP and on a control sample of virgin Kerr-McGee material. The test was performed using Rotap particle size analyses with 20 8-mm-diameter glass beads placed on each sieve. Particle size was determined initially without the glass beads (t = 0), and after vibrating with the beads for 15, 30, and 45 minutes. The data indicate that the rate at which particle size is reduced is similar for both reclaimed AP and virgin AP. After 45 minutes, the mean particle size of all samples was reduced by approximately 10 microns.

A grinding evaluation was performed with reclaimed AP and with virgin Kerr-McGee AP. Three grinds were made for each type of AP at the nominal settings determined for virgin AP target particle sizes of 5, 20, and 75 microns. Four composite samples from each grind were analyzed for particle size using Microtrac. The 75- and 20-micron grinds were completed with a 60 air classified mill, and the 5-micron grinds were completed with a 12-inch fluid energy mill. The data were analyzed using the student-t statistic at the 95 percent confidence level and indicate that reclaimed AP is comparable to virgin material and that acceptable particle sizes can be obtained per standard grinding methods.

Standard Thiokol safety tests were performed on the test material and on virgin Kerr-McGee material. Testing included: (1) Thiokol's tests for friction, impact, electrostatic sensitivity, and thermal stability; and (2) Allegheny Ballistics Laboratory's safety tests for friction and impact. Results are presented below. The values obtained for recrystallized/reclaimed AP were comparable to virgin Kerr-McGee material and indicate that the reclaimed AP presents no special shipping or handling problems over virgin 200-micron AP.

Test	Nominal Kerr-McGee AP 7229-0139	Recrystallized/Reclaimed AP 60000993-001
TC indirect impact (in.), 50%	44.0	43.2
ABL impact (cm), T.I.L.	21	21
TC strip friction (lb), 50%	>64	>64
ABL sliding friction, T.I.L.	560 at 8 ft/sec	660 at 8 ft/sec
TC ESD (Joules), 50%	>8	>8
Simulated bulk autoignition (onset exotherm)	402°F	410°F

ONE-GALLON PROPELLANT DEMONSTRATION

One-gallon Space Shuttle propellant mixes were made with the recrystallized/reclaimed AP. Three five-mix standardization matrices of TP-H1148 propellant were made using the same raw materials except for the AP. The five-mix matrix is used in Space Shuttle raw material evaluations to determine mechanical and ballistic property responses to HB/ECA and iron oxide levels, respectively. Five mixes were processed with 100 percent reclaimed AP, five mixes were processed with 100 percent virgin AP, and five mixes were processed with virgin AP in the unground fraction and reclaimed AP in the ground fraction.

Rheological, mechanical, and ballistic properties were determined from each mix. Standard Thiokol safety tests were performed on samples of uncured and cured propellant, and the results are presented below. All values were comparable to values for propellant processed with virgin AP. The initial 1-gallon data showed that acceptable rheological,

mechanical, ballistic, and safety properties could be achieved from propellant made with reclaimed AP.

UNCURED TP-H1148 PROPELLANT SAFETY PROPERTIES			
	Control (AB9570)	100% Reclaimed (AB9575)	Virgin Unground/ Reclaimed Ground (AB9580)
TC indirect impact (in.), 50%	13.3	15.6	14.5
ABL impact (cm), T.I.L.	41	26	80
TC strip friction (lbs), 50%	63.0	>64	>64
ABL sliding friction, T.I.L.	180 at 8 ft/sec	320 at 8 ft/sec	800 at 8 ft/sec
TC ESD (Joules), 50%	>8	>8	>8
TC confined ESD (Joules), 50%	8	8	8
Simulated bulk autoignition (onset exotherm)	365	363	372

CURED TP-H1148 PROPELLANT SAFETY PROPERTIES		
	Nominal	100% Reclaimed (2093116)
TC indirect impact (in.), 50%	12 - 14	18.5
ABL impact (cm), T.I.L.	11 - 13	33
TC strip friction (lbs), 50%	42 - >64	62.5
ABL sliding friction, T.I.L.	50 - 240	130 at 8 ft/sec
TC ESD (Joules), 50%	>8	>8
Simulated bulk auto ignition (onset exotherm)	340°F	360°F

Six additional 1-gallon propellant mixes were made to evaluate cast and cure properties. Two mixes each were made with 100 percent reclaimed AP, 100 percent virgin AP, and virgin AP in the unground fraction/ reclaimed AP in the ground fraction. Each mix was processed at the formulation determined for target mechanical properties, 110 psi maximum stress: 100 percent reclaimed AP mixes 86.9 percent PBAN polymer in the binder (HB), control AP mixes 86.9 percent HB, and virgin unground/reclaimed ground mixes 87.0 percent HB.

Cast properties were evaluated using a standard 1-gallon castability box. After 4 days' cure at 135°F, the height of each section was measured. The results indicate that casting properties for propellant made with reclaimed AP were comparable to the control and that propellant made with reclaimed AP has acceptable cast properties.

Cure properties were evaluated using propellant cast into 1- by 4- by 11-inch cartons. The cartons were cured at 135°F for 96, 120, 144, and 168 hours and postcured for 1 hour prior to testing. Mechanical properties were determined from four horizontal JANNAF Class C tensile specimens tested at 2 ipm, ambient temperature and pressure. Cure equations for maximum stress (σ_m), initial tangent modulus ($E^{2.6}$), and minimum strain at maximum stress ($\varepsilon_{\bar{m}}$) were determined from best fit regression analyses and are presented below.

Maximum Stress

(1) Virgin AP σ_m (psi) = -9.92 + 28.68 ln (time) $R^2 = 0.829$

(2) 100% reclaimed AP σ_m (psi) = -21.58 + 30.51 ln (time) $R^2 = 0.998$

(3) Mixed AP σ_m (psi) = 4.16 + 24.29 ln (time) $R^2 = 0.982$

Initial Tangent Modulus

(4) Virgin AP $E^{2.6}$ (psi) = -3.63 + 128.03 ln (time) $R^2 = 0.943$

(5) 100% reclaimed AP $E^{2.6}$ = 3.13 + 134.04 ln (time) $R^2 = 0.708$

(6) Mixed AP $E^{2.6}$ (psi) = 27.02 + 120.69 ln (time) $R^2 = 0.839$

Minimum Strain at Maximum Stress

(7) Virgin AP $\varepsilon_{\tilde{m}}^{2.6}$ (%) = 71.90 - 5.53 ln (time) $R^2 = 0.890$

(8) 100% reclaimed AP $\varepsilon_{\tilde{m}}^{2.6}$ (%) = 64.01 - 4.22 ln (time) $R^2 = 0.239$

(9) Mixed AP $\varepsilon_{\tilde{m}}^{2.6}$ (%) = 82.59 - 7.89 ln (time) $R^2 = 0.851$

For the cure equations listed above, the slope controls the rate the propellant reaches its ultimate property. Although there are minor differences in cure rate between reclaimed AP propellant and the control, these differences are not alarming; similar differences in cure rate are observed between nominal Kerr-McGee and WECCO AP. Overall, the data indicate that acceptable mechanical properties can be obtained from propellant processed with reclaimed AP and cured per nominal propellant standards.

FIVE-GALLON EVALUATION

Five 5-gallon mixes of TP-H1148 propellant were processed with 100 percent reclaimed AP in accordance with the same matrix and raw materials as used in the 1-gallon evaluation. For comparison, five additional 5-gallon control mixes were processed at the same formulations with the same raw materials except virgin Kerr-McGee AP. The control mixes were completed as part of the Space Shuttle raw material standardization program.

End-of-mix (EOM) properties, which include total solids, percent ammonium perchlorate, percent aluminum plus ferric oxide, percent HB polymer, and liquid strand burn rate (LSBR) at 1500 psig and 100°F, were determined for each mix and indicate that acceptable propellant was processed. The LSBR regression equations are shown below.

(10) Virgin AP LSBR (in./s) = 0.4776 + 0.2375 (% Fe_2O_3) $R^2 = 0.990$

(11) 100% reclaimed AP LSBR (in./s) = 0.5006 + 0.2100 (% Fe_2O_3) $R^2 = 0.946$

The reclaimed AP propellant LSBR regression equation was compared to both the control and historical Space Shuttle regression equations (RSRM Flights 1 through 44). The reclaimed AP slope is comparable to the control at the 95 percent confidence level (student-t test) and falls well within the historical 3-sigma control limits. However, the intercept is statistically different from the control at the 95 percent confidence level (reclaimed AP has a slightly higher intercept). This may be due to the slightly smaller particle size of the

unground reclaimed AP. In any case, the predicted LSBR at 0.3 percent iron oxide is well within the historical 3-sigma control limits and indicates acceptable uncured ballistic properties. A plot of the comparisons is presented in Figure 1.

The end-of-mix (EOM) rheological properties, including EOM viscosity corrected to 145°F, Brookfield potlife at 135°F, and Haake viscosities for six shear rates at 135°F, were determined for each mix. Rheological properties help to characterize propellant flow and processability. The EOM viscosity and potlife values obtained for the reclaimed AP propellant were compared to both the control and to the historical database (RSRM Flights 1 through 39). The values are comparable to the control at the 95 percent confidence level (student-t test) and fall well within the historical 3-sigma control limits. Plots of the comparisons are presented in Figures 2 and 3. The data indicate that acceptable rheological properties can be achieved from propellant made with reclaimed AP.

Cured mechanical properties were determined from two half-gallon cartons cast from each mix. Cartons were cured for 96 ± 4 hours at 135°F and postcured for between 4 and 7 days prior to testing. The mechanical properties were determined from 12 JANNAF Class C tensile specimens tested at 2 ipm at ambient temperature and pressure. Regression equations for maximum stress (σ_m), initial modulus ($E^{2.6}$), and minimum strain at maximum stress ($\varepsilon_{\tilde{m}}$) as functions of HB polymer level are presented below.

Maximum Stress

(12) Virgin AP σ_m (psi) = 3976.8 - 44.64 (% HB) $R^2 = 0.999$

(13) 100% reclaimed AP σ_m (psi) = 3884.7 - 43.57 (% HB) $R^2 = 0.998$

Initial Tangent Modulus

(14) Virgin AP $E^{2.6}$ (psi) = 25,393.7 - 287.14 (% HB) $R^2 = 0.998$

(15) 100% reclaimed AP $E^{2.6}$ = 23,848.8 - 269.29 (% HB) $R^2 = 0.994$

Minimum Strain at Maximum Stress

(16) Virgin AP $\varepsilon_{\tilde{m}}$ (%) = -273.8 + 3.57 (% HB) $R^2 = 0.934$

(17) 100% reclaimed AP $\varepsilon_{\tilde{m}}$ (%) = -120.5 + 1.79 (% HB) $R^2 = 0.781$

The reclaimed AP propellant mechanical property regression equations were compared to both the control and historical (RSRM Flights 1 through 42) regression equations. The slope and intercepts are comparable to the control at the 95 percent confidence level (student-t test) and fall within the historical 3-sigma control limits. Nominal mechanical properties are predicted at 86.5 percent HB polymer. Plots of the comparisons are presented in Figures 4 through 6. The data indicate that acceptable mechanical property requirements can be achieved from propellant processed with reclaimed AP.

Cured ballistic properties were determined from three TU-131 motors (5-inch C.P. motors) cast from each mix and cured for 96 ± 4 hours at 135°F. The motors were tested at 625 psia and 60°F. The burn rate vs. iron oxide content regression equations are shown below.

(18) Virgin AP TU-131 R_b = 0.3338 + 0.1030 (% Fe_2O_3) $R^2 = 0.986$

(19) 100% reclaimed AP TU-131 R_b = 0.3429 + 0.1043 (% Fe_2O_3) $R^2 = 0.981$

The reclaimed AP propellant TU-131 regression equations were compared to both the control and historical (RSRM Flights 1 through 44) regression equations. The slope and intercept are comparable to the control at the 95 percent confidence level (student-t test) and fall within the historical 3-sigma control limits. Nominal ballistic properties are predicted at 0.3 percent iron oxide. A plot of the comparison is presented in Figure 7. The data indicate that acceptable ballistic property requirements can be achieved with propellant processed from reclaimed AP.

Five additional 5-gallon mixes were processed with reclaimed AP to standardize the raw materials used in the 600-gallon mix. The formulation determined to meet target mechanical and ballistic properties (110 psi maximum stress and 0.363 ips TU-131 burn rate at 625 psia, respectively) was 86.7 percent HB and 0.236 percent iron oxide.

FULL-SCALE EVALUATION

The 600-gallon mix was processed on January 6, 1994. The EOM viscosity was 14.5 kP at 144°F, and the Brookfield potlife to 40 kP at 135°F was 6.4 hours. Haake viscosities between 0.017 and 0.544 sec^{-1} shear rates were nominal for Space Shuttle propellant. End-of-mix acceptance properties, which include total solids, percent ammonium perchlorate, percent aluminum plus ferric oxide, and LSBR at 1500 psig and 100°F, were also determined to be nominal.

Mechanical properties were determined from 62 half-gallon loaf cartons cured at 135°F for 96 ± 4 hours. Standard quality assurance properties were determined from 12 JANNAF Class C tensile specimens tested at 2 ipm, ambient temperature and pressure. The results are presented below, along with the nominal values for Space Shuttle production (RSRM Flights 1 through 45). The data indicate that nominal TP-H1148 properties were obtained.

600-GALLON MIX QUALITY ASSURANCE MECHANICAL PROPERTIES

	Reclaimed AP Mix	RSRM Nominal (Flights 1-45)
Maximum stress, psi	117	112 (s = 5.9)
Minimum strain at maximum stress, %	35	36.5 (1.7)
Initial tangent modulus, psi	543	519 (52)
Strain at failure, %	44	48.7 (2.9)

Additional uniaxial characterization tests were performed at 25, 75, and 125°F, at ambient and 1000 psi pressure. Crosshead rates of between 0.02 and 20 ipm were used. Five JANNAF Class C tensile specimens were tested at each condition, and the results are presented in Table III. Failure envelopes were constructed at ambient and 1000 psi pressure and are shown in Figures 8 and 9, respectively. Historical TP-H1148 responses are also shown on each plot for comparison. The failure boundaries for propellant processed with reclaimed AP are well within the historical TP-H1148 propellant database and indicate that propellant processed with reclaimed AP has nominal failure parameters.

Stress relaxation tests were conducted at 25, 75, and 125°F, at ambient pressure. Five JANNAF Class A tensile specimens were tested at each temperature. The specimens were strained 5 percent at 250 ipm and the relaxation modulus, E_R, was determined between 0.1 and 1000 seconds. The master relaxation curve generated is shown in Figure 10, along with

historical TP-H1148 curves. The master curve is well within the historical TP-H1148 propellant database and indicates nominal material capabilities.

The propellant coefficient of linear thermal expansion (CLTE) was determined to be 6.06×10^{-5} in./in. ÷ °F. These results correlate well with the historical value of approximately 6.1×10^{-5} in./in. ÷ °F and indicate nominal CLTE properties.

The mechanical properties of propellant processed with reclaimed AP correlate very well to the historical TP-H1148 database. Quality assurance, variable rate/temperature uniaxial tests, stress relaxation, and CLTE analyses indicate that propellant processed with reclaimed AP has nominal material capabilities.

One 800-pound BATES motor, three 70-pound BATES motors, and twenty-two 5-inch C.P. motors (approximately 7 pounds) were fabricated for ballistic property evaluation. The 5-inch C.P. motors were tested at the Thiokol test facility between -35 and 135°F, and between 250 and 1000 psia. A summary of the results is presented in Table IV. The burn rate at 625 psia and 60°F is 0.365 in./sec. This is well within the RSRM historical 3-sigma control limits of 0.352 to 0.371 (RSRM Flights 1 through 45). The burn rate pressure relationship (n) was determined to be 0.312 from a logarithmic regression of the 16 motors tested at 60°F. This is comparable to the nominal TP-H1148 value of 0.311 at the 95 percent confidence level (student-t test). The pressure-temperature sensitivity (π_k) was determined to be 0.113 percent/°F from multivariant analyses of Motors 1 through 9. This correlates very well with the current TP-H1148 value of 0.11 percent/°F.

The data indicate that 5-inch C.P. ballistic properties of propellant processed with reclaimed AP correlate very well to the historical TP-H1148 database.

The three 70-pound BATES motors were static-tested at the Phillips Laboratory on Pad 5B. A summary of the results is presented in Table V. The results for each motor are from two independent pressure transducers. The first motor tested (347A-010) had an anomalous trace between about 1.25 and 2.25 seconds. An investigation concluded that both pressure transducer ports became blocked during testing, resulting in the anomalous trace. The remaining motors (347A-011 and 347A-012) had nominal traces and were used to calculate average performance.

Performance of the reclaimed AP propellant motors is compared to the historical 70-pound BATES baseline in Figures 11 through 13. An average burn rate of 0.442 ips at 958 psia was obtained for the reclaimed AP propellant motors, very near the target of 0.423 ips at 1000 psia. The reported and theoretical specific impulse of 294- and 316-lbs*sec/lb are well within the 3-sigma historical control limits, as is the resultant efficiency of 93.2 percent.

The 70-pound BATES data indicate that target properties were obtained and that ballistic properties of propellant processed with reclaimed AP correlate very well to the historical database.

The static test firing of the 800-pound BATES motor was also performed at the Phillips Laboratory. As with the 70-pound BATES motors, the pressure data were measured with two independent pressure transducers. The thrust measurement was obtained from the summation of three parallel load cells. The trace of the thrust data indicted an uncharacteristic ringing of the test stand at ignition. This ringing is a measurement anomaly and is not believed to be related to the propellant performance. However, since the ringing was large enough to shift the load cell readings, the thrust data are unreliable. Because motor efficiency is calculated from thrust data, efficiency values are also unreliable. This anomaly is being investigated so that the thrust data can be adjusted to show the true thrust

generated by the motor. The remaining data obtained from the motor firing were nominal. All results are presented in Table VI.

The values obtained from the 800-pound BATES firing compare very well to the 70-pound BATES data. The chamber pressure and burn rate for the motors are nearly identical. The measurements from the 800-pound motor firing indicate that the propellant processed from reclaimed AP has nominal propellant properties.

TABLE I
KERR-MCGEE RECRYSTALLIZED/RECYCLED AP
ACCEPTANCE LABORATORY ANALYSES

Test	Reclaimed AP 60000993-0001	Kerr-McGee Nominal	RSRM Specification	
			Minimum	Maximum
Iron, as ferric oxide (%)	0.000	0.0003	--	0.0036
Chlorate, as ammonium chlorate (%)	0.00	0.005	--	0.02
Chloride, as ammonium chloride (%)	0.00	0.01	--	0.155
Phosphate, as tricalcium phosphate (%)	0.14	0.16	0.10	0.25
Bulk density ($g/in.^3$)	19.1	18.9	18.0	
pH	5.9	6.4	5.0	6.6
Acid insolubles (%)	0.01	0.008	--	0.04
Bromate, as ammonium bromate (%)	0.000	0.000	--	0.004
Perchlorate, as ammonium perchlorate (%)	99.0	99.4	98.3	--
Sulfated ash, as sodium perchlorate (%)	0.4	0.3	--	0.9
Total moisture (%)	0.02	0.02	--	0.06
External moisture (%)	0.0	0.01	--	0.02
Internal moisture (%)	0.01	0.01	--	0.04
Particle size distribution, percent retained				
40 sieve	0	<1	0	1
50 sieve	8	8	6	11
70 sieve	35	39	33	43
100 sieve	64	70	66	76
140 sieve	87	91	88	95
200 sieve	98	98	97	100

TABLE II
KERR-MCGEE RECRYSTALLIZED/RECLAIMED AP
CHARACTERIZATION ANALYSES

Stock-Lot		MDL	Reclaimed 60000993-1	Virgin 7229-0139
Anions:	Chloride (ppm)	25	ND	ND
	Sulfate (ppm)	30	41.6	64.6
	Nitrate (ppm)	30	107	117
Metals (ppm):	Al	2.50	ND	ND
	Sb	5.00	ND	ND
	Ar	5.00	ND	ND
	Ba	0.10	ND	ND
	Be	0.10	ND	ND
	Cd	0.30	ND	ND
	Ca	1.00	683	786
	Cr	0.50	ND	ND
	Co	0.30	ND	ND
	Cu	0.20	ND	ND
	Fe	0.50	ND	1.64
	Pb	2.50	ND	ND
	Mg	0.10	5.22	9.07
	Mn	0.10	0.22	0.22
	Hg	NA	NA	NA
	Mo		0.279	0.279
	Ni	1.00	ND	
	K	40.00	94.0	80.0
	Se	5.00	ND	ND
	Si		0.418	0.418
	Ag	0.30	ND	ND
	Na	1.0	31.2	45.1
	P		ND	ND
	Tl	5.00	ND	ND
	Sn	2.00	ND	ND
	V	0.20	ND	ND
	Zn	0.40	ND	0.86
Volatile organics (ppm)		1	ND	ND
Nonvolatile organics (ppm)		40	179	200
Particle size (μ):	10%		118	131
	50%		197	211
	90%		321	337

MDL = Method Detection Limit
ND = Not Detected
NA = Not Tested

TABLE III
KERR-MCGEE RECLAIMED/RECRYSTALLIZED AP TP-H1148 PROPELLANT UNIAXIAL TENSILE PROPERTIES

Temperature (°F)	Pressure (psi)	Rate (ipm)	$E^{2.6}$ (psi)	ε_{m+}^{t} (%)	ε_{f}^{t} (%)	σ_{m} (psi)	σ_{m}^{tc} (psi)	ε^{tc} (%)
25	Ambient	0.02	815	34.0	42.2	131	178	40.4
		0.2	1067	36.8	46.0	165	231	41.3
		2	1640	32.2	46.1	227	316	41.0
		20	2900	28.3	47.2	331	451	39.0
25	1000	0.02	1090	40.1	42.4	329	461	41.2
		0.2	1460	40.1	43.6	433	610	41.7
		2	2460	35.5	38.2	599	814	36.9
		20	3320	32.5	36.1	694	925	34.7
75	Ambient	0.02	555	27.7	31.3	93.7	121	31.4
		0.2	571	33.3	39.3	105	141	36.8
		2	726	36.7	48.2	126	176	43.3
		20	925	40.5	56.0	162	234	49.6
75	1000	0.02	690	34.2	35.6	181	243	34.9
		0.2	624	36.6	41.0	211	288	37.5
		2	930	38.3	46.5	254	356	42.2
		20	1090	45.4	63.3	338	501	53.8
125	Ambient	0.02	438	21.4	23.7	65.5	79.5	21.7
		0.2	447	25.3	29.6	74.7	94.3	27.4
		2	572	28.8	36.2	87.9	115	33.3
		20	661	33.8	45.6	111	153	41.5
125	1000	0.02	488	29.1	29.7	118	152	29.2
		0.2	610	32.1	33.7	145	191	32.0
		2	742	34.9	39.3	179	243	36.5
		20	830	40.2	56.2	232	331	45.4

Values determined from five JANNAF Class C tensile specimens

TABLE IV
KERR-MCGEE RECLAIMED/RECRYSTALLIZED AP TP-H1148 PROPELLANT
5-INCH C.P. MOTOR DATA SUMMARY

Motor No.	Temperature (°F)	Pressure (psia)	Burn Rate (ips)
1	60	648	0.366
2	60	654	0.375
3	60	650	0.367
4	-35	591	0.341
5	-35	583	0.333
6	-35	584	0.335
7	135	711	0.403
8	135	707	0.400
9	135	711	0.402
10	60	240	0.267
11	60	242	0.272
12	60	239	0.271
13	60	502	0.338
14	60	502	0.340
15	60	508	0.343
16	60	782	0.393
17	60	764	0.387
18	60	765	0.389
19	60	1058	0.428
20	60	1056	0.429
21	60	1046	0.425
22	60	650	0.371

TABLE V RECLAIMED AP 70-POUND BATES BALLISTIC SUMMARY						
Firing No.:	347A-010	347A-010	347A-011	347A-011	347A-012	347A-012
Propellant weight (lbs)	73.83	73.83	73.78	73.78	73.40	73.40
Expansion ratio (A/A*)	9.952	9.952	9.966	9.966	10.337	10.337
Average pressure (psia)	872.2	869.5	949.7	945.2	971.3	967.7
Average thrust (lbs)	3898.08	3899.89	3835.96	3824.33	3971.32	3973.98
Action time (sec)	4.609	4.607	4.620	4.620	4.532	4.532
Burn rate average (ips)	0.451	0.451	0.429	0.429	0.455	0.455
Burn rate (ips at 1000 psia)	0.471	0.472	0.436	0.437	0.459	0.460
Delivered specific impulse (lbs*sec/lb)	243.343	243.352	243.259	243.252	245.179	245.242
Delivered specific impulse (vacuum)(lbs*sec/lb)	259.781	259.703	263.818	263.988	266.115	266.394
Report specific impulse (vacuum)(lbs*sec/lb)	296.022	296.122	293.505	293.619	295.103	295.418
Theoretical specific impulse (vacuum)(lbs*sec/lb)	316.018	316.018	316.018	316.018	316.018	316.018
Efficiency	93.672	93.704	92.876	92.912	93.352	93.491

TABLE VI RECLAIMED AP 800-LB BATES PRELIMINARY BALLISTIC SUMMARY		
Firing No.:	347L-001	347L-001
Propellant weight (lbs)	784.99	784.99
Expansion ratio (A/A*)	9.353	9.353
Average pressure (psia)	971.747	972.523
Average thrust (lbs)	29000.479	29040.432
Action time (sec)	6.190	6.191
Burn rate average (ips)	0.429	0.429
Burn rate (ips at 1000 psia)	0.433	0.433
Delivered specific impulse (lbs*sec/lb)	228.664	229.052
Delivered specific impulse (vacuum)(lbs*sec/lb)	246.873	247.276
Report specific impulse (vacuum)(lbs*sec/lb)	276.198	276.648
Theoretical specific impulse (vacuum)(lbs*sec/lb)	316.018	316.018
Efficiency	87.399	87.542

5-GALLON TP-H1148 UNCURED PROPELLANT PROPERTIES

HISTORICAL DATA ● VIRGIN AP ■ 100% RECLAIMED AP

FIGURE 1.

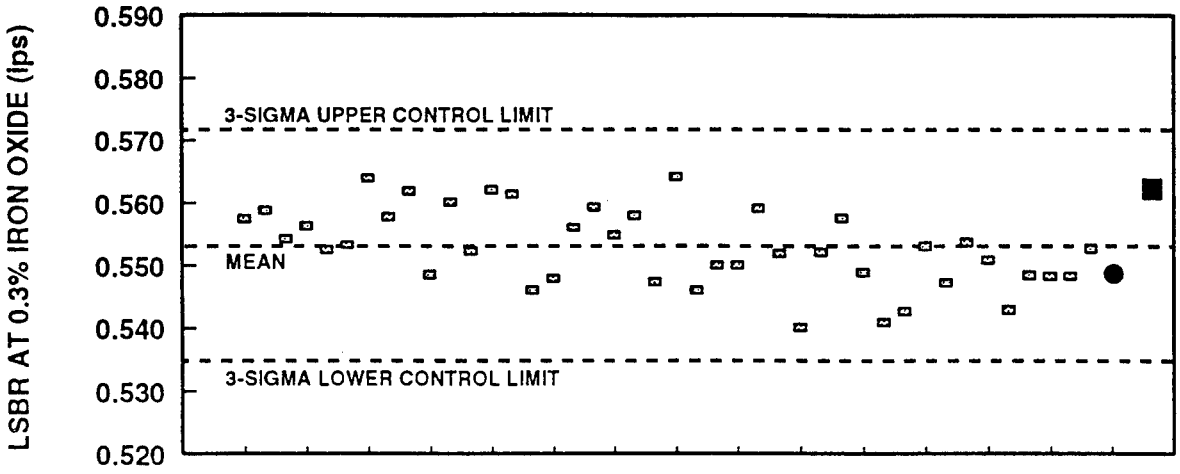


FIGURE 2.

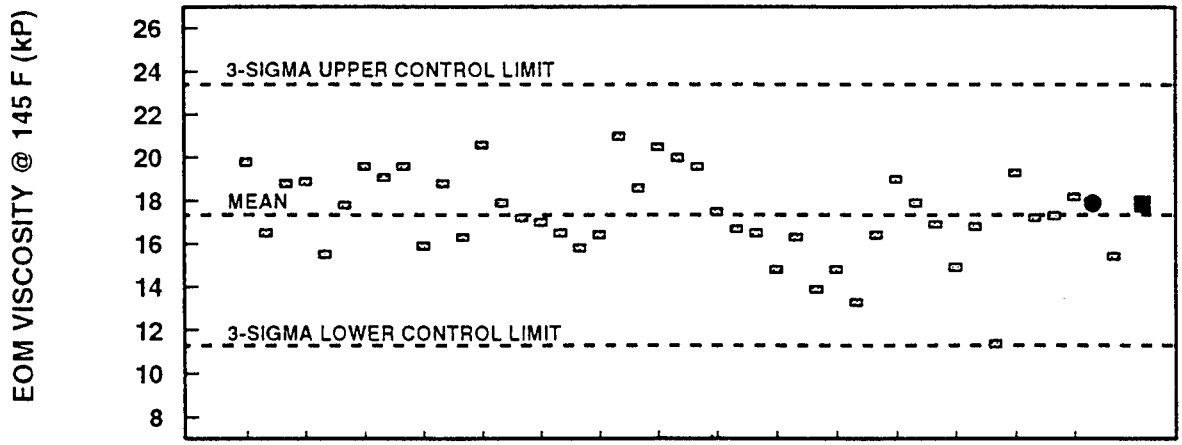
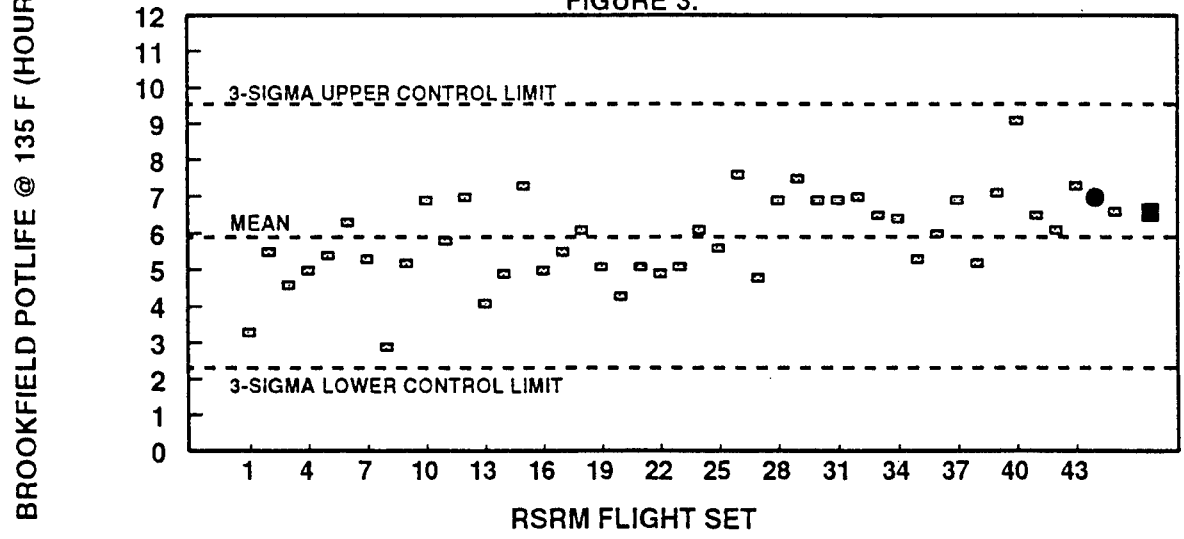


FIGURE 3.



K.F. MIKS 18 MAY 1994 JANNAF1.DRW

5-GALLON TP-H1148 PROPELLANT MECHANICAL PROPERTIES

HISTORICAL DATA ● VIRGIN AP ■ 100% RECLAIMED AP

FIGURE 4.

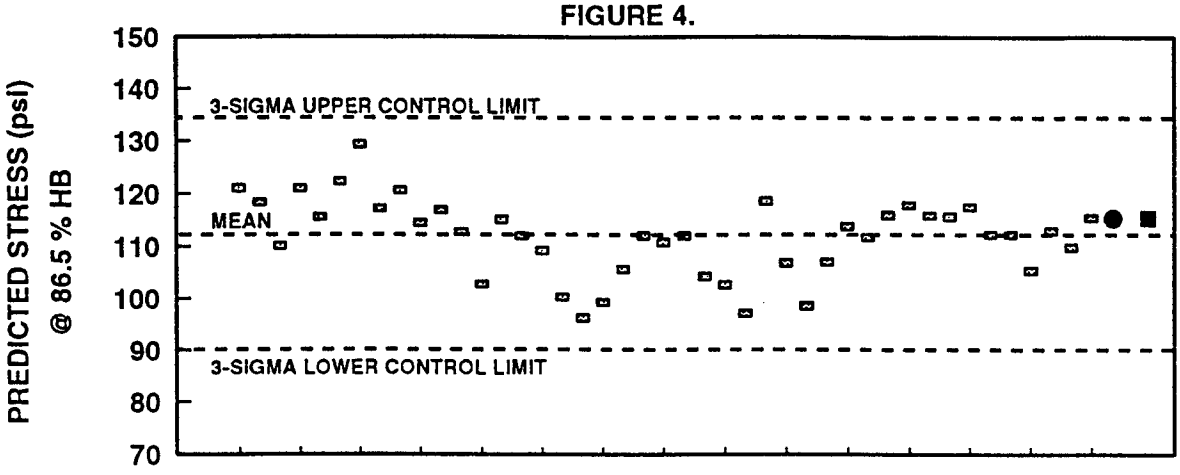


FIGURE 5.

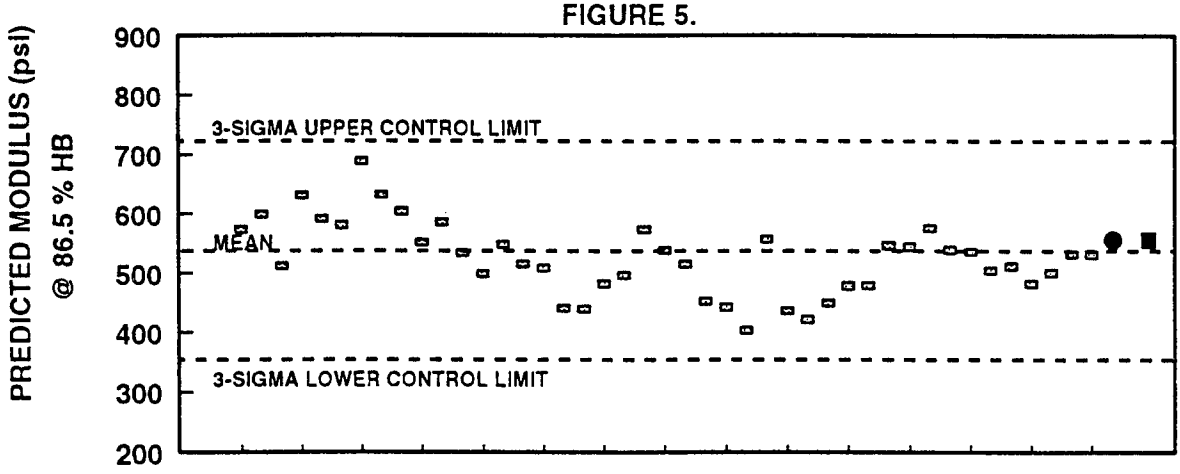
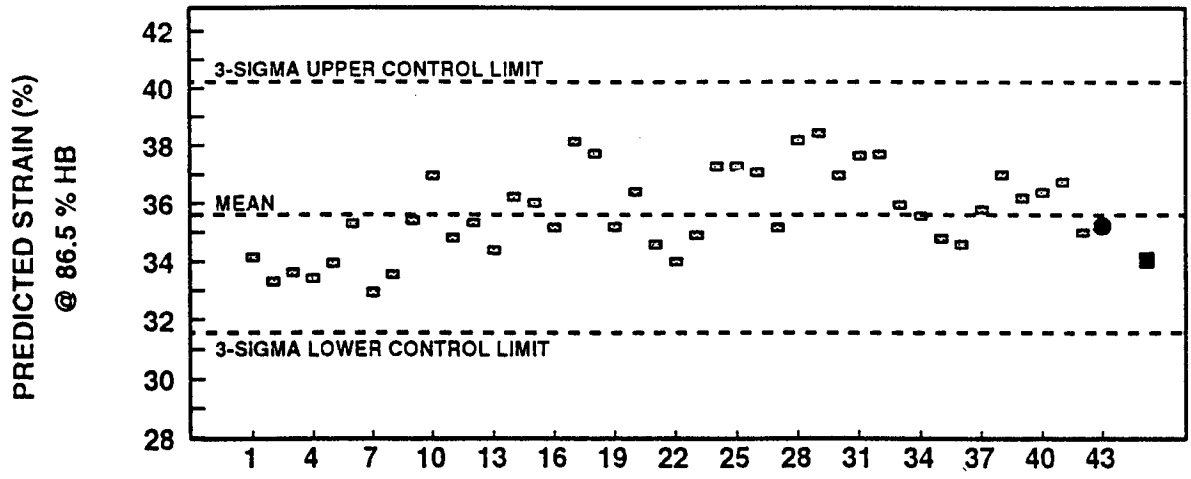


FIGURE 6.



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5-GALLON TP-H1148 PROPELLANT BALLISTIC PROPERTIES

FIGURE 7.

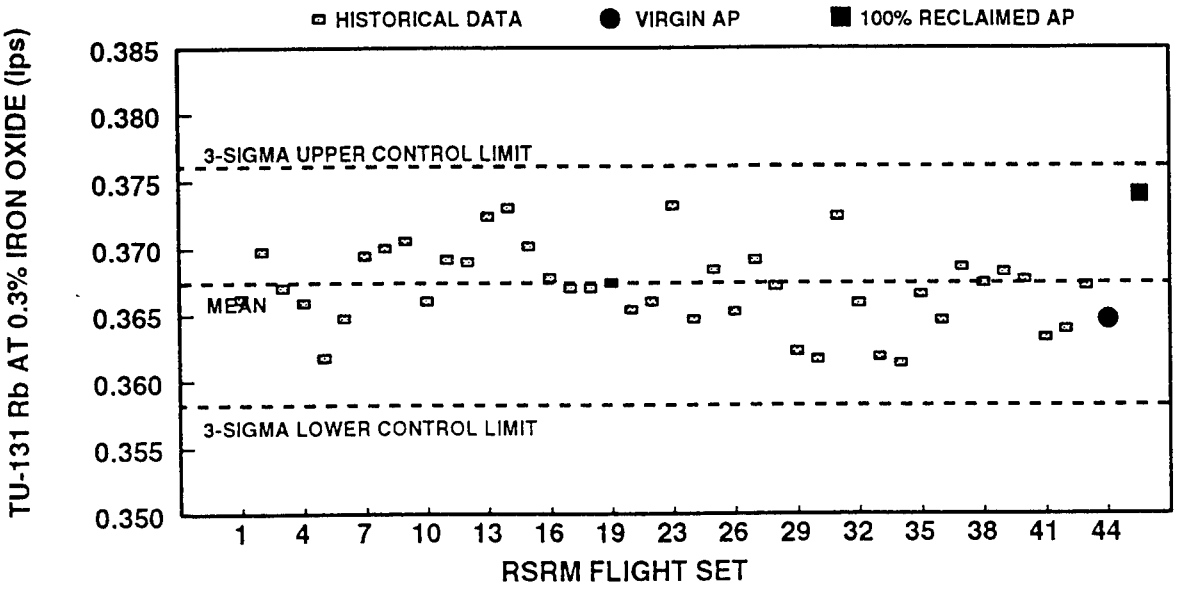

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Figure 8.

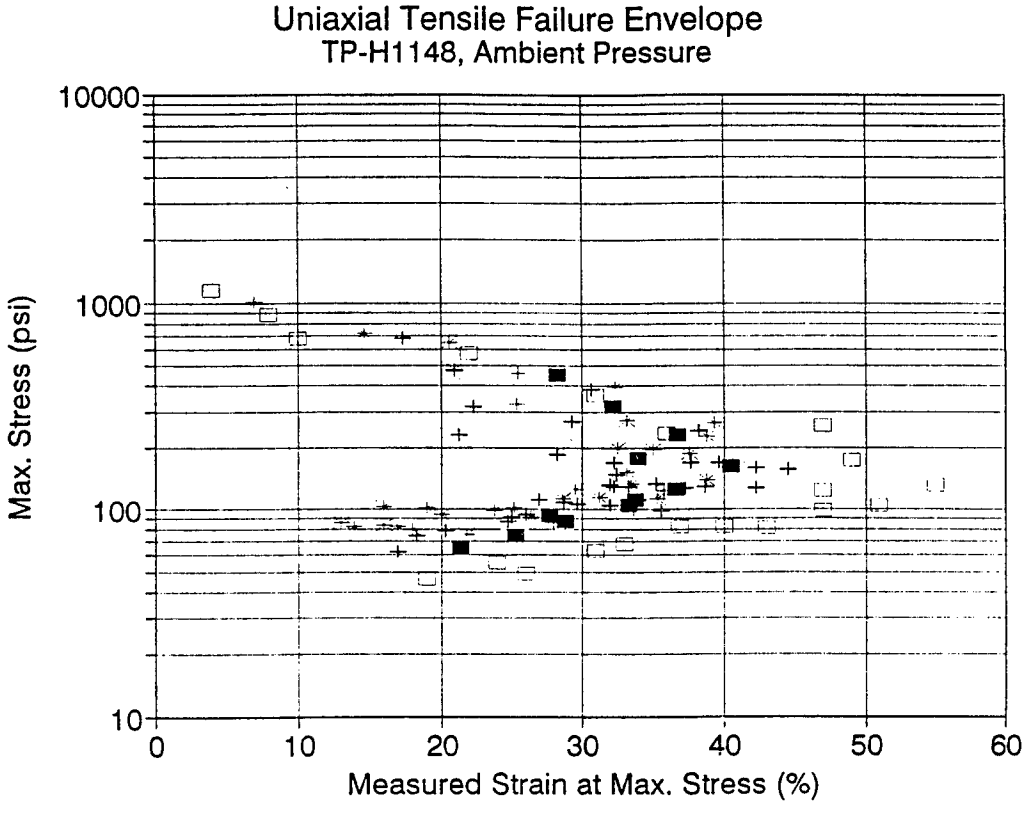


Figure 9.

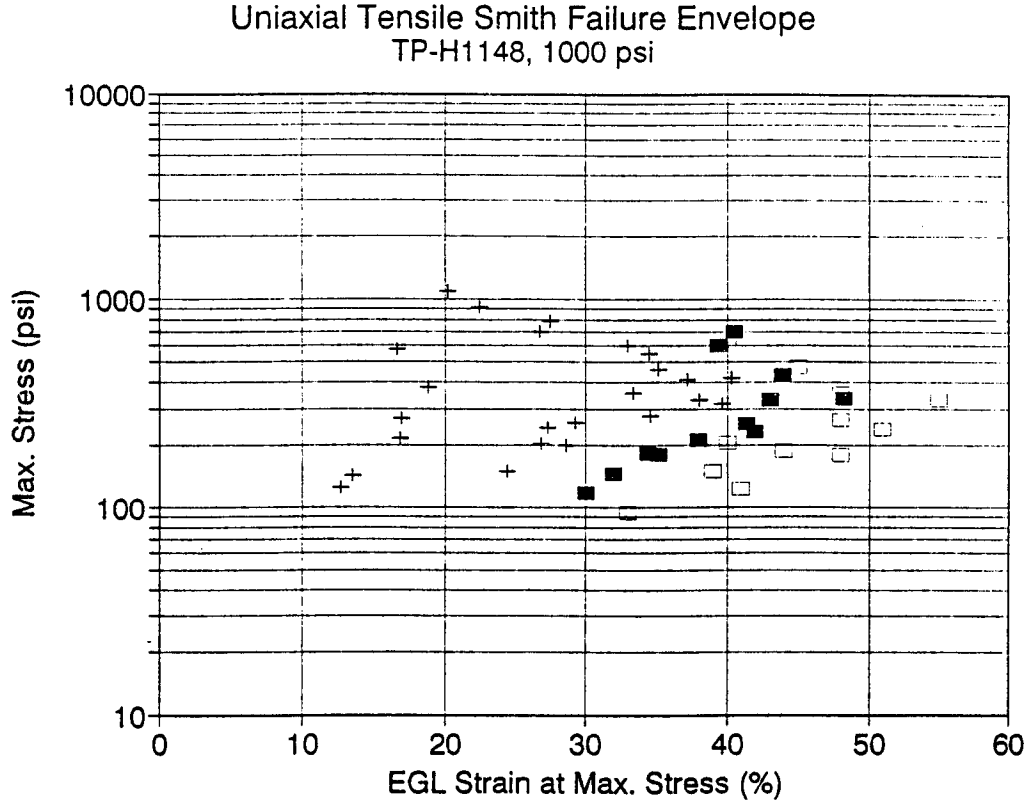
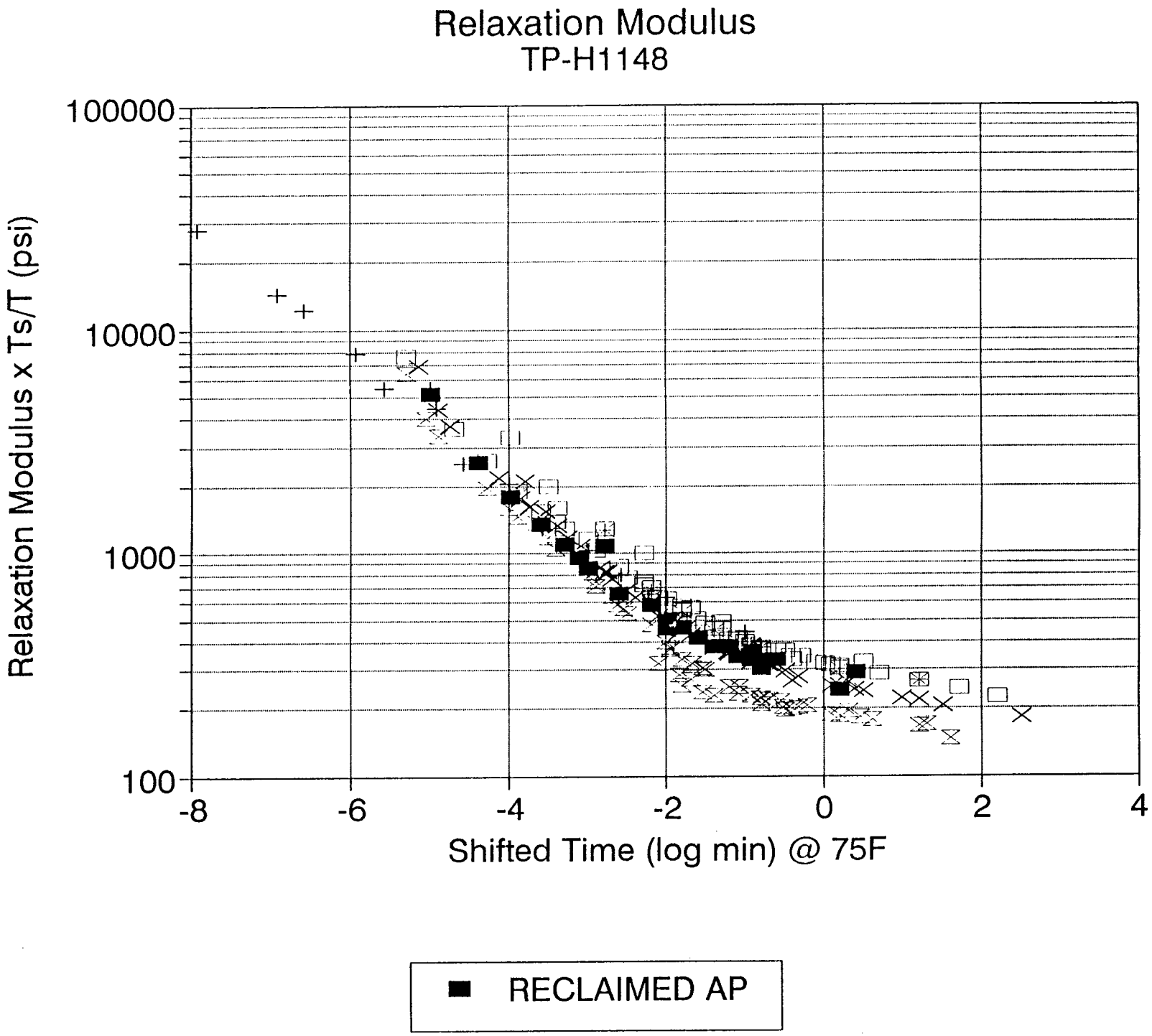


Figure 10.


Relaxation Modulus
TP-H1148
Relaxation Modulus x Ts/T (psi)
100000
10000
1000
100
-8
-6
-4
-2
0
2
4
Shifted Time (log min) @ 75F
RECLAIMED AP

70-POUND BATES BALLISTIC PROPERTIES
TP-H1148 PROPELLANT

FIGURE 11.

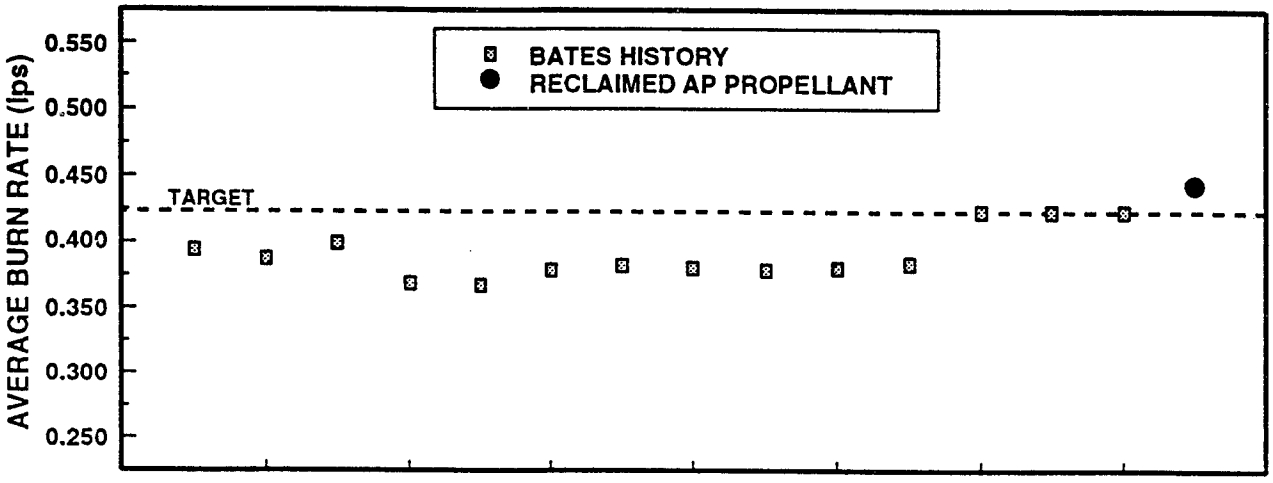


FIGURE 12.

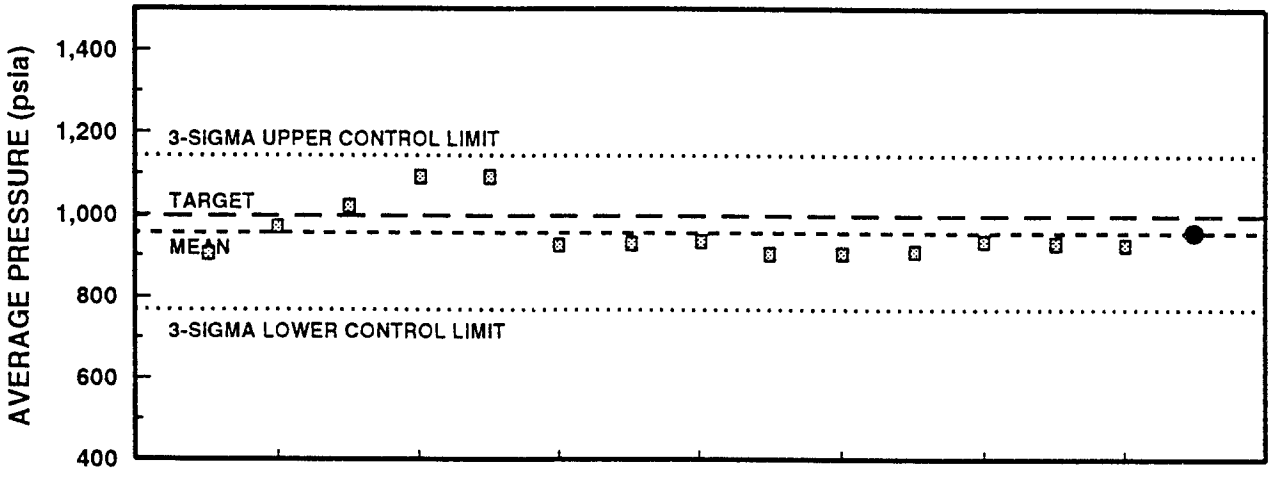
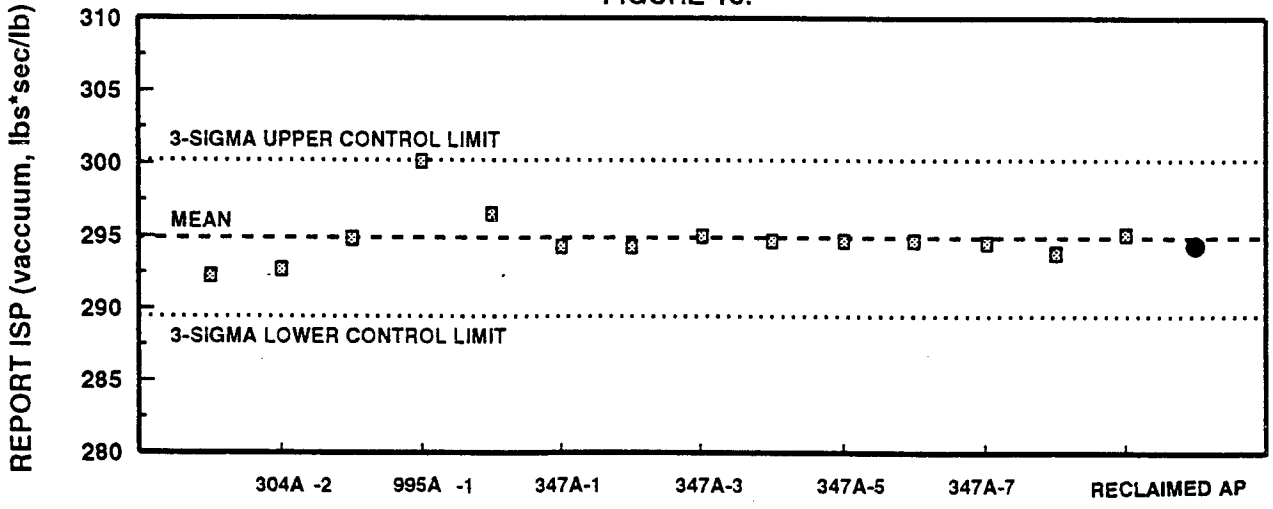


FIGURE 13.



K.F. MIKS 19 MAY 1994 JANNAF5.DRW

ENHANCED ALKALINE HYDROLYSIS AND BIODEGRADABILITY STUDIES OF NITROCELLULOSE-BEARING MISSILE PROPELLANT

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ABSTRACT

Large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations must be disposed of in an environmentally sound manner. Historically, the method of choice for destruction of obsolete or aging energetic materials has been open burning or open detonation (OB/OD). This destruction approach has become undesirable due to air pollution problems. Therefore, there is a need for new technologies which will effectively and economically deal with the disposal of energetic materials. Along those lines, we have investigated a chemical/biological process for the safe destruction and disposal of a double base solid rocket propellant (AHH), which was used in several 8 inch projectile systems. The solid propellant is made of nitrocellulose and nitroglycerin as energetic components, two lead salts which act as ballistic modifiers, triacetin as a plasticizer and 2-Nitrodiphenylamine (2-NDPA) as a stabilizer. A process train is being developed to convert the organic components of the propellant to biodegradable products and remove the lead from the process stream. The solid propellant is first hydrolyzed through an enhanced alkaline hydrolysis process step. Following lead removal and neutralization, the digested liquor rich in nitrates and nitrites is found to be easily biodegradable. The digestion rate of the intact ground propellant as well as the release of nitrite and nitrate groups were substantially increased when ultrasound were supplied to the alkaline reaction medium compared to the conventional alkaline hydrolysis. The effects of reaction time, temperature, sodium hydroxide concentration and other relevant parameters on the digestion efficiency and biodegradability have been studied. The present work indicates that the AHH propellant can be disposed of safely with a combination of physicochemical and biological processes.

INTRODUCTION

Significant quantities of energetic materials (rocket motor propellants, propellant charges, etc.) have been generated as part of the US. Army demilitarization program. Energetic materials are classified as reactive (40 CFR §261.21) and are listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste. Historically, the method of choice for destruction of obsolete or aging energetic materials has been open burning or open detonation (OB/OD). This treatment approach has become restrictive over the past several years due to the promulgation of legislation to manage the handling and treatment of hazardous materials.

The goal of the present study is to develop a treatment process and ultimately a pilot scale demonstration facility for AHH. The AHH formulation is used in several 8 inch projectile systems. The Army currently plans to eliminate the 8 inch weapon systems by the FY98. Ultimately, the processes developed as a result of this study could be applied to a significant quantity of AHH propellant from the demilitarization of 8 inch projectiles. Moreover, it is anticipated that a considerable amount of information obtained from the AHH studies will establish the basis for broader application of the technology. Optimization of these chemical/biological treatment systems could provide a viable means of safe and cost effective disposal for a broad array of energetic materials. The compelling benefits from the development of an innovative bioremediation technology are numerous. This technology would significantly reduce disposal and remediation costs of toxic and hazardous components facing both defense and manufacturing communities. In addition this technology could be utilized for a variety of applications, including, but not limited to the destruction of hazardous manufacturing wastes, excess military munitions, and treatment of contaminated soils and waters.

APPROACH

The composition of AHH, a double-base propellant is given in Table 1. Nitroglycerin and nitrocellulose are the energetic components. Triacetin is a plasticizer used to convert nitrocellulose from its natural fibrous state into a gel state required during the mixing and casting fabrication process of the propellant. Triacetin also acts as a desensitizer and prevents the formation of neat nitroglycerin. 2-NDPA is added as a stabilizer to prevent the auto catalytic decomposition of the propellant with decomposition products. Finally the lead salts act as ballistic modifiers for the propellant.

TABLE 1: AHH Propellant Composition.

Component	Wt % Composition
Nitrocellulose	53.9 min.
Nitroglycerin	31.6 nom.
Triacetin	8.8 nom.
2-Nitrodiphenylamine (2-NDPA)	0.9 min.
Lead Salicylate	1.2 nom.
Lead 2-Ethyl Hexoate	2.0 nom.

Bioremediation has been proven effective in the transformation and complete mineralization of some energetic compounds. Simply stated, bioconversions are chemical transformations (reactions) of organic compounds catalyzed by specific enzymes synthesized by microorganisms. It is generally assumed that access to the active site of an enzyme is available only to compounds dissolved or dispersed in the reaction medium. The propellant itself is highly insoluble in water and it must be pre-treated with solvent(s) in order to increase its solubility[1,2]. However the use of solvents introduce an additional component in the system that has to be removed or treated later in the process. Most solvents are toxic to microorganisms when there are present at concentrations that exceed a specific threshold limit. Therefore, this approach limits the amount of solvent that can be used and the incoming stream must be diluted, to minimize adverse effects on the biomass, which will increase the overall volume of the waste stream. Another technique which can be used when the substrate does not suit the desired bioconversion is to carry out first a chemical modification of the substrate. For example, the alkaline hydrolysis of nitrocellulose has been shown to provide a useful mean to degrade chemically the water insoluble nitrocellulose[3,4]. This alkaline hydrolysis process results in complete digestion of nitrocellulose. Kenyon and Gray[4] documented the presence of a wide variety of organic and inorganic products resulting from the alkaline digestion of nitrocellulose such as nitrates, nitrites, ammonia, cyanide, malic, oxalic, glycolic, trioxyglutaric, dioxybutyric, malonic, tartonic and other unidentified complex acids, sugars, modified celluloses and their nitrates, and partially denitrated cellulose nitrate. Wendt and Kaplan[3], reported that after neutralization, dilution to control nitrate levels and addition of a suitable carbon source (glucose) the digested nitrocellulose liquor is biodegradable. Alkaline decomposition of nitroglycerin produces ammonia, carbon dioxide, formic acid, acetic acid, alkali nitrates, alkali nitrites and intermediate peroxides according to Kenyon and Gray[4]. In the present work, the effect of ultrasound on the alkaline digestion of the AHH propellant has been explored.

The treatment process train tested for the destruction of AHH is illustrated in Figure 1. The propellant is ground and digested in sodium hydroxide solutions, the lead is removed by chemical precipitation and finally the resultant solution, which is rich in organic carbon and nitrogen, is treated biologically to remove carbonaceous and nitrogenous BOD. The final selection of the most suitable option will depend on the kinetics and stoichiometry of the denitrification of the digested propellant and the biological capabilities of nearby wastewater sewage treatment plant. In addition to the alkaline hydrolysis of the propellant mixture, the hydrolysis of pure nitrocellulose was investigated in order to compare the nitrogen releases in the two systems.

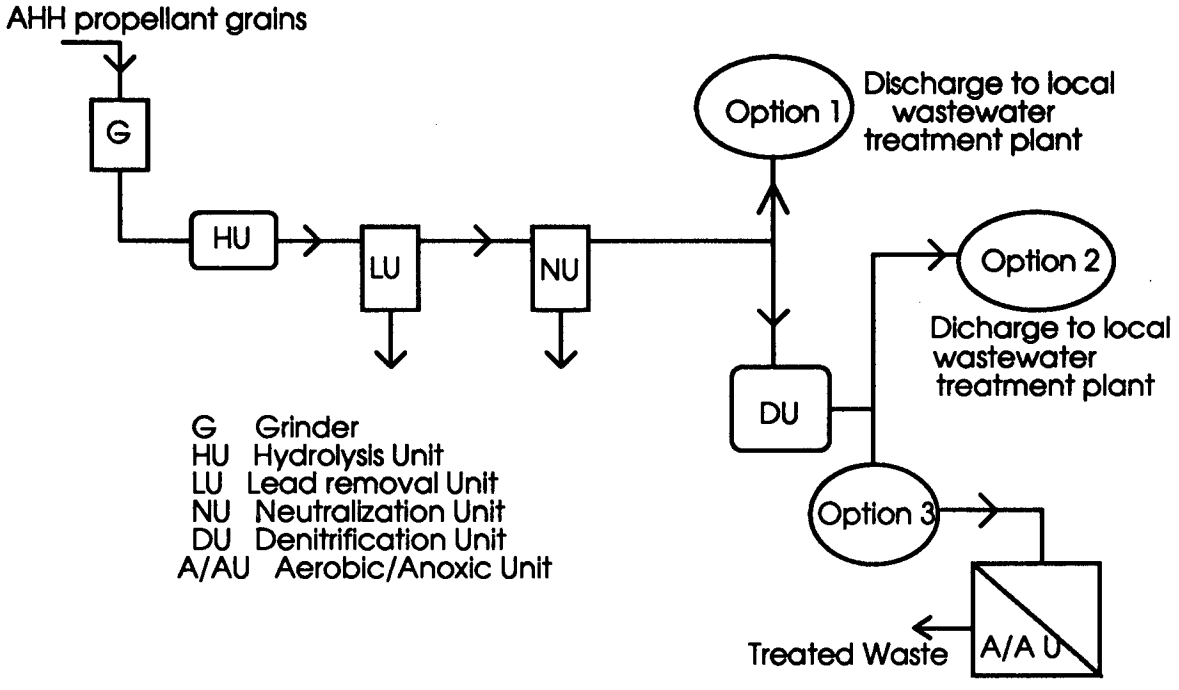

FIGURE 1: Synoptic Diagram for the AHH Propellant Treatment Process

EQUIPMENT AND METHODS

Pure nitrocellulose containing approximately 12.2% nitrogen was obtained from Aqualon, a division of Hercules Incorporated. AHH propellant samples were supplied by Picatinny Arsenal personnel. A sample was prepared from a war reserve M753 rocket motor downloaded at Picatinny Arsenal in 1992. The motor was disassembled per FSAC standard operation procedures. The irregular shaped grain segment was inserted horizontally in the bed of a lathe chuck. Without cutting fluid, a one inch hole was bored in the base of the grain segment. The resulting shavings were collected and stored under environmentally controlled conditions. Next, a grinder (Thomas Wiley Intermediate Mill) was used to process the shavings into 20 Mesh size granules. No fluids were introduced during this operation.

The digestion of the solid propellant and nitrocellulose was carried out in Erlenmeyer flasks. Approximately 0.5 grams of solids were added to fifty milliliters (50 mL) of aqueous sodium hydroxide solution in a 100 mL flasks. This resulted in 1% by weight solids mixture. The flasks were immersed in a sonicator equipped with a water bath capable of maintaining a maximum temperature of 95°C. The sonicator (Fisher Scientific, Model FS14) had a constant power output of 270 watts and 43kHz frequency. In a typical experiment at a given temperature and sodium hydroxide concentration, the alkaline hydrolysis was carried out for 30 to 60 minutes. After digestion the solution was cooled to room temperature and prepared for precipitation of lead by pH adjustments, and sodium sulfide addition. The pH of the decomposition mixture was adjusted with sulfuric acid. Upon removal of lead, the BOD and COD of the mixture were

determined. The lead free supernatant solution, rich in carbon and nitrogen, was neutralized and passed through an acclimated denitrification reactor.

The nitrite and nitrate concentrations were determined by direct injection of collected aliquots using High Pressure Liquid Chromatography (HPLC) on a Varian LC Workstation equipped with a diode array detector, and a Universal Anion 4.6×150 mm, 5μm (Alltech Associates Inc., Deerfield, IL) chromatographic column. Total Kjeldahl Nitrogen (TKN), a measure of nitrogen in the trinegative state, was determined according to Standard Methods[5]. Ammonia was measured by an ammonia selective electrode[5]. Measurements of BOD and COD were also performed following Standard Methods[5] procedures. The concentration of lead in the digestion liquor was determined by Atomic Absorption using a Varian Zeeman 400 Graphite Furnace equipped with an autosampler.

RESULTS AND DISCUSSION

Alkaline Hydrolysis

The effects of reaction time, temperature, and sodium hydroxide concentration on the digestion efficiency were examined. Digestion experiments were carried out at 35, 45, 55, 65, 75, 85 and 95°C in different sodium hydroxide solutions ranging from 2 to 15 % by weight. The sonication power was kept constant and no mechanical mixing was provided. Results for three sodium hydroxide concentrations are presented in Figure 2. The percent digestion is defined as $[(m_i-m_f)/m_i]\cdot 100$ where m_i and m_f are the initial and final mass of solid propellant respectively. Figure 2 shows that the digestion efficiency increases with temperature and sodium hydroxide concentration.

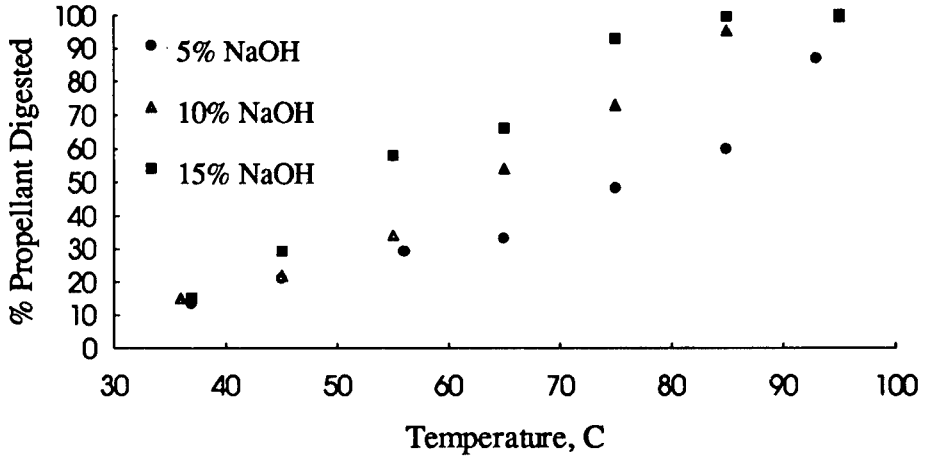

FIGURE 2: Digestion of AHH at Various NaOH Concentrations and Reaction Temperatures.

Experiments were also performed with mechanical agitation of the reaction medium and a combination of sonication and mechanical mixing. Mechanical agitation resulted in significant increases of the digestion rates, at all temperatures, over the rates obtained by sonication alone. However, combination of sonication and mechanical agitation produced higher digestion rates

than sonication or mixing alone. For instance, in an experiment conducted at 90°C with 0.25g AHH in 50 ml 2 wt% NaOH under well mixed conditions for 1 hour the observed digestion was 78.82%. When the experiment was repeated with the sonicator turned on, 84.80% of the propellant was hydrolyzed. Data presented in Table2correspond to another typical experiment conducted with 0.5 g AHH in 50 ml 2 wt% NaOH solution.. Although the results indicate that a significant increase in digestion rate and total nitrogen release, this may not be sufficiently high to justify the costs associated with the installation of large sonicators in a full-scale system. Therefore, the economic advantages of sonication must be carefully examined. It should be noted that sonication power requirements can be significantly reduced by intermittent application of ultrasound[6].

TABLE 2: Effect of reaction type on alkaline digestion of AHH propellant

Reaction type	Digestion wt %	$[NO^-_2]$ ppm	$[NO^-_3]$ ppm	Total N ppm
Good Mixing and no sonication	56.73	1522.80	1014.30	665.50
Sonication plus "poor mixing"	64.78	1630.20	1100.00	744.55
Sonication plus "good mixing"	77.79	2038.30	1427.80	942.76

The nitrogen released from the decomposition of AHH was compared to nitrogen released by alkaline hydrolysis of NC under identical experimental conditions. The results obtained from the alkaline hydrolysis of AHH and pure NC are presented below.
Experiments at 90°C with varying alkali to propellant ratio and sonication were carried out using 50 mL NaOH solutions and 0.5 grams of ground propellant with sonication only. The nitrate and nitrite production was monitored during the course of the reaction and is presented in Figure 3 for different NaOH concentrations. The total nitrogen produced in the forms of nitrate and nitrite is proportional to the amount of propellant digested and appears to be independent of NaOH concentration. The ratio of nitrite to nitrate is approximately 2 to 1 regardless of the degree of digestion. The theoretical amount of nitrogen in solution containing 1% solids, based on the nominal propellant composition and assuming 13.5% nitration of cellulose, is about 1312 mg/L. In a typical experiment at 97.50 % digestion of the propellant 768.33 mg/L of nitrite-N, and 385.23 mg/L of nitrate-N, were released. Approximately 60 % of the original nitrate groups were reduced to nitrite. The total nitrogen produced as nitrate and nitrite accounts for 90.12 % of the nitrogen originally present in the propellant.

The nitrite and nitrate measurements indicated that about 10% of the original nitrogen was unaccounted and apparently bound to post-degradation organic carbon residuals. In an attempt to close the nitrogen mass balance we performed TKN measurements of the digested liquor. The TKN was found to be about 23 mg/L or 1.8 % of the original nitrogen. Ammonia was also a product of decomposition and was detected in solution at a concentration of 0.5 mg/L as NH_3-N. However, most of the ammonia formed was probably stripped-off due to the strong basic environment which shifts the acid-base equilibrium reaction in favor of ammonia formation. Cyanide, another degradation product, could combine with hydronium ions to form the volatile hydrocyanic acid. Ammonia and small amounts of cyanide may account for the missing 10% of original nitrogen. Considering that nominal compositions of nitrocellulose and nitroglycerin were

used to compute the total expected nitrogen in the propellant, and the heterogeneity of the samples used during digestion, the nitrogen mass balance is quite satisfactory.

NC decomposition was studied at 90°C with varying alkali to nitrocellulose ratio and sonication by preparing 1% solids solutions and various NaOH strengths. The degree of digestion and the concentrations of nitrite and nitrate were monitored for one hour reaction time. Typical results of NC hydrolysis are illustrated in Figure 4. Pure NC appears to degrade faster than the AHH formulation and 100% digestion is achieved within one hour at 2% NaOH dosage. The ratio of nitrite-N to nitrate-N is approximately 2.8 regardless of the degree of digestion. This finding is in good agreement with the results obtained by Kenyon and Gray[4] who found 0.075 mole of nitrite and 0.025 mole of nitrate per liter of alkaline decomposition mixture. Moreover, the independence of this ratio from the degree of digestion suggests that the hydrolysis of nitrocellulose and nitroglycerin is a single step process where nitrates and nitrites are formed directly from the cleavage of the parent molecules. Wendt and Kaplan[3] also demonstrated that the decomposition of NC in alkaline environments proceeds in a single step, by determination of the nitrogen, carbon and oxygen contained in the residual (undigested) NC during the course of the reaction.

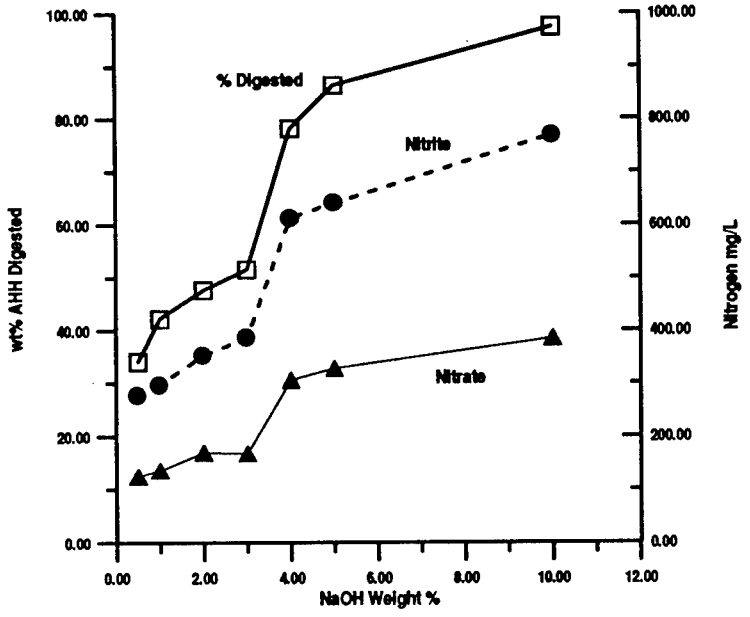

FIGURE 3: Nitrate and Nitrite Release During AHH Decomposition

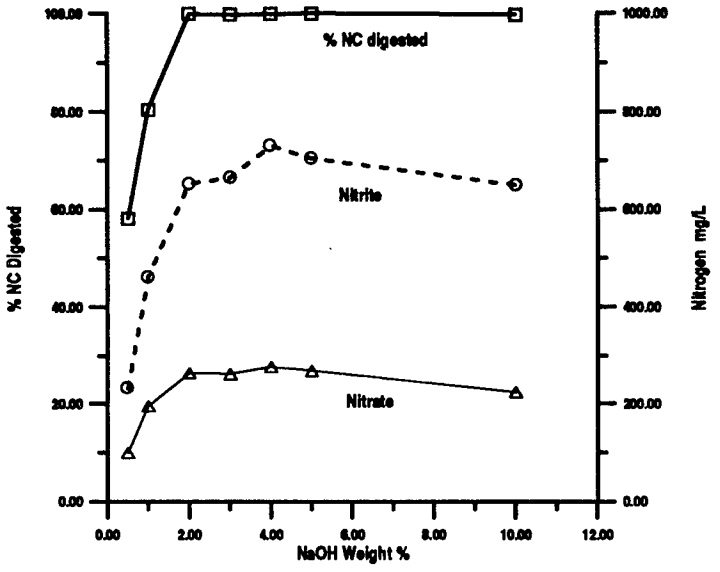

FIGURE 4: Nitrate and Nitrite Release During NC Decomposition

The theoretical amount of nitrogen in a 1% NC solids (12.2% nitration) mixture is 1220 mg/L. The conversion of the original nitrate-N to nitrite-N is about 80%. The TKN of the decomposition mixture was found to be 116 mg/L or 9.5% of the original nitrogen. The total amount of nitrogen accounted for in the forms of nitrate, nitrite and TKN is 89.5 %. Loses of ammonia and HCN, which are known decomposition products, from the system may account for portion of the remaining 10.5% of nitrogen. However, no attempt was made to quantify other nitrogen-containing degradation products.

Lead Removal

The propellant contains a substantial amount of lead, approximately 1.6% wt, which must be removed prior to biological treatment of the digestion liquor. The initial total Pb concentration in the digestion liquor ranges from 65 ppm to 70 ppm and at these concentrations it will be highly toxic and inhibitory to microbial growth. Since PbS is highly insoluble in water, it was decided to dose the solution with Na_2S and precipitate lead as PbS. To facilitate precipitation, the pH of the solution was adjusted to the minimum PbS solubility. According to the theoretical solubility diagram, PbS exhibits minimal solubility at pH of around 8. After pH adjustments, various amounts of Na_2S are added in order to determine an optimal dosage. The results of a typical experiment are shown in Figure 5. For this particular experiment the initial Pb concentration was 55 ppm. The highest percent removal (99.36) was observed at a sodium sulfite dosage of 1.0 mM. Lead removal may also be facilitated by the formation and co-precipitation of lead sulfate, lead hydroxide and lead carbonate due to the presence of the corresponding anions and pH adjustments.

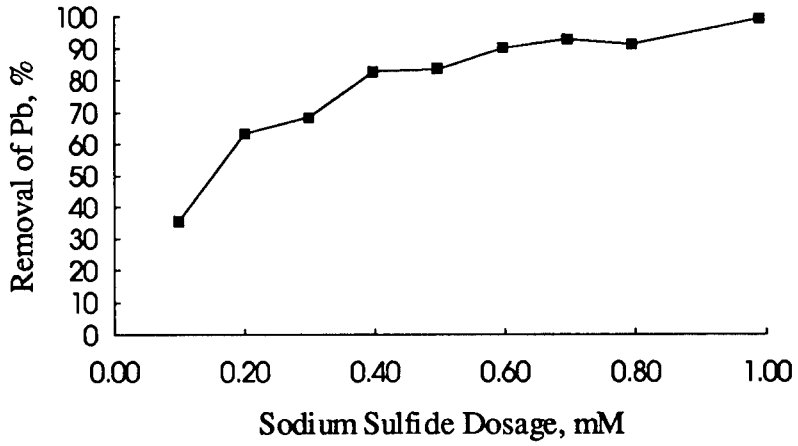

FIGURE 5: Lead Removal at Various Sodium Sulfide Concentrations

The solubility of lead sulfide in the presence of the post-degradation organic compounds was investigated in 0.5 mM sodium sulfide solutions and various pH environments. The results are presented in Table 3. Maximum lead removal was observed at pH around 9. Although sodium sulfide is added in excess of stoichiometric requirements for total lead precipitation, it appears that the precipitation process is greatly affected by the formation of lead complexes. A solubility diagram was constructed for this system and compared with the theoretical pC-pH diagram for PbS. This comparison showed that the solubility of Pb was much higher than that predicted by theoretical considerations and suggests the formation of organo-lead complexes which substantially increase the solubility of lead.

TABLE 3: pH Effects on Lead Removal by Sodium Sulfide Precipitation at 0.5 mM.

Final pH	Initial Lead Concentration [ppm]	Final Lead Concentration [ppm]	Lead Removal (%)
6.50	67.41	7.75	88.50
6.58	59.77	13.63	77.66
7.36	62.79	5.55	91.16
7.97	63.19	6.38	89.90
8.18	64.93	7.65	88.22
8.43	54.14	5.48	89.88
8.72	53.59	3.62	93.24
9.02	35.26	2.10	94.06
9.17	21.00	4.74	77.44
10.00	11.03	2.37	78.56
10.41	15.59	4.19	73.15
11.73	52.02	8.76	83.17

Five days biological oxygen demand tests were carried out directly with the neutralized digested propellant. The average BOD and COD of three samples before lead removal were 1480 mg/L and 2960 mg/L respectively. After lead removal the BOD and COD were found to be 435 mg/L and 2295 mg/L respectively.

Denitrification

The BOD and COD results reported above, indicate that the neutralized digested propellant is biodegradable. Since the digested liquor is very rich in nitrates and nitrites, anoxic denitrification experiments were conducted with lead-free digested liquid, to convert them to nitrogen gas. Results showed complete conversion of nitrate and nitrite to nitrogen gas in an acclimated reactor without addition of external carbon source within 30 hours with mixed cultures that have been acclimated for two months. This acclimation period was necessary because it was observed that high initial shock loads of nitrite were inhibitory. In a typical experiment, initial nitrite and nitrate concentrations of 123.3 mg/L and 90.5 mg/L respectively were reduced completely to nitrogen gas within 30 hours.. The initial COD in the reactor was 1274 mg/L and after total nitrite and nitrate conversion, 1168 mg/L of COD were remaining in the system. The COD consumed per unit mass of nitrogen (2 mg COD/mg nitrogen) is close to the values reported in the literature[7]. The complete conversion of nitrite and nitrate and a residual BOD of 94 mg/L in the system prove conclusively that external carbon sources are not necessary for denitrification of the digested propellant. Since BOD is present in excess of the amount required for nitrite and nitrate conversion an additional step is required for complete mineralization of the hydrolysis products. In another set of experiments, fresh activated sludge obtained from a nearby sewage treatment plant was added to the reactor by replacing 1 liter of the prevailing acclimated mixed culture. Following a short acclimation period of 4 days, 135 ml of lead free digested propellant was added to the 2 L reaction volume. The pH was maintained slightly above 7, the agitation speed was 250 rpm and the temperature of the reaction medium was maintained at 30 °C. Results of the time course of the reaction are shown in Figure 6. The results indicate that nitrite is reduced more rapidly than the nitrate. COD measurements indicate that in this case 2.63 mg COD were consumed per mg of nitrogen. The TSS was 1180 mg/L. The difference with the COD/N ratio of 2 reported above might be attributed to cell synthesis since one liter of acclimated mixture culture (acclimated for two months) was replaced by fresh activated mixed culture.

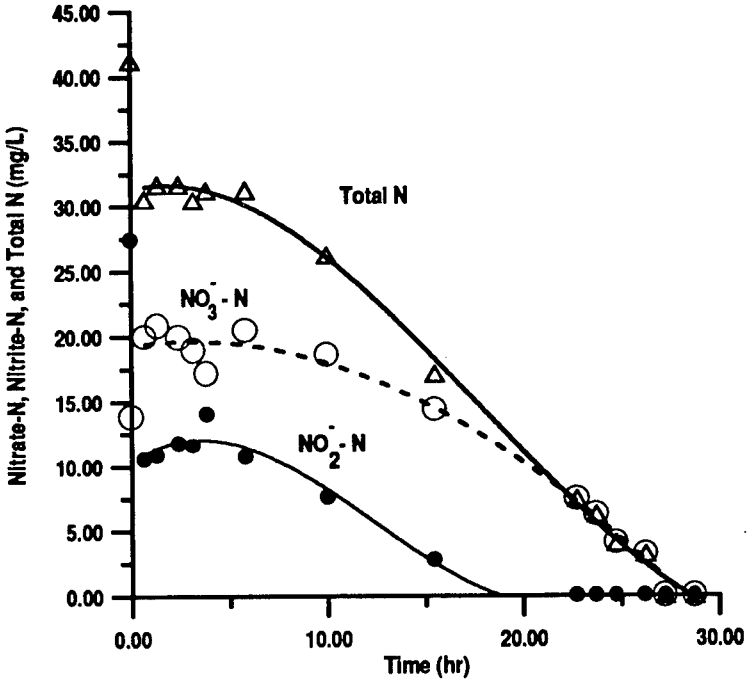

FIGURE 6: Time History of Nitrogen Reduction Under Anoxic Environment

CONCLUSIONS

Simultaneous mixing and sonication appear to significantly enhance the rates of decomposition of AHH in sodium hydroxide solutions. Alkaline hydrolysis decomposes AHH into biodegradable products that can be treated by conventional biological treatment technologies. Approximately 60% of the original nitrate groups of nitrocellulose and nitroglycerin are reduced to nitrite. The amount of nitrogen released in the form of nitrites and nitrates accounts for 90% of the original nitrogen. The remaining 10 % appears to be bound on post-degradation organic carbon or converted to ammonia and other nitrogen compounds. Digestion of nitrocellulose releases 80 % of the original nitrogen as nitrite-N and nitrate-N, and 9.5% as TKN. The lead present in the digestion liquor of the decomposed AHH mixture is effectively removed by precipitation with sodium sulfide. Complexation of lead with organic and inorganic digestion products appears to be responsible for the observed increase in lead solubility. Complete denitrification of the of nitrite and nitrate present in the decomposition mixture is achieved without addition of external carbon sources.

ACKNOWLEDGMENT

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REFERENCES

1. Goodhue, C.T., "The methodology of Microbial Transformation of Organic Compounds" in *Microbial Transformation of Bioactive Agents*, Rosazza, J.P, Ed., CRC Press Inc., Boca Raton, Fla. (1982)

2. Marsheck, W.J., "Current Trends in the Microbiological Transformation of Steroids", Prog. Ind. Microbiol., 10, 49-103 (1971)

3. Wendt, T.M., and A.M. Kaplan, A Chemical Biological Treatment Process for Cellulose Nitrate Disposal, *Journ. WPCF* **48**, 660-668 (1976)

4. Kenyon W.V., and H. LeB. Gray, "The Alkaline Decomposition of Cellulose Nitrate I. Quantitative Studies", *Amer. Chem. Soc. Journ.*, **8**, 1422-1427 (1936)

5. Greenberg, A. E., L. S. Clesceri, and A. D. Eaton. *Standards Methods for the Examination of Water and Wastewater,* 18th Edition. American Public Health Association, American Water Works Association, and Water Environment Federation, 1992

6. Pesic, B., and T. Zhou, "Application of Ultrasound in Extractive Metallurgy: Sonochemical Extraction of Nickel", Metallurgical Transactions, 23B, 13-22 (1992)

7. U.S. Environmental Protection agency: *Process Design Manual for Nitrogen Control*, Office of Technology Transfer, Washington, DC., October 1975

Environmentally Compatible Solid Rocket Propellants

By

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Abstract

Hercules' clean propellant development research is exploring three major types of clean propellant: (1) chloride-free formulations (no chlorine containing ingredients), being developed on the Clean Propellant Development and Demonstration (CPDD) contract sponsored by Phillips Laboratory, Edwards Air Force Base, CA; (2) low HCl scavenged formulations (HCl-scavenger added to propellant oxidized with ammonium perchlorate [AP]); and (3) low HCl formulations oxidized with a combination of AN and AP (with or without an HCl scavenger) to provide a significant reduction (relative to current solid rocket boosters) in exhaust HCl. These propellants provide performance approaching that of current systems, with less than 2% HCl in the exhaust, a significant reduction (≥70%) in exhaust HCl levels. Excellent processing, safety, and mechanical properties were achieved using only readily available, low cost ingredients.

Two formulations, a sodium nitrate ($NaNO_3$) scavenged HTPB and a chloride-free hydroxy terminated polyether (HTPE) propellant, were characterized for ballistic, mechanical, and rheological properties. In addition, the hazards properties were demonstrated to provide two families of class 1.3, "zero-card" propellants. Further characterization is planned which includes demonstration of ballistic tailorability in subscale (one to 70 pound) motors over the range of burn rates required for retrofit into current Hercules space booster designs (Titan IV SRMU and Delta II GEM).

Introduction

The national initiatives to reduce the amount of hazardous substances released into the environment have expanded to include solid rocket propellants. The environmentally more compatible propellants are known in the industry as "clean propellants" and feature HCl levels at least an order of magnitude lower than conventional propellants. These propellants are typically formulated with either chlorine scavengers such as sodium nitrate or chlorine-free oxidizers such as ammonium nitrate[1,2,5].

Hercules initiated development on chloride-free propellants formulated with ammonium nitrate as early as 1986. Shortly thereafter, work was also initiated to develop low-HCl using a combination of oxidizers such as ammonium nitrate, ammonium perchlorate and sodium nitrate (an HCl scavenger). The Air Force/Phillips Laboratory Clean Propellant Development and Demonstration Contract[4] was awarded in 1989 to provide a chloride-free propellant for the Advanced Launch System. Promising candidate formulations were identified and a baseline propellant was selected. Funding for further propellant development, scaleup, and characterization work was discontinued in 1991 and then partially restored in the fourth quarter of 1993. Plans for scaleup and demonstration of an improved version of the baseline propellant are on hold pending additional funding.

Discussion

Formulation

Hercules' chloride-free propellants are formulated with low energy HTPE (hydroxy terminated poly ether) binders, ammonium nitrate oxidizer, and magnesium-aluminum metal alloy fuels. Low energy binders utilize an energetic plasticizer such as BuNENA (n-butyl 2-nitratoethyl nitramine) or TEGDN (triethylene glycol dinitrate) in order to increase burning rates, improve combustion efficiency, and increase performance. These improvements are needed to compensate for the use of ammonium nitrate as the primary solid oxidizer. The amount of energetic plasticizer is limited, however, to maintain a hazard classification of 1.3 and a critical diameter of greater than six inches. Magnesium-aluminum metal alloy fuels are utilized for the same reasons that low energy binders are used. It is necessary to use an alloy rather pure magnesium in order to avoid compatibility problems. Ammonium nitrate was selected for use, even though it adversely affects ballistics, because of its availability, low cost, and lack of chlorine.

Hercules has done work to develop two types of low HCl propellants. The first type is an HTPB/AP/$NaNO_3$/Al-based propellant specifically formulated for retrofit of the Titan IV SRMU booster. The second type of low HCl propellant being developed is similar to the chloride-free propellant already described except it utilizes a low level of ammonium perchlorate in combination with aluminum powder as the primary metal fuel. Up to 20% ammonium perchlorate can be utilized, without an HCl scavenger, before exceeding an HCl level of ~6% in the exhaust.

Propellant Trade Studies

Trades studies comparing the performance, HCl levels, ballistics, and ingredient costs of these clean propellants, along with selected alternative clean propellants, are summarized in Tables I through III. Titan SRMU and Delta GEM booster propellants (QDT and QDL respectively) are included as references. Performance trade-off analyses were conducted using payload partials derived for Hercules expendable launch vehicles.

Only two propellants currently offer the potential of a completely chloride-free exhaust. These propellants include our (Hercules) HTPE chloride-free propellant and the HAN/AN/Al emulsion propellant currently being developed by Aerojet. Aerojet's propellant is formulated with an eutectic of hydroxy ammonium nitrate (HAN) and ammonium nitrate. Both chloride-free propellants offer roughly the same theoretical payload capabilities in the Titan IV SRMU and Delta II GEM boosters (i.e., 86-93% and 93-97% respectively). However, both propellants currently only deliver Isp efficiencies of about 90%.

The burning rate of the emulsion propellants can be tailored over a fairly broad range; however, these propellants reportedly also have a very high pressure exponent (~0.82)[3]. Pressure exponents of less 0.50 are needed for any type of space booster retrofit application. The emulsion propellants reportedly have a shock sensitivity of greater than zero cards and, therefore, a critical diameter of less than three inches[3]. A demonstrated critical diameter of greater than six inches is required to verify that the clean propellants hazards characteristics are similar to those of current large space booster propellants. In addition, the HAN/AN/Al emulsion propellants soften over time, presumably due use of highly hygroscopic oxidizers[3].

Hercules' HTPE chloride-free propellant currently can only be tailored over a fairly limited burn rate range (0.20 to 0.30 in/sec); however, the pressure exponent for these propellants has been measured to be less than 0.50. In addition, HTPE chloride-free propelants have been shown to have a card gap sensitivity of 0 cards and are estimated to have critical diameter of greater than six inches.

Based on this assessment, the Air-Force's Phillips Laboratory has designated Hercules' HTPE propellant as a near term development chloride-free propellant. A summary of the properties measured for the Hercules HTPE chloride-free propellant, WFS, are shown in Table IV.

Assuming a limited amount of HCl will be acceptable in the exhaust from future space boosters, a number of propellant options exist. Of these options, the scavenged (HTPB/$NaNO_3$/AP/Al) propellants appear to offer the best overall trade-offs. HCl levels as low as 2% can be achieved while still providing 91% to 96% of the current payload capability of Titan IV SRMU and Delta II GEM boosters. These propellants also offer a broad range of ballistic tailorability and ingredient costs which are comparable to those of existing low cost space booster propellants. Hercules's HTPB/$NaNO_3$/AP/Al scavenged clean propellant, QEH-1, has also been shown to have mechanical and rheological properties which would allow it to be retrofit into Titan SRMU boosters (Table IV).

Summary and Conclusions

Hercules' HTPB/$NaNO_3$/AP/Al scavenged clean propellant is currently available for a retrofit of the Titan IV SRMU and Delta II GEM boosters. This propellant is readily tailorability to provide the optimum burn rate for both motors, and is only a minor refinement of the current formulations. The scavenged propellant reduces the exhaust HCl level from ~21% to ~2%.

Hercules' HTPE propellants offer the potential for completely chloride-free exhaust without drastically reducing payload capabilities. They are also estimated to have critical diameters of greater than 6 inches and rheological/mechanical properties which would allow for the retrofit of existing space boosters. Additional development is still needed to resolve the following key issues: (1) Isp efficiency needs to be improved by reducing two-phase flow losses and increasing the flame temperature, and (2) burn rate tailorability is limited and higher rates are necessary for a Titan retrofit.

Future Work

During the remainder of the 1994 calendar year, we will select, scale up and demonstrate in subscale (~15 lb.) motors an improved HTPE chloride-free propellant. This formulation will be tailored to provide a burn rate approaching that required for a Titan IV SRMU retrofit. Next year, if funding is available, we will scale up this or a similar formulation for characterization and demonstration in an 800-lb. or larger scale motor. At the completion of these projects, we anticipate that a viable chloride-free propellant will be ready for additional characterization and demonstration in larger scale (1,700 to 33,000-lb.) demonstration motors. Parameters of potential demonstration motors are given in Table V.

TABLE I
Preliminary Performance/HCl Level Trade-Off Used to Select the Most Viable Clean Propellant Candidate

PROPELLANT APPROACH	PAYLOAD (lbm)		HCl (%)
	DELTA II (TO GTO)	TITAN IV (TO LEO)	
TITAN - QDT	---	40,000	21.3
DELTA - QDL	4,000	---	21.1
HTPE			
CHLORIDE-FREE (AN/MgAl)	3,722	34,304	0
LOW HCl (AN/AP/Al)	3,855	36,981	6.0
SCAVENGED			
HTPB/$NaNO_3$/AP/Al	3,845	37,032	2.0
HTPB/AP/Mg-NEUTRALIZED	3,675	33,388	15.2
HAN/AN/Al EMULSION	3,867	37,250	0

TABLE II
The Ballistic Properties of Current Clean Propellant Formulations are Nearly Equivalent to Those of the Titan IV SRMU and Delta GEM Propellants

APPROACH	BALLISTICS		COMMENTS
	r_{1000} (in/sec)	n	
TITAN IV SRMU - QDT	0.32	0.30	88% solids HTPB/AP/Al baseline propellants.
DELTA GEM - QDL	0.26	0.34	
HTPE			
CHLORIDE-FREE (AN/MgAl)	0.20-O.30	0.45	Limited burn rate range with chloride-free option, lower pressure exponent needed for low HCl option.
LOW HCl (AN/AP/Al)	0.25-0.50	0.60	
SCAVENGED HTPB/$NaNO_3$/AP/Al	0.20-0.60	0.40	Already demonstrated to have acceptable ballistics and combustion efficiency (800-lb. demonstration).
HTPB/AP/Mg-NEUTRALIZED[4]	0.30-0.50	0.40	2,000-lb. demonstration motor tested.
HAN/AN/Al EMULSION[3]	0.30-0.60	0.82	Significantly lower pressure exponent needed.

TABLE III
The Cost of Clean Propellant Ingredients is Similar to That of Conventional Propellants

APPROACH	INGREDIENT COST ($/lb.)	COMMENTS
TITAN IV SRMU - QDT DELTA GEM - QDL	1.80 2.60	QDT utilizes low cost R45AS, atomized Al, and E/A bonding agent.
HTPE CHLORIDE-FREE (AN/MgAl) LOW HCl (AN/AP/Al)	 5.74 [3.08]* 5.23 [3.15]*	Higher costs related to use of liquid nitramine plasticizer (currently $18/lb.) partially compensated for by low cost AN.
SCAVENGED HTPB/$NaNO_3$/AP/Al	 1.90	Cost reduced by use of $NaNO_3$ - higher cost R45M used.
HTPB/AP/Mg NEUTRALIZED[4]	3.20	Higher cost related to use of R45M and HX-752.
HAN/AN/Al EMULSION[3]	5.12	High cost associated with HAN - potentially lower processing costs.

* Values in brackets based on estimated future ingredient costs for large quantities.

TABLE IV
Clean Propellants Currently Being Tailored to Meet Estimated Titan IV SRMU Retrofit Requirements

PROPERTIES	SRMU RETROFIT REQUIREMENTS	HERCULES PROPELLANTS	
		QEH-1	WFS
HCl (%) PAYLOAD (lbm)	--- *	2 36,314	0 34,247
BALLISTICS r_{1000} (in/sec) n	 0.33 - 0.35** < 0.50	 0.26 - 0.36 0.39	 0.24 - 0.29 0.46
MECHANICAL PROPERTIES TENSILE STRENGTH (psi) ELONGATION (%)	 100 35	 134 52	 114 39
PROCESSABILITY EOM VISCOSITY (kP) POT LIFE (hr)	 <10 >15	 5 16	 1 25

* Current maximum payload to LEO is 40,000 lbm.
** Estimated burn rates needed to achieve equivalent thrust.

TABLE V Hercules Has Several Options for Large Scale Demonstration of Chloride-Free Propellants				
MOTOR OPTIONS	PARAMETERS			COMMENTS
	ACTION TIME (sec)	DIAMETER (in.)	PROPELLANT WEIGHT (lb.)	
GEM BOOSTER	63	40.0	29,950	High L/D ratio, comparable to larger booster. Vectorable nozzle demonstrated April 1994.
ORION 50S-XLG	69	50.2	33,229	High L/D ratio, larger diameter, ground launched, vectorable nozzle.
ORION 50	74.5	50.2	6,665	Larger diameter, vectorable nozzle.
ORION 38	64.4	38.0	1,700	Can accommodate higher burn rate by adjusting throat diameter, vectorable nozzle, lowest cost motor.

References

(1) Bennett, R. R., Clean Propellants and the Environment, AIAA/SAE/ASME/ASEE 28th Joint Propulsion Conference and Exhibit, July 6-8, 1992, Nashville, TN, Thiokol Corporation, Brigham City, Utah

(2) Hawkins, T. W. and Wilkerson, B. E., Environmental Propellant: Current Issues and Assessments, 1992 JANNAF Propulsion Meeting, Volume II, Fort Benjamin Harrison, Indianapolis, IN, 24-27 February 1992, Phillips Laboratory, Edwards AFB, CA

(3) Katzakian, A., Emulsion Propellant Technology Program (Redirected) Final Report, Air Force Phillips Laboratory's Report # PL-TR-91-3067, June 1992, Aerojet Propulsion Division

(4) Magann, T. F., Doll, D. W., Clean Propellant Feasibility Motor Demonstration Final Report, Air Force Astronautics Laboratory, Contract F04611-89-C-0024, Thiokol Corporation, January 1990

(5) McDonald, A. J., Bennett, R. R., Hinshaw, J. C., Barnes, M. W., "Chemical Rockets and the Environment," Aerospace America, June 1991

(6) Clean Propellant Development and Demonstration, Contract No. F04611-89-C-0082, Phillips Laboratory, Edwards Air Force Base, CA, April 1989

LOW ACID PRODUCING SOLID PROPELLANTS

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Abstract

The potential environmental effects of the exhaust products of conventional rocket propellants have been assessed by various groups. Areas of concern have included stratospheric ozone, acid rain, toxicity, air quality and global warming. Some of the studies which have been performed on this subject have concluded that while the impacts of rocket use are extremely small, there are propellant development options which have the potential to reduce those impacts even further. This paper discusses the various solid propellant options which have been proposed as being more environmentally benign than current systems by reducing HCl emissions. These options include acid neutralized, acid scavenged, and nonchlorine propellants. An assessment of the acid reducing potential and the viability of each of these options is made, based on current information. Such an assessment is needed in order to judge whether the potential improvements justify the expenditures of developing the new propellant systems.

Introduction

A good deal of effort has been expended in recent years to develop and demonstrate solid rocket propellants which are more environmentally benign. These alternate propellants have often been grouped together and termed 'clean' propellants, but this appellation is misleading and tends to cloud the issue since each of the various propellant options has its own merits and drawbacks. From what is currently known, there are no rocket propellants, liquid oxygen/liquid hydrogen systems included, which are completely benign to the environment. This paper is an assessment of the various low acid solid propellant options either available or at some stage of development, with particular focus on recent solid propellant work. Although most of the published literature (NASA, Prather, Schmalzer (1985, 1986), Potter, Bennett (1992), AIAA), focuses on the environmental impact of burning propellants, it must be kept in mind that the testing and launching of rockets represents only a part of their impact. In order to make a complete assessment of the various propellant systems, one must look at the entire 'cradle to grave' impact. This includes not only the end use of the rockets, but also their manufacture, the manufacture of all the components, the disposal of waste generated in the manufacturing process, and the disposal of unwanted components in the future.

A report issued by the AIAA in October 1991 (AIAA) concluded that the use of rockets with the current production propellants has a very minor impact on the environment. However, in spite of the technical evidence of a very minor environmental impact, if substances emitted during the manufacture or use of rockets are regulated, restricted, or banned, alternate processes or fuel formulations may be required. The example is given (Hawkins) of HCl as an emission product which technically appears to have very little environmental impact, but which has been attacked in the press as a harmful to the environment (Halverson), and which may be subjected to stringent emission regulations in the future.

In order to make a rational decision about which rocket fuel to use for a propulsion system, a detailed cost/benefit analysis must be performed. Changing from a conventional fuel to one of the alternates on the basis of environmental impact does not mean simply pouring the new propellant into a rocket chamber in place of the old fuel. One must also consider the impact to the system performance,

hazards, reliability, cost, operability, material availability, and long term system stability, and decide whether or not the expected improved environmental impact is worth the price.

Discussion

Many more factors besides the specific target environmental issue must be addressed prior to the serious consideration of a propellant for use in a rocket motor. In order for a rocket motor to meet its mission requirements, it must have sufficient thrust to deliver its payload. The performance of a propellant in a given system will be a function of its specific impulse, the mass of propellant used, and the overall system weight. These, in turn, are dependent upon such things as the chemical makeup of the propellant, the propellant density, the motor chamber pressure and temperature, the reproducibility and magnitude of the propellant mechanical and ballistic properties, and the erosion characteristics of the nozzle and insulation materials.

Cost will always be a system driver, especially in commercial launch vehicles. Cost of the raw materials themselves is only a part of the system costs to which the propellant contributes. Manufacturing of motors must be considered. If the process is very labor or time intensive, cost is added, as it is if special environmental conditions for storage of materials or motors are required. The fulfilling all of the environmental regulation requirements, including waste disposal, is becoming increasingly expensive, and may be a major cost driver.

Material hazards before, during, and after mixing, will always be a concern. The propellant hazards classification, 1.1 (detonable at more than a 69 card gap) or 1.3 (non-detonable at more than a 69 card gap), usually impacts propellant formulation development. For example it is questionable whether a class 1.1 propellant (or perhaps even a class 1.1 ingredient in a class 1.3 propellant) would ever be approved for manned flight use in the U.S. Individual material hazards, such as aluminum dusting or isocyanate (propellant curative) toxicity, must be controlled during propellant process.

System reliability has always been a major concern in the rocket industry, and is especially important for manned space flight and very expensive satellite launches. System reliability depends in many ways upon the propellant used, including the reproducibility of propellant ballistic and mechanical properties, the consistency in the propellant ignition, satisfactory safety factors, and the complexity and soundness of the propellant grain design. The operability of a system is important in maintaining mission flexibility and minimizing costs. Questions such as how quickly a motor can be put onto the launch pad and readied for launch, how many environmental restrictions are required, how long the motor may be left on the pad, and how much turnaround time is required after the launch must all be addressed before a propellant system can be used.

Finally, the availability of materials must be considered. A propellant may have all of the properties one desires, but if one or more of its component materials is not readily available in sufficient quantities, it cannot be considered for production. Factors such as the scale of raw material production, the manufacturing location and frequency are important considerations.

The development of 'clean' propellants has been an evolutionary process. The issues of launch site acidification and stratospheric ozone impact were identified and addressed in the Space Shuttle Environmental Impact Statement (NASA). Although the authors were working with limited data, they concluded that both impacts would be minor and the Shuttle program proceeded. The amount of data available on both issues has increased significantly in recent years, but the original conclusions of a minor impact remain the same. However, public awareness of these and other environmental issues has been greatly heightened, as has the number of environmental regulations. As a result, in the 1980s, a number of 'clean' propellant programs were begun to specifically address the acidification

issue. This paper will deal only with the HCl issue. Additional reviews have been published by the author regarding the impacts of chemical propulsion on the stratospheric ozone (e.g. Bennett (1992)).

Acid Production and Propellant Options

The deposition of acidic species on the area around the Space Shuttle launch pads at the Kennedy Space Center and their impact on the local environment is well documented (Schmalzer (1985, 1986)). On a regional or global scale, acid deposition due to the HCl in solid rocket exhaust represents an extremely small portion of acidic species deposited in the atmosphere. If only anthropogenic sources in the U.S. are considered, heating and power production deposit about 33,000 kilotons of acid producing chemicals (mainly sulfur oxides and nitrogen oxides) into the atmosphere annually; transportation about 9,100 kilotons; and industrial processes about 6,100 kilotons (Schwartz). This compares with about 2.3 kilotons (of HCl) from chemical propulsion systems worldwide (1.8 kilotons from U. S. launches) at the 1991 launch rate estimated in the AIAA workshop report. The global impact will be smaller still. HCl is a very common tropospheric species, produced naturally by the reaction of sodium chloride in marine aerosols with atmospheric nitric acid. One estimate is that worldwide, the oceans alone produce about 330,000 kilotons of HCl annually (Symonds).

On a local level, Space Shuttle launches at Kennedy Space Center cause near field (< 2,500 ft) acidification effects due to the SRB (Solid Rocket Booster) exhaust (Schmalzer (1985, 1986)). There are some fish and plant mortalities and a reduction in plant speciation, but only in a very localized area of about 0.08 square miles near each of the two launch pads. Far field acid effects (> 2,500 ft) seem to be limited to leaf spotting as the exhaust plume is dispersed over a wide area.

In order to put the extent of the near field area affected by the HCl into perspective, a comparison was made of the area at the Kennedy Space Center permanently affected by near-field acidification with that affected by buildings, roads, parking lots, launch pads and landing facilities. The KSC buildings occupy 0.13 sq. miles, which is almost as much area as is affected by the HCl cloud. When the roads, parking lots, launch pads and landing facilities are included, an area of 1.6 sq. miles has been covered. This means the HCl from the SRB exhaust permanently affects the flora and fauna of an area which is about 10 percent as large as the area completely covered by other facilities.

In spite of what seems to be a relatively minor impact, the development of reduced acid propellants continues for several reasons. The technical evidence notwithstanding, the perception reflected in the popular press has been that the problem is significant. At least two lawsuits were filed to prevent NASA from proceeding with the testing of the Advanced Solid Rocket Motor (ASRM) in Mississippi on environmental grounds (Space News). Political decisions are often made on the basis of public opinion rather than technical facts. Since HCl emissions may very well be regulated in the future, it is important to have a back-up system from which HCl emissions have been substantially reduced. Finally, though it appears unlikely at this time, there may be long-term environmental effects of HCl which have not yet been detected, and which would make the use of low HCl propellants desirable.

Several options exist for reducing the amount of HCl in the propellant exhaust. They can be subdivided into various families: neutralized, scavenged, and nonchlorine; each of which has its own unique challenges and advantages which are a function of the chemistry and physical properties of the materials used. Table I lists the major categories of solid propellants to be discussed, their primary constituents and exhaust products, and their density and specific impulse. For the products listed in Table I, it was assumed that all of the hydrogen and carbon monoxide emitted react with atmospheric oxygen to form water and carbon dioxide. This is likely true for altitudes below about 25 km. Model calculations also suggest that some of the HCl produced in the motor chamber is converted to Cl_2 in the

TABLE I
The Composition and Exhaust Products of Conventional and Alternate Solid Propellants

Propellant Ingredient	Purpose	Space Shuttle	Nominal Class 1.1	Neut.	Scav.	HAN/AN	Nitrate Ester Plast. AN	GAP/AN	PGN/AN
PBAN/ECA	Binder	14.00							
HTPB/NCO	Binder			12.00	10.00				
PEG/NCO	Binder		7.00						
PGA/NCO	Binder						5.91		
GAP/NCO	Binder							20.90	
PGN/NCO	Binder								20.90
PVA	Binder					15.00			
NG	Plasticizer		17.00						
BuNENA	Plasticizer						16.09		
AP	Oxidizer	69.75	8.00	65.70	29.54				
AN	Oxidizer					3.25	51.00	52.00	52.00
HMX	Oxidizer		47.00		15.00				
$NaNO_3$	Oxidizer				23.21				
HAN	Oxidizer					57.20			
$KClO_4$	Oxidizer							5.00	5.00
Aluminum	Fuel	16.00	20.00		22.00	20.00	13.50	21.00	21.00
Magnesium	Fuel			22.00			13.50		
MNA	Stabilizer		0.50						
2-NDPA	Stabilizer		0.20						
NC	Crosslinker		0.30						
Fe_2O_3	Ball. Accel.	0.25		0.30	0.25			0.60	0.60
Carbon	Additive							0.50	0.50
H_2O	Additive					0.33			
Amphos	Additive					0.65			
BIPY	Additive					0.65			
GNX	Additive					2.60			
Dequest	Additive					0.32			
Isp(vac)		285.3	295.6	281.1	273.3	279.9	283.9	277.9	278.1
Density		0.06408	0.06707	0.06075	0.06898	0.06321	0.05910	0.06398	0.06578
Isp*Density$^{0.6}$	54.87	58.43	52.35	54.94	53.39	52.01	53.40	54.33	
Major Exhaust Products				Mass Produced/100g Propellant Burned[a]					
HCl		19.22	2.11	0-14.5[c]	1.44	0.89		0.18	0.39
Cl_2[d]		2.14	0.23	<1.4	0.16	0.10		0.02	0.04
H_2O		28.35	21.95	28.34	22.03	37.80	36.88	33.66	31.82
CO_2		41.67	55.18	37.55	40.04	33.44	34.20	30.73	26.66
Al_2O_3		30.43	36.48		41.69	37.96		39.89	39.98
NOx[b]		6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
N_2		8.78	21.42	6.72	13.21	19.24	21.12	26.76	20.89
$Mg(OH)_2$				30-45[c]			17.73		
$MgCl_2$				5-22[c]					
NaCl					12.08				
Na[O]*					>1.50				
KCl								2.28	1.82
K[O]*								>0.18	>0.33
$MgAl_2O_4$							35.60		

TABLE I (cont.)
The Composition and Exhaust Products of Conventional and Alternate Solid Propellants

Propellant Ingredient	Purpose	TEP[f]	Minimum Smoke
Nitrocellulose	Binder	yes	
PEG/NCO	Binder		3.00
PCP/NCO	Binder		2.91
BTTN	Plasticizer	yes	15.23
TMETN	Plasticizer		7.61
AN	Oxidizer	yes	
HMX	Oxidizer		20.25
RDX	Oxidizer		47.25
Aluminum	Fuel	yes	
MNA	Stabilizer	yes	0.50
Various Additives			3.25
Isp(vac)		285	268.6
Density		0.066	0.06187
Isp*Density$^{0.6}$		55.80	50.58

Major Exhaust Products	Mass Produced/100g Propellant Burned[a]
HCl	
Cl_2[d]	
H_2O	28.01
CO_2	73.81
Al_2O_3	1.00
NOx[b]	6.0
N_2	29.65
Pb	1.35

[a]Assumes all H_2 is converted to H_2O, and all CO to CO_2.
[b]NOx estimate for Shuttle based on data in (Karol). Other propellants assumed to produce the same relative amount.
[c]Actual values depend on effectiveness of neutralization process. Lab data suggests HCl produced is at least less than 3%. MgO is an nozzle exit species of this propellant. The table assumes that all MgO is hydrated and converted to $Mg(OH)_2$. Thermochemical calculations predict 4.8 g $MgCl_2$/100 g propellant at the nozzle exit plane. 22 g will be produced if all HCl is neutralized.
[d]Thermochemical code predicts essentially no Cl_2 at the nozzle exit, but some is produced during afterburning. Measurements of captured exhaust plumes of Shuttle propellant at Thiokol show that about 10% of the HCl is converted to Cl_2. The same HCl/Cl_2 ratio is assumed for other propellants.
[e]Thermochemical code predicts elemental sodium or potassium at the nozzle exit plane. They will certainly be oxidized in the plume, but the final compounds produced are not known.
[f]Formulation is proprietary, however, propellant contains no chlorine.

plume. Various estimates of the extent of this reaction have been given (NASA, Hoshizaki). The values given in Table I assume that the models for HCl vs. Cl_2 cited in (NASA) are correct since they are consistent with experimental measurements made at Thiokol Corp. The NO_x production from afterburning is based on data given by Karol et al.(Karol), and is fairly consistent with NO_x measurements obtained from an airborne flythrough of a Titan launch (Stewart).

Neutralized Propellants

The first of the three families of reduced acid propellants relies on simple acid-base chemistry to neutralize the HCl in the exhaust plume (Doll). In the neutralized propellants, magnesium is used in the place of aluminum as the metal fuel. All other ingredients remain essentially the same. Approximately 70 percent of the formulation by weight is ammonium perchlorate, 12-14 percent is polymeric binder, and 16-18 percent is magnesium. As the propellant burns, the magnesium is oxidized to form magnesium oxide (eq. (1)). Upon contact with water, the magnesium oxide forms magnesium hydroxide (eq. (2)). This is a very basic material, which reacts readily with HCl to form magnesium chloride and water (eq. (3)).

$$Mg + O \text{ --> } MgO \quad (1)$$

$$MgO + H_2O \text{ --> } Mg(OH)_2 \quad (2)$$

$$Mg(OH)_2 + 2HCl \text{ --> } MgCl_2 + H_2O \quad (3)$$

It was shown in the laboratory and in small scale motors that the neutralization reaction does indeed occur, and also that water is an essential component of the mechanism. The lab data suggested that the neutralization reaction has the potential of completely removing HCl from the exhaust plume, almost certainly if a $MgO/H_2O/HCl$ aerosol is formed. In order to better assess the extent of neutralization in a more realistic environment, a 2000 lb motor containing this propellant was static tested, with an array of HCl measuring devices, including an airborne instrument platform (Bennett (1993)). It was found in this test that only about 1/2 of the HCl was neutralized, apparently because of the rapid dispersion of the exhaust cloud. For aerosol deposition such as that observed with the Shuttle launches as the plume mixes with the sound suppression water, the data still suggest that complete neutralization would occur.

As outlined above, there are several other factors which must be evaluated prior to seriously considering the use of a propellant in a rocket motor. For the neutralized propellant, the processing is essentially the same as conventional propellants, so the waste generation and disposal would remain unchanged. The specific impulse of the neutralized propellant is close to that of conventional aluminized propellants (281.8 vs. 285.3), but the density is considerably lower (0.0591 vs. 0.0641 lb/in^3). It is unlikely that this would be an acceptable option for a retrofit of an existing volume limited motor, but it would be a potential candidate for a new system designed specifically for its properties. Table I compares the theoretical performance for a typical first stage or booster application for the nominal Class 1.3 Space Shuttle propellant along with the various alternate formulations. For this application, it is estimated that the performance is equal to the product of the specific impulse and the density raised to the 0.6 power. Among the ten propellants evaluated, the neutralized propellant ranks eighth in total performance in a volume limited system because of its low density.

The cost of such a system would be about the same as conventional motors, since all materials but one are the same. The only additional processing concern would be that the magnesium needs to stay as dry as possible. An extensive hazards characterization has been performed on this propellant under the Solid Propulsion Integration and Verification (SPIV) program (Cragun), and has shown it to be Class 1.3 similar to the Space Shuttle and Peacekeeper Stage I propellants. A full scale propellant and bondline characterization study has been performed, and shows the neutralized propellant to be

robust and versatile. Propellant aging capability is still largely unknown. From the available data, reliability, operability and material availability should be comparable to existing systems. Of the proposed alternate solid propellants, the neutralized and scavenged propellants are the most mature.

Scavenged Propellants

The second of the reduced acid propellant families are the scavenged propellants. In these propellants, sodium nitrate is used in place of about 1/2 of the AP. As the propellant burns in the rocket chamber, the sodium ions scavenge most of the chloride ions to form NaCl, preventing them from forming HCl. Laboratory measurements and theoretical calculations indicate that the HCl emissions are reduced by about an order of magnitude from conventional propellants. An accurate quantification of the acid reducing capability of the scavenged propellants during an open air test has not yet been made, although there are plans to do so in the future.

Replacement of AP with sodium nitrate exacts a specific impulse penalty. Depending on the formulation, 15 - 20 seconds are lost compared to conventional Space Shuttle propellant. Some of this (5 - 10 seconds) is regained if an energetic nitramine, such as HMX, is used (Table I), but attaining Space Shuttle Isp with a sodium nitrate propellant is not realistic. However, because of its increased density of sodium nitrate over AP, a scavenged propellant appears to be practical in a volume limited, booster/first stage application. The loss in specific impulse can be compensated for by virtue of the fact that a greater mass of propellant can be used in the motor. It appears that essentially the same overall performance as the Space Shuttle can be achieved in a scavenged propellant by a combination of the addition of HMX and a higher solids loading. Table I shows that a scavenged propellant formulated at 90 percent solids and 15 percent HMX has total performance (Isp x density$^{0.6}$) of 54.94 compared with Space Shuttle's 54.87.

As with the magnesium propellant, conventional processing techniques would be used for the scavenged propellant, with about the same amount of waste generation. Material costs would be slightly higher if HMX were used. Manufacturing costs might also be somewhat higher because a larger number of ingredients means more storage space and material control work. Though a complete hazards characterization has not yet been performed, the tests run to date show the hazards of the scavenged propellants to be about the same as those of conventional class 1.3 composite propellants. HMX is a Class 1.1 material, but it can be used in moderate amounts without making the propellant Class 1.1. In fact at least 15 percent HMX can be added without detonating a zero card gap pipe.

Sodium nitrate formulations have been scaled up to full scale (600 gallon) mixes, and have been tested in motors of various sizes up to about 2000 lb, showing the expected properties. Mechanical properties are not as robust as the neutralized propellants, with somewhat lower strain capability, but they appear to be about as good as the conventional Minuteman Stage I propellant (30 percent strain and 130 psi maximum corrected stress). The reliability of the propellant should be reasonably good, though the increased number of ingredients may result in somewhat higher propellant variability, but this is purely speculative. Operability and availability of materials are likely to be about the same as for conventional propellants.

Reduced Chlorine Propellants

The final family of reduced acid propellants does not depend on the acid neutralization or scavenging reactions to reduce the acid in the exhaust, it simply contains little or no chlorine in the first place. A wide variety of approaches exist for reducing the amount of chlorine in the propellants, and each presents its own set of challenges or drawbacks. In concept, the simplest approach is to replace

the AP with a nonchlorine oxidizer.

For class 1.3 composite propellants, ammonium nitrate (AN) has been extensively studied. More recently, the more energetic hydroxyl ammonium nitrate (HAN) has been used in conjunction with AN to form a eutectic mixture which is a liquid at room temperature. This liquid oxidizer has then been mixed with polyvinyl alcohol and aluminum (if desired) to form a gel propellant (Katzakian). Other potential oxidizers such as ammonium dinitramide (ADN) are under preliminary investigation on the lab scale. Since the replacement of AP by AN results in a substantial performance loss and very limited ballistic tailorability, more energetic binder and plasticizer systems are being investigated.

AN presents other challenges in addition to lower performance capability. Studies to date have shown little ballistic or mechanical property tailorability. AN propellant burn rate is typically quite low, and burn rate slope quite high. The mechanical property capability of AN propellants has generally been rather poor, with strains in the 10 - 20 percent range at a stress level of 160 psi (Weyland), or about 30 percent at a stress level of 80 psi (Bradford). At equivalent solids loading, processing is generally more difficult than AP propellants, and AN has a number of crystalline phase transitions in the temperature range normally associated with propellant cure and storage requirements. Since the different phases have different densities, if the AN crystalline phase is not stabilized by an additive, the propellant grain tends to increase in volume as it is temperature cycled, disrupting its integrity. AN is also more moisture sensitive than AP. While none of these difficulties appears insurmountable, they do represent a significant challenge to propellant chemists and engineers. AN propellants have been static tested in at least 70 lb. motors.

As mentioned, energetic polymers and plasticizers have been considered for some time in connection with improving the performance of AN oxidized propellants. Among those polymers considered are glycidyl azide polymer (GAP), polyglycidyl nitrate (PGN), polyoxetanes, and polynitramines. Some of these materials are available in large enough quantities to be considered for production propellants.

One promising new approach under investigation by Thiokol, given the acronym TEP, is to use a nitrate ester to plasticize and gel nitrocellulose. Although this ingredient combination has been used for quite some time, unique processing techniques have imparted greatly improved mechanical properties, with strains of about 100 percent and stresses approaching 1000 psi. Aluminum and ammonium nitrate can be added to improve performance, with performance identical to Space Shuttle easily achievable. Minimum signature TEP formulations have been shown to be Class 1.3. The processing and gel mechanisms of TEP and other gelled solid propellants are considerably different than conventional propellants. No chemical cross linking is employed, giving them the potential to significantly reduced propellant waste streams. In addition, the TEP propellant has an indefinite working life and is insensitive to low levels of moisture contamination. Nitrate ester plasticizers have been used in other AN propellant formulations as well. These propellants show some promise, but are not mature enough to know if they are viable for production motors.

The HAN/AN gel propellants exhibit greatly improved strain capability (in excess of 250 percent) over conventional class 1.3 composite propellants (Katzakian). A HAN/AN propellant has been tested in an 800 lb Super BATES motor at Edwards AFB. The HAN/AN/PVA binder system is water soluble, so motors could conceivably be washed out easily; however, this very fact raises concerns about aging this propellant with exposure to atmospheric humidity. Both the specific impulse and the density of the HAN/AN propellants are lower than conventional Shuttle propellant, so motors could not likely be retrofit with them. While some success has been achieved in tailoring the HAN/AN propellant burn rate, the burn rate exponent remains higher than is desirable (> 0.6).

Cost, reliability, operability, hazards, aging characteristics, and material availability all remain

open issues with the Class 1.3 AN and gel systems. They are considerably less mature than the scavenged and neutralized propellants. While ADN looks promising on paper, it is currently available in very limited quantities in the U.S., although the Soviet Union apparently produced a large amount of the material for some time (Pak). It still appears that the practical use of ADN in U.S. rocket motors is at least several years distant.

If the Class 1.3 requirement does not apply, conventional high energy, Class 1.1 propellants can be used in order to reduce the HCl in the exhaust. These generally consist of polyethylene or polyester binders, plasticized with nitrate esters. HMX is used as the main solid oxidizer, with only 8-10 percent AP present for ballistic tailoring. These propellants have been used for years in submarine launched ballistic missiles such as C-4 and D-5, and in tactical minimum smoke applications. When aluminized, they outperform the conventional class 1.3 composite propellants (Table I), are easily processed and have excellent mechanical and ballistic property capabilities, both as produced and with aging. They typically cost more than Class 1.3 propellants, because of the price of the nitrate esters and the HMX. Reliability and availability of materials are similar to Class 1.3 propellants. Their major perceived drawback is their hazards properties, since by definition they will detonate at greater than 69 cards, and hence have very small critical diameters. This could impact operability for space launch systems. Despite the potential for detonation, motors loaded with Class 1.1 propellants enjoy a very good safety record in the field; however, none of the current space launch vehicles use this family of propellants.

In summary, there are several approaches to reducing the acid content of the exhaust plume. The most mature are the conventional high energy Class 1.1 propellants, which have been in production for many years, but are viewed as being more hazardous than the Class 1.3 propellants. For the Class 1.3 propellants, the neutralized and scavenged propellants are the most mature, having been made in full scale mixes, cast and tested in large subscale motors, and characterized extensively. The AN propellants, both gel and conventional, are not as mature, and have more technical challenges to be overcome. The extent of acid reduction by the magnesium neutralized propellants depends on the environmental conditions under which it is used, and is in the range of 0 - 10 percent. The sodium nitrate and high energy propellants have the potential of reducing the HCl in the exhaust by about an order of magnitude, to 1-3 percent, while the nonchlorine propellants eliminate it entirely.

References

1. AIAA, 'Atmospheric Effects of Chemical Rocket Propulsion,' October 1991, Report of an AIAA Workshop held in Sacramento, California, 28-29 June, 1991.

2. Bennett, R. R., Wallace, I. A., Richtsmeier, S. C., and Goldstein, N., 'Characterization of the Exhaust Cloud of a 37-Inch Magnesium Fueled Rocket Motor,' 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, Las Cruces, NM, August 10, 1993.

3. Bennett, R. R., Hinshaw, J. C., and Barnes, M. W., 'The Effects of Chemical Propulsion on the Environment,' Acta. Astronautica **26(7)**, 531 (1992).

4. Bradford, D. J., et al., 'Clean Propellant Development Demonstration,' report prepared for the Astronautics Laboratory (AFSC), Contract No. FO4611-89-C-0082, Report Nos. 13 and 16, 1991.

5. Cragun, B. C., 'Hazards Properties of a Magnesium Neutralized Clean Propellant,' paper presented at the 1992 JANNAF Prop. Sys. Haz. Sub. Conference, Silver Springs MD, April 1992.

6. Doll, D. W. and Lund, G. K., 'Magnesium-neutralized Clean Propellant,' paper No. AIAA-91-

2560, presented at the 27th AIAA Joint Propulsion Conference, Sacramento, CA June 24-26, 1991.

7. Halverson, T., 'Proposed Rocket Tests Puts NASA on the Defensive,' Flor. Today, Oct. 28, 1991.

8. Hawkins, T. W. and Wilkerson, B. E., 'Environmental Propellant: Current Issues and Assessment,' 1992 JANNAF Propulsion Meeting, Indianapolis, Indiana.

9. Hoshizaki, H. et al, 'Aircraft Wake Microscale Phenomena,' in The Stratosphere Perturbed by Propulsion Effluents,' Climate Impact Assessment Program, Monograph 3, DOT-TST-75-53, U. S. Department of Transportation, September 1975, p. 2-68.

10. Karol, I. L., Ozolin, Y. E., and Rozanov, E. V., 'Effect of Space Rocket Launches on Ozone and Other Atmospheric Gases,' presented at a European Geophysical Assoc. Conference, Wiesbaden, 1991.

11. Katzakian, A., Jr., 'Alternate Clean Propellant Development,' report prepared for the Astronautics Laboratory (AFSC), Report No. LHL-M-04, 20 October 1990; Katzakian, A., Jr., Bruenner, R. S., Clark, G. M., Grix, C. E., Lou, R. L., and Oberth, A., E., 'Development of a New High Performance Clean Solid Propellant,' paper presented at the 1992 JANNAF Propellant Development and Characterization Subcommittee Meeting, Kennedy Space Center, Florida, 7-9 April, 1992.

12. NASA, 'Space Shuttle Program Environmental Impact Statement,' April, 1978.

13. Pak, Z. 'Some Ways to Higher Environmental Safety of Solid Rocket Propellant Application,' Paper #AIAA-93-1755, AIAA 29th Joint Propulsion Conference, Monterey, CA, June 28-30, 1993

14. Potter, A. E., 'Environmental Effects of the Space Shuttle,' J. Environ. Sci., **21**, 15 (1978).

15. Prather, M., Garcia, M. M., Douglass, A. R., Jackman, C. H., Ko, M. K. W., and Sze, N. D., 'The Space Shuttle's Impact on the Stratosphere,' J. Geophys. Res. **95(D11)**, 18,583 (1990).

16. Schmalzer, P. A., Hinkle, C. R., and Breininger, D., 'Effects of Space Shuttle Launches STS-1 Through STS-9 on Terrestrial Vegetation of John F. Kennedy Space Center, Florida,' NASA Tech.

17. Schmalzer, P. A., Hinkle, C. R., and Dreschel, T. W., 'Far-Field Deposition from Space Shuttle Launches at John F. Kennedy Space Center, Florida,' NASA Tech. Mem. 83104 (1986).

18. Schwartz, S. E., 'Acid Deposition: Unravelling a Regional Phenomenon,' Science **243**, 753 (1989); Robinson, E. and Robbins, R. C., 'Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants,' Stanford Research Institute, Report SRI Project PR-6755, February 1968. Supplemental Report, June, 1969; National Acid Precipitation Assessment Program, 'Interim Assessment: The Causes and Effects of Acidic Deposition,' (Government Printing Office, Washington, D. C. 1987).

19. Space News, 'Lawsuits Threaten ASRM Tests,' November 4-10, 1991.

20. Stewart, R. B. and Gomberg, R. I., 'The Production of Nitric Oxide in the Troposphere as a Result of Solid-Rocket-Motor Afterburning,' NASA Technical Note D-8137, March 1976.

21. Symonds, R., Rose, W., and Reed, M., 'Contribution of Cl and F Bearing Gases to the Atmosphere by Volcanoes,' Nature **334**, 415 (1989).

22. Weyland, H. H. and Miller, R. R., 'Clean Propellant for Large Solid Rocket Motors,' Final report prepared for the Astronautics Laboratory (AFSC), Report No. AL-TR-90-016, 1990.

IMPROVED HYBRID ROCKET FUEL

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ABSTRACT

McDonnell Douglas Aerospace, as part of its Independent R&D, has initiated development of a clean burning, high performance hybrid fuel for consideration as an alternative to the solid rocket thrust augmentation currently utilized by American space launch systems including Atlas, Delta, Pegasus, Space Shuttle, and Titan. It could also be used in single stage to orbit or as the only propulsion system in a new launch vehicle. Compared to solid propellants based on aluminum and ammonium perchlorate, this fuel is more environmentally benign in that it totally eliminates hydrogen chloride and aluminum oxide by products, producing only water, hydrogen, nitrogen, carbon oxides, and trace amounts of nitrogen oxides. Compared to other hybrid fuel formulations under development, this fuel is cheaper, denser, and faster burning. The specific impulse of this fuel is comparable to other hybrid fuels and is between that of solids and liquids. The fuel also requires less oxygen than similar hybrid fuels to produce maximum specific impulse, thus reducing oxygen delivery system requirements.

Introduction

The nineties is the decade in which new governmental regulations drove industry to develop and utilize alternative, more environmentally benign products and processes. In the area of rocket propulsion, one effect of the peace dividend has been a reduction in military funding for systems designed to meet military needs, leaving an increased emphasis on commercial launch systems. As a result, technology drivers are being broadened from those of the military, which emphasize low volume and long term storage coupled with immediate readiness, to those established or anticipated to be established by regulatory agencies, which place additional emphasis on safety and being more environmentally benign.

Propulsion Background

The standard rocket propulsion options, the technologies around which all launch systems in use today have been designed, comprise two well defined categories--solids and liquids. Solids tend to be easily stored for considerable periods of time, are smaller, are less expensive to develop, are less expensive in mass production, and are available for use at a moment's notice. However, with minor exceptions, they cannot be turned off once ignited until they have completed propellant burnout. In contrast, liquids allow stop, start, restart, and throttling capability, and are favored for launch vehicle main engines. Commercial systems in use today - - Delta (figure 1), Atlas, and Titan, were

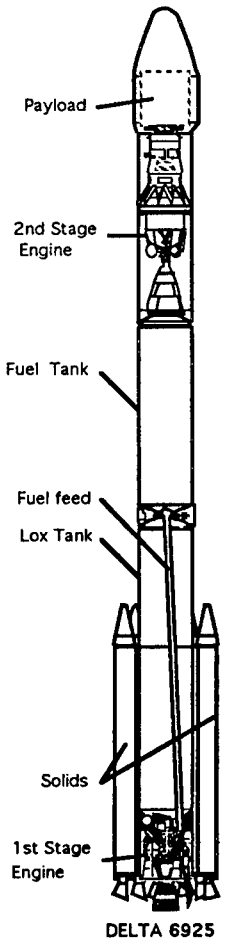

FIGURE 1. DELTA ROCKET

on a hydrocarbon binder system filled with a second hydrocarbon of a slightly different composition. The performance of the MDA hybrid fuel compared to that of the Government/Industry Team's hybrid fuel as well as another possible propulsion alternative is shown in Table 2. The specific impulse developed by the MDA hybrid fuel system compares favorably with others in Table 2. It can be seen that the specific impulse of hybrid fuels is substantially higher than that of typical solids, and is very close to that of existing liquid systems.

Analysis Conditions: Shifting equilibrium, chamber pressure of 1000 psia, solid--70% AP and 18% Al, O/F ratios for RP-1 and hybrids 2.56, 2.4, and 2.0 respectively.

One of the advantages of the MDA hybrid fuel is its higher density compared to other fuels as shown in Table 3. The reason the Space Shuttle needs such a large external tank is that liquid hydrogen has a very low density and occupies a relatively large volume for a given weight. The higher density of the improved hybrid fuel means that the motor case to hold it can be smaller than that required for other hybrid fuels, enabling greater system integration capability with the launch vehicle.

Another advantage of the improved hybrid fuel is its lower oxidizer requirement as shown in table 4. The lower oxygen requirement is advantageous in that a smaller oxygen tank can be used and either a smaller pump or less pressurant will be required to move it, thus reducing weight and cost.

TABLE 1. MOLE PERCENT OF CHEMICAL SPECIES IN ROCKET EXHAUST (AT EQUILIBRIUM)

Exhaust Product	Typical Solid Propellant	MDA Hybrid Propellant
HCl (hydrogen chloride gas)	16.1	none
Al_2O_3 (solid particulate)	9.1	none
CO (carbon monoxide gas)	22.4	27.6
CO_2 (carbon dioxide gas)	1.7	23.2
H_2O (water vapor)	12.4	34.8
H_2 (hydrogen gas)	29.1	6.9
N_2 (nitrogen gas)	8.2	6.2
Total percent accounted for	99.0	98.7

TABLE 2. COMPARATIVE SPECIFIC IMPULSE (I_{SP}) OF DIFFERENT PROPELLANTS IN LBF SEC/LBM

	Solid Propellant	Liquid (RP-1/ O_2)	Government/ Industry Team Hybrid	MDA Hybrid
1 atm	263.1	304	299.2	299.1
Vacuum	288.3	331.2	326.3	326.3

TABLE 3. COMPARATIVE DENSITIES OF DIFFERENT PROPELLANTS

	Liquid Hydrogen	Liquid RP-1	Government/ Industry Team Hybrid	MDA Hybrid
Density in g/ml	0.07	0.81	1.0	1.1

TABLE 4. COMPARATIVE O/F RATIOS FOR DIFFERENT FUELS

	Liquid RP-1	Government/ Industry Team Hybrid	MDA Hybrid
O/F ratio at maximum Isp	2.56	2.4	1.9-2.0

The Hybrid Alternative

Hybrid rocket propulsion is an alternative in which hazardous and environmentally less desirable solid rocket propellants containing ammonium perchlorate can be replaced with a much safer, relatively inert, environmentally benign fuel to be burned with oxygen. A hybrid rocket propulsion system is shown in figure 4. Some of the salient features are 1) the fuel is stored adjacent to the nozzle in what becomes the combustion chamber analogous to solid motors, 2) the total volume of the hybrid motor will be intermediate between a solid and a liquid designed to produce the same total impulse, 3) only the oxidizer needs to be moved to the combustion chamber during operation reducing the number of moving parts compared to an all liquid system, and 4) the complex engine is replaced with a much simpler combustion chamber.

Hybrids--in the form of a solid fuel burned with fluid oxygen--embody many of the advantages of solids. These are a) lower cost via relatively easy design and fabrication to virtually any intermediate size and b) relative simplicity compared to all liquid propulsion systems, since half of the pumping and piping as well as the engine have been eliminated. Hybrids are more advantageous than solids in that they are less costly to handle and process since they are not energetic. From a pollution standpoint, hybrid fuels are advantageous because they can easily be formulated to contain only carbon, hydrogen, oxygen, and nitrogen, (just like liquid fuels) and thus produce primarily water, oxides of carbon, hydrogen, and nitrogen--relatively benign species--during operation. While oxides of nitrogen are possible, the results of analysis obtained via the SPP (Standard Performance Prediction Program) indicate that they are very minor products. Results from this code also show that hybrid systems deliver higher specific impulse than solids.

McDonnell Douglas Aerospace--Huntsville has formulated and tested an advanced family of hybrid rocket fuels. These fuels contain only carbon, hydrogen, oxygen, and nitrogen making them clean burning. The fuels contain no oxidizing species, making them safe to handle, process, and store. The hybrid propulsion system can be started, stopped, restarted, and throttled, and it exhibits more design flexibility than existing hybrid fuels. Tests to date, both in the MDA program and elsewhere, indicate that limited cracks, debonds, or voids in the fuel grain lead to only moderate, slowly developed increases in pressure, making operation safer. These characteristics

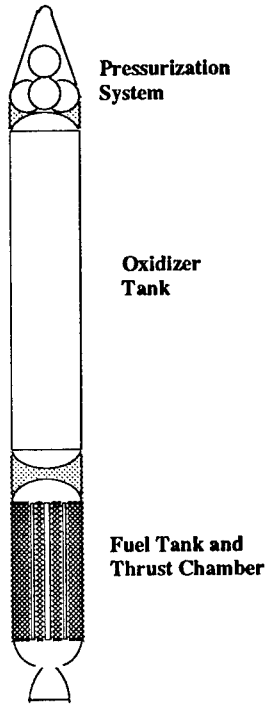

FIGURE 4 HYBRID PROPULSION FOR A SPACE LAUNCH VEHICLE

enable a much wider variety of design options as well as a significantly lowered environmental impact for a rocket propulsion system compared to commercialized solid propulsion technologies.

Characteristics of the Improved Hybrid Fuel

The exhaust products of a typical solid propellant are compared with those of one of the MDA hybrid propulsion options (fuel plus oxygen) in Table 1. The solid propellant formulation is an 18% aluminum, 70% ammonium perchlorate composition, with the percentages being weight percents. The hybrid fuel is burned at an oxidizer to fuel (weight ratio) of 2.0, the ratio at which the specific impulse is maximum. It can be seen that by changing to a hybrid propulsion system which was formulated to be clean, all HCl and Al_2O_3 are eliminated from the exhaust products. The more hazardous of the two, HCl, is eliminated by replacing the solid oxidizer, ammonium perchlorate, with oxygen. Aluminum was also deliberately removed from this particular hybrid formulation, thus eliminating aluminum oxide from the exhaust.

The hybrid fuel formulation currently being examined by the NASA Marshall Space Flight Center Government/Industry Team is based

Solid propellant is significantly more dense than the components in liquids. Typical solid propellants used in thrust augmentation have densities of 1.84 g/cc. As a result the volume required to hold solid propellant producing a given amount of total impulse is significantly smaller than the volume required for a liquid system designed to produce the same total impulse.

Solid propellants fall into two general types from a safety standpoint. These are class 1.1 and class 1.3, which are explosive hazard classifications. Class 1.1 propellants can react very rapidly in detonation mode as well as more slowly in deflagration mode. Class 1.3 propellants can only deflagrate. However, the difference is only in the rate of reaction, and a slow detonation is very similar to a rapid deflagration. Technically, a detonation proceeds at a supersonic rate. For some compositions under some conditions, a deflagration can accelerate and become a detonation. Because of the relative hazard potential, class 1.3 propellants are preferable to class 1.1 propellants, and class 1.3 propellants are much more common. The fuel in class 1.3 propellants is usually aluminum, while the oxidizer is usually ammonium perchlorate. Thrust augmentation propellants for Delta, Atlas, Titan, and the Space shuttle are all class 1.3.

Solid propellants consist primarily of a fuel and an oxidizer, intimately mixed at the factory long before flight. In most cases the fuel and oxidizer are held together by some sort of rubbery binder material. The common class 1.3 propellants are prepared by mixing the oxidizer and fuel with a liquid prepolymer and a curative. Prior to cure, the mixture is poured or cast into the combustion chamber or motor case. Such motors are known as case bonded since the propellant is bonded directly to the case. (Technically there are intermediate layers of liner and insulation, but they are all bonded together, and the outside layer is bonded directly to the case wall.) The propellant cures in the motor case which becomes the combustion chamber once the motor is ignited and burned.

Two significant chemical by-products produced when class 1.3 propellants burn are hydrogen chloride and aluminum oxide. Hydrogen chloride is a pollutant which contributes primarily to acid rain. The chlorine portion of the molecule can adversely affect the ozone layer. Particulate aluminum oxide can adversely affect the ozone layer if it is deposited in the stratosphere. However, the total amounts of either of these chemicals generated and deposited by rockets is small compared to that generated by all other sources.

Characteristics of Liquids

Liquid propellant systems consist of fuel and oxidizer which are stored and handled separately until they reach the combustion chamber in the rocket engine. Because they are stored and handled separately, liquids are less hazardous than either solid propellants or solid propellant ingredients, especially the solid oxidizers. The most common liquid fuels are hydrocarbons similar to gasoline or jet fuel. The Delta 6925 uses a hydrocarbon called RP-1, which has a density of approximately 0.8 g/cc. The most common liquid oxidizer is oxygen, which is normally handled as a cryogenic fluid to maximize its density and to limit the weight of the tank required to hold it. The density of liquid oxygen is about 1.1 g/cc. The explosive hazard for liquid systems is generally lower than that for solids as neither the fuel nor the oxidizer can explode by itself. However, mixtures of certain ratios can explode and/or detonate. The primary combustion products formed during engine operation are water, hydrogen, carbon dioxide, and carbon monoxide.

Since the fuel and oxidizer are held separately in the rocket, liquid systems utilize pumps to move the liquids into the engine which consist of the inlets, injector, combustion chamber, and nozzle/exit cone. Starting, stopping, and throttling are controlled primarily by varying the pumping rates. There are a large number of moving parts, many moving at very high speeds.

A diagram of one engine (complete with nozzle and exit cone) that is used in the liquid propulsion portion of a space launch system is shown below in Figure 3. Large inlet pipes and powerful high speed turbo pumps are used to supply the engine with fuel and oxidizer during operation.

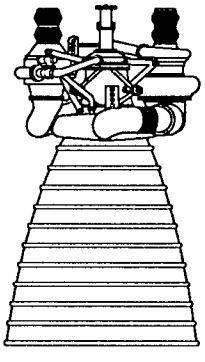

FIGURE 3 LIQUID ENGINE FOR A SPACE LAUNCH VEHICLE

originally designed to use only liquid propulsion. However, over the years, each has subsequently added solid propellant, strap-on, thrust augmentation as a lower cost route to increase payload capability in an incremental fashion.

A good example of a launch system is the 6925 configuration of the McDonnell Douglas Delta Launch System shown in figure 1. This is a two (or three) stage system, with the first stage utilizing a combination of liquids and solids. In the first stage, the weight ratio of oxygen needed for a given amount of fuel is about 2.2. As a result, the oxygen tank is larger than the fuel tank and is positioned closer to the engine. Oxygen is stored as a low temperature, cryogenic liquid, usually referred to as LOX, short for liquid oxygen. At the base of the launch vehicle is the engine in which the fuel and oxygen are combined and burned. The hot gases are ejected through the nozzle throat and expand as they pass through the exit cone shown at the very bottom of the figure 1. Supplementing the liquid main engines, grouped around the base of the first stage are several thrust augmentation units in the form of solid rockets.

The second stage of the Delta 6925 shown in figure 1 consist of a smaller liquid engine with a large exit cone. The much lower external pressure at the high altitudes where this stage operates allows higher engine performance via greater expansion of the hot gases in the large exit cone. The fuel is Aerozine-50, the oxidizer is nitrogen tetroxide, a liquid at ambient temperatures enabling it to be stored without venting which is required for cryogenic liquids. After the second stage is fired, the payload is delivered into a low earth orbit.

In this illustration, the payload is to go into a final higher orbit, and contains a payload assist motor for the last leg of the trip, making the entire package a three stage launch system. Payload assist motors are usually solid rockets, as solid rocket motors are compact and easily stored for long periods of time. This simplifies payload integration, as the payload can be stored and ready well in advance of readying the basic two stage launch system.

Characteristics of Solids

A cross section of the solid rocket motor used for thrust augmentation on the current Delta 7925 Launch System, the Hercules graphite epoxy motor or GEM, is shown in Figure 2. A major difference between the Delta 6925 and the Delta 7925 Launch Systems is that on the 7925, each

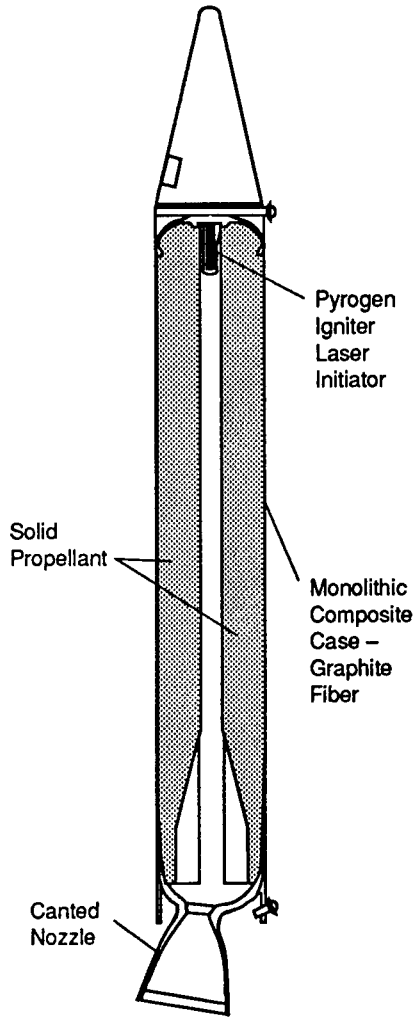

FIGURE 2. THE GRAPHITE EPOXY MOTOR (GEM)

solid propellant motor is larger and utilizes a lightweight graphite epoxy case instead of a metal case.

By examination of figure 2 it can be seen that solid rocket motors are relatively simple, consisting mostly of propellant, case to hold it, an igniter to start it, and a nozzle/exit cone to direct the hot gases. The form of the solid fuel is usually referred to as a propellant grain or a web. In this case, the propellant grain has a hollow core running down the center from the igniter to the nozzle. This type of grain design is commonly referred to as CP, which stands for center perforated. The center perforation is not limited to circular cross sections. The larger open space toward the bottom in this grain indicates some sort of star cross section in part of the grain. The propellant is ignited by an electrical signal and a laser.

McDonnell Douglas has conducted a vigorous IRAD program during 1993 and 1994 to develop these new hybrid fuel formulations. Over 39 motor firings of 2" diameter fuel grains have been conducted with various fuel formulations. The results of the motor firings indicate that the improved fuel exhibits a regression rate approximately twice that of the NASA Marshall Space Flight Center Government/Industry Team formulation. The increase in regression rate will enable a much greater flexibility in grain design. Current regression rate limitations drive the grain design to either a very long, slender, single port grain, or else a complex multiport grain. The increased regression rate will either enable shortening of the single port grain or else a decrease in the number of openings in the multiport design. One net effect will be an increase in the average density since there will be less empty space required in the motor. The resultant decrease in motor size will reduce costs and each launch vehicle integration operations.

During operation the hybrid motor is throttleable and restartable. This provides design flexibility for thrust variation as the vehicle passes through maximum Q compared to solid boosters which provide nearly constant thrust. Test results have also shown that hybrid motors are much less susceptible to overpressurization due to exposure of additional grain surfaces. Cracks in solid propellant grains have a tendency to expose additional propellant surface area which very rapidly produces a positive feedback loop leading to destructive overpressurization. Cracks in hybrid fuel grains have generally been found to lead to only moderate pressure increases since the (fixed) oxygen flow rate limits the total oxidation and formation of additional gas that can occur. In a fairly extreme case which occurred during testing on this IRAD program, grain disintegration and a rapid increase in surface area produced a fairly rapid increase in pressure. However, even under these adverse conditions, detection of the overpressure condition and immediate oxidizer flow shut off resulted in successful corrective action and avoidance of destructive overpressurization.

Potential Uses of Hybrid Rocket Propulsion

Probably the easiest route to implementation of hybrid rocket propulsion technology is through development of thrust augmentation units for use on existing launch systems such as Delta, Atlas, or Titan. The requirements are well defined and the performance of the motor could be extensively validated via a qualification program.

New propulsion systems could also be designed to take advantage of the unique characteristics of the hybrid. One possibility is in the single stage to orbit, reusable launch system. The first iteration in design based the propulsion system entirely on hydrogen/oxygen, a system with a large volume requirement. Subsequent designs have included use of a second liquid fuel with a density much greater than hydrogen, which trade studies have shown results in a gain in overall performance. Since the MDA hybrid fuel exhibits another step up in density, the use of MDA hybrid fuel as part of the SSTO propulsion system should lead to a further increase in system performance. MDA is in the process of evaluating this possibility.

A third possibility for use of hybrid rocket propulsion is a stand alone hybrid for a new expendable launch system. The American rocket Company in conjunction with Martin Marietta plans to fly a small system of this type in 1996.

Ancillary Benefits

In the history of technological development, it has generally been performance first cost second. First determine if it can be done, then determine if it can be done cost effectively. Total cost is made up of indirect as well as direct components. It is easy to obtain cost of raw materials in dollars per pound, and the improved hybrid fuel plus oxygen is significantly cheaper than solids as well as being cheaper than alternative hybrid formulations. However, the total costs of using class 1.3 solid propellants include loss of facilities and buildings, need for additional buildings and land for remote storage and remote processing, and much travel to and from between remote buildings as well as accidents that are inevitable even with stringent attention to safety and quality procedures that have been established for working with energetic materials.

Summary

A family of promising, new, improved hybrid fuels has been developed which offers a number of advantages over solid propellants which they can replace. These advantages include a more environmentally benign system via elimination of hydrogen chloride and aluminum oxide as by-products, lower cost, higher density, higher degree

of safety, lower oxygen requirements, and higher regression rates. The advantages are obtained without sacrificing performance as measured by specific impulse. Hybrid propulsion utilizing MDA's new higher performance fuel offers unique characteristics which can potentially increase the performance of the next generation SSTO, or lower costs in existing launch systems as they develop and utilize new larger thrust augmentation units in order to deliver the larger payloads of tomorrow.

Acknowledgments:

MDA-HSV wishes to thank Professor M. K. Hudson, PhD candidate R. B. Shanks, and co-workers in the Department of Electronics and Instrumentation, University of Arkansas at Little Rock for assistance in fuel grain fabrication and for conducting motor firing tests.

All values involving rocket motor exhaust products or performance were generated using "The Solid Propellant Rocket Motor Performance Prediction Computer Program" (SPP), produced for the United States Air Force by G. R. Nickerson, D. E. Coats, A. L. Dang, S. S. Dunn, D. R. Berker, R. L. Hermsen, and J. T. Lamberty and documented in AFAL-TR-87-078.

The work described herein was performed entirely on MDA-HSV IRAD funding. However, MDA-HSV has recently been awarded a NASA MSFC contract to further refine the advanced hybrid fuel formulations and to validate performance in 11" hybrid motors.

Technology Transfer Into the Solid Propulsion Industry

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Abstract

This paper is a survey of the waste minimization efforts of industries outside of aerospace for possible applications in the manufacture of solid rocket motors (SRM) for NASA. The Redesigned Solid Rocket Motor (RSRM) manufacturing plan was used as the model for processes involved in the production of an SRM. A literature search was conducted to determine the recycling, waste minimization, and waste treatment methods used in the commercial sector that might find application in SRM production. Manufacturers, trade organizations, and professional associations were also contacted. Waste minimization efforts for current processes and replacement technologies, which might reduce the amount or severity of the wastes generated in SRM production, were investigated. An overview of the results of this effort are presented in this paper.

Introduction

This paper was prepared under the direction of NASA/MSFC in support of the NASA Operational Environment Team headquartered at MSFC. This paper was prepared from a Technical Report, by the authors, produced for the Solid Rocket Motor Design Branch of the Propulsion Laboratory at NASA/MSFC [1]. The objective of this paper is provide a review of lessons learned from the commercial sector that might be applicable to the SRM industry. Issues related to propellant disposal technology and the operational uses of SRMs were excluded from this study due to the large ongoing efforts in these areas elsewhere.

The RSRM program was chosen as the model for this paper because of it's large size and obvious importance to NASA. Thiokol Corporation has an ongoing waste minimization effort and has reported good progress in reducing and eliminating unnecessary waste. The intention of this paper is not to evaluate the waste treatment or minimization efforts at Thiokol. However, it is hoped this paper will provide some useful ideas for the SRM manufacturers in waste minimization, treatment, new technologies, and recycling.

This effort was begun by reviewing the various processes that go into the production of the RSRM. These include, but are not limited to, case preparation and refurbishment, insulation/inhibitor preparation, propellant mixing and casting, and manufacture of composite materials. Each of these processes generates its own series of wastes that require recycling or treatment and disposal. The generic characteristics of each of these processes were listed and used to identify processes in commercial industries that are similar in nature.

The automotive industry was of particular interest because of its large production capacity, varied manufacturing steps, and diversity of materials used. The production of an automobile, in the broad sense, uses the same types of materials and processes as an SRM. The materials and processes of particular interest are metal fabrication, metal cleaning, painting operations, and polymer recycling and disposal.

Little information was found concerning composites outside of aerospace related industries. The most attractive use for the waste composites that was located is for engineered building materials. With the new materials composed of waste composites and comingled municipal plastic wastes.

Discussion

This paper will highlight four examples of technology that are applicable in the aerospace industry. These four samples that will be cited are the Automotive Pollution Prevention Project, treatment of oily wastewater, removal of zinc from an oily wastewater, and recycling of waste composites from the aerospace industry. Each of these will be discussed in limited detail and are examples from the report prepared for NASA/MSFC.

Automotive Pollution Prevention Project

The Automotive Pollution Prevention Project (APPP) is a voluntary partnership between General Motors Corporation, Chrysler Corporation, Ford Motor Company, American Automobile Manufacturers Association, the State of Michigan, and the United States Environmental Protection Agency. The APPP is chartered with the task of 1) identifying persistent toxics that have been released into the Great Lakes Basin, 2) advancing a pollution prevention agenda within the auto industry, 3) reducing releases of persistent toxic substances, and 4) addressing regulatory barriers that inhibit pollution prevention efforts[2].

The APPP prepared a list of Great Lakes Persistent Toxics (GLPT) which the use and release of was to be reduced or eliminated, where possible. Many of the chemicals listed as GLPT are found in the manufacture of a typical SRM. Some of those listed as GLPT are*:

Methyl Chloride	Methylene Chloride
Phenol	Toluene
Chromium	Zinc

*This is a sampling of the GLPT and not an inclusive list.

Another goal of the APPP is to foster technology transfer among the three major U.S. Auto companies and their suppliers to aid in pollution prevention and treatment. The APPP produced a series of case studies, in a synopsis format. Among the accomplishments cited by the APPP is the annual reduction in the release of GLPT. Their progress since 1988 is detailed in Figure 1. The auto companies also report that a 27.3% reduction has been achieved in the release of GLPT on a per car produced basis.

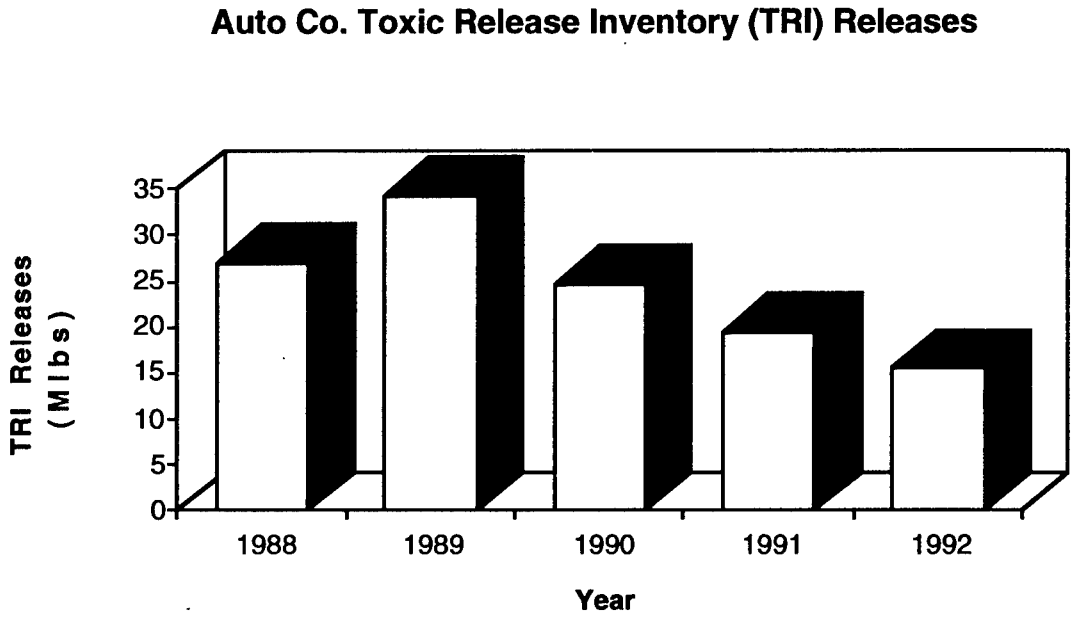

Figure 1 Release of GLPT Substances by the Auto Companies [2].

Many of the case studies are also of interest to the SRM industry. Two of the studies will be reviewed here. They are the elimination of Trichloroethane degreasing and reduction in the use of ozone depleting substances (ODS) for spot metal cleaning.

General Motors in its Lansing Auto Division, as a late as 1990, was using 15,000 pounds per year of chloroflourocarbons (CFCs) for spot metal cleaning. The CFC used was in the form of Freon 11 and Freon 12 in aerosol spray cans. The Freon 11 and Freon 12 were replaced by HCFC-141B. Although HCFC-141B is also an ODS, it has only 12% of the ozone destroying potential of the CFC. The amount of cleaner was also reduced from the 15,000 pounds per year to 9,000 pounds per year.

Ford replaced trichloroethylene vapor degreasing with aqueous cleaning. The plant used vapor degreasing to clean high surface area aluminum parts used in heat exchanging equipment. Although the degreasing unit had a vapor reclamation system, the high surface area aluminum retained a significant amount of TCE which evaporated after

removal from the cleaner. This TCE vapor degreasing process accounted for a large percentage of the chlorinated solvents released by Ford.

As is true with any new process, there is concern as to whether it will be as reliable as the previous one. There was concern that going to an aqueous degreasing processing would etch the aluminum or adversely effect the brazing process in assembling the completed units. A pilot process was established to test detergent solutions. This unit consisted of 1) a prewash to remove easily removed oils, 2) a detergent wash to loosen and remove more stubborn oils, and 3) a water rinse. The pilot plant operation was found to be compatible with current and planned brazing operations and did not adversely effect the aluminum surface.

On the basis of on the results from this program, the Ford Climate Control Division has recommended that Ford replace all TCE degreasers with aqueous cleaning world-wide.

Treatment of Oily Wastewater

General Motors installed a membrane biological reactor system (MBR) to treat effluent from a sheet metal machining operation. The water effluent from this operation was heavily contaminated with synthetic machining oils. The manufacturing operations generated a wastewater flow of 151 m^3/day. The untreated effluent contained a chemical oxygen demand (COD) of approximately 6000 mg/l. A new treatment plant would be required to meet stricter effluent standards [3].

The existing treatment plant was 35 years old and required a high degree of operator attention. The waste treatment facility consisted of standard physical and chemical treatments. This treatment scheme generally left soluble organics untreated and discharged them in the effluent.

The new membrane biological reactor consists of a suspended growth biological unit combined with an ultrafiltration unit. The ultrafiltration unit provides a means to assure adequate liquid-solids separation. This combination allows for very high levels of biomass growth in the reactor unit without any being released in the effluent. This technology has the added benefit of treating soluble organics in the waste stream that had previously been discharged untreated.

The installation of the MBR at the plant was a success. The MBR yielded a 94% reduction in COD, reducing oils and greases in the effluent to less than 25 mg/l. The unit met or exceeded design specification even though the COD volumetric loading was more than twice the design parameters.

Removal of Zinc From Oily Wastewater

In another example from General Motors an innovative process was employed to remove zinc from oily wastewater in a transmission facility. This example differs from the previous example in technology in that it is a retrofit to an existing facility. The new treatment system was required to meet new effluent guidelines. Zinc was to be reduced from the current effluent level of 2-5 mg/l to 0.37 mg/l in a flow of 2160 m^3/day and meet a deadline of less than one year [4].

In the removal of zinc from a waste water, it is critical that the oil level be as low as possible. The influent contained approximately 35 g/l oil. This level necessitated that the current oil removal system be optimized. The current system for oil removal consisted of a corrugated plate interceptor and dissolved air flotation and skimming. Enhancement of the existing oil removal system was accomplished by addition of a rotary screen to remove solids, and improve distribution of waste into the dissolved air flotation unit.

To meet the new effluent requirements for the wastewater, the zinc level had to be reduced from 5-10 mg/l to 0.35 mg/l. This reduction was planned to be accomplished with a solids contact clarifier, with chemical floculation. The clarifier was followed by an upflow sand filter. The sand filter was added, because of the tight regulatory time frame, to assure adequate zinc removal. Upon installation and checkout of the system it was determined that the sand filter was not needed to meet effluent requirements. The removal of the upflow sand filter helped to reduce the complexity of the system and served to reduce the amount of solid wastes requiring disposal. The new system flowsheet is shown in Figure 2.

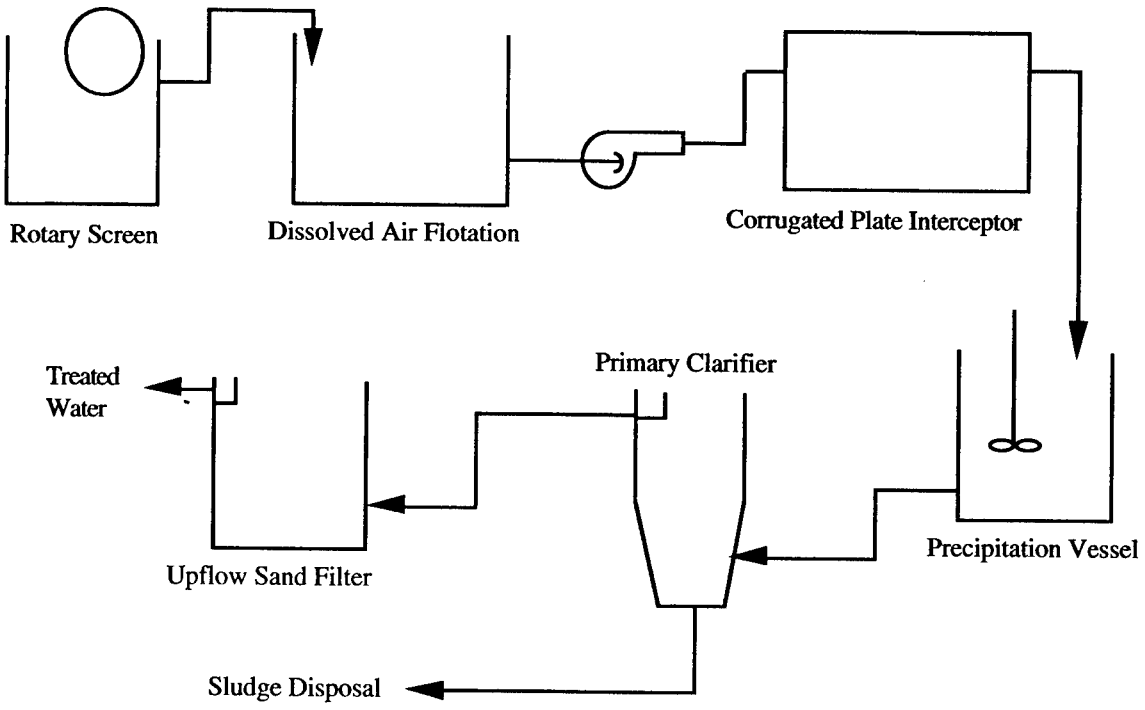

Figure 2 Schematic of Improved Zinc Removal System [4].

Reuse of Composites

Foster-Miller has developed a process to produce engineered building materials from waste materials. The Foster-Miller process combines comingled plastics from municipal wastes with fiber filled composites from the aerospace industry to produce construction materials. They report that their material

has the potential of matching the mechanical properties of wood and to be competitive in cost on a life-cycle basis [5].

The product consists of plastic wastes (largely high density polyethylene), fiber filled composites, and resin. The material has exceptional low temperature properties that make it suitable for low temperature structural applications. Foster-Miller believes that the products material properties can be tailored to specific applications by optimizing the fiber orientation and length. Some proposed applications are as structural members, siding, and decking.

Conclusion & Recommendations

The Foster-Miller process, to use waste composites, could provide immediate benefits in the aerospace industry. The reuse of the composites will eliminate the costs associated with their disposal while possibly recouping some of the production costs. The two wastewater treatment processes presented can be adapted for SRM case production and refurbishment facilities. The automobile industry has many more applications that are applicable to SRM production than are reviewed in this paper. Technology such as reduction in solvents used in paint formulations and new finish application technologies are both applicable to SRM production.

This paper is a small sampling of the wealth of innovative technology in the commercial sector that could be applied to the aerospace industry. There are many ongoing efforts within the aerospace industry to reduce or eliminate waste. These efforts are generally shared among the various producers of hardware. There is also a great deal of emphasis placed on finding commercial applications for the technology being developed in aerospace. However, it should be remembered that there is a tremendous amount of high quality technology developed in the commercial sector that can find application within the aerospace industry. Using a synergistic approach to handling production effluents offers the best chance at preserving the environment at the least cost.

References

1. Thomson, L.J., Campbell, R.L. "Technology Transfer into the Solid Propulsion Industry." Sverdrup Technology NASA/MSFC Group, 311-202-94-012, August, 1994.

2. "Automotive Pollution Prevention Project: Progress Report." American Automobile Manufacturers Association, February, 1994.

3. Knoblock, M.D., et.al. "Membrane Biological Reactor System for Treatment of Oily Wastewaters." Water Environment Research, Vol. 66 No. 2, March/April, 1994, pp. 133-139.

4. Garret, L.D., Doran, T.M. "Utilization of Innovative Technology for Zinc Removal from Transmission Plant Wastewater." SAE Int. No. 920188, February, 1992.

5. Correspondence with Foster-Miller Company.

Prioritization Methodology for Chemical Replacement

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ABSTRACT

Since United States of America federal legislation has required ozone depleting chemicals (class I & II) to be banned from production, The National Aeronautics and Space Administration (NASA) and industry have been required to find other chemicals and methods to replace these target chemicals. This project was initiated as a development of a prioritization methodology suitable for assessing and ranking existing processes for replacement "urgency."

The methodology was produced in the form of a workbook (NASA Technical Paper 3421). The final workbook contains two tools, one for evaluation and one for prioritization. The two tools are interconnected in that they were developed from one central theme -- chemical replacement due to imposed laws and regulations. This workbook provides matrices, detailed explanations of how to use them, and a detailed methodology for prioritization of replacement technology. The main objective is to provide a *GUIDELINE* to help direct the research for replacement technology.

The approach for prioritization called for a system which would result in a numerical rating for the chemicals and processes being assessed. A Quality Function Deployment (QFD) technique was used in order to determine numerical values which would correspond to the concerns raised and their respective importance to the process. This workbook defines the approach and the application of the QFD matrix.

This technique:

1. provides a standard database for technology that can be easily reviewed,

2. provides a standard format for information when requesting resources for further research for chemical replacement technology.

Originally, this workbook was to be used for Class I and Class II chemicals, but it was specifically designed to be flexible enough to be used for any chemical used in a process (if the chemical and/or process needs to be replaced).

The methodology consists of comparison matrices (and the smaller comparison components) which allow replacement technology to be quantitatively compared in several categories, and a QFD matrix which allows process/chemical pairs to be rated against one another for importance (using consistent categories). Depending on the need for application, one can choose the part(s) needed or have the methodology completed in its entirety. For example, if a program needs to show the risk of changing a process/chemical one may choose to use part of Matrix A and Matrix C. If a chemical is being used, and the process must be changed; one might use the Process Concerns part of Matrix D for the existing process and all possible replacement processes. If an overall analysis of a program is needed, one may request the QFD to be completed.

INTRODUCTION

This methodology serves to define a system for effective prioritization of efforts required to develop replacement technologies mandated by imposed and forecast legislation. The methodology used is a semi-quantitative approach derived from quality function deployment techniques (QFD Matrix). QFD is a conceptual map that provides a method of transforming customer wants and needs into quantitative engineering terms. This methodology aims to weight the full environmental, cost, safety, reliability, and programmatic implications of replacement technology development to allow appropriate identification of viable candidates and programmatic alternatives.

EXPLANATION OF MATRICES

Matrix A

Matrix A is a "chemical and use" matrix. The objective of this matrix is to define the target chemicals by the part and process in which they are used (the how and where the targeted chemicals are used). This matrix has some "bookkeeping" areas to help in tracking the particular chemical/part/process combination in other matrices. Parts of Matrix A will be used in all matrices. Each component of

Matrix A may not need to be filled out. The following is an explanation of the requested information for this matrix.

• *the target chemical*

The Class I or Class II chemical which has to be eliminated due to regulation should be put in this column. Any other chemical which needs evaluation for replacement could also be put in this column. It should be noted that some materials may contain several "target" chemicals. Those materials which have several chemicals should be grouped for identification purposes. This information will be necessary for subsequent matrices.

• *a chemical registry #*

This is the standard number (as might be found on a Material Safety Data Sheet (MSDS)) for the chemical. This is requested so that actual values necessary for evaluation can be found.

• *a chemical reference #*

This a bookkeeping number. It is assigned by the person filling out the chart. It is recommended that for every chemical the number is consistent (i.e. for all uses of TCA the number is 1, for all uses of CFC113 the number is 2, etc.). This number will be used throughout the rest of the matrices in the "chem #" column.

• *material*

This is the material that the chemical is in, identified for the specific process. This is a reference to assist defining the processes and parts. Generally this will be the manufacturing or common name.

• *the process in which the chemical is used*

This is the current process for which the chemical is being used. This process is dependent on the part, surface, etc. that will be affected. The process will be necessary for subsequent matrices.

• *a description of the part/component/subsystem which is being processed*

The part/component/ subsystem that will be processed will be completed in this part of the matrix.

• *a reference number for the specified part/component/subsystem*

This is a number assigned to the part/component/subsystem that will be processed. This number can be manufacturer specific as long as it can be referenced to the FMEA (NASA specific risk assessment). This number will be used in Matrix C - Risk Assessment and possibly in Matrix D for specifications of surface requirements.

• *the surface being considered*

After the part has been defined, a surface on the part may need to be specified to better define the process and requirements.

• *process # (Reference)*

This is the bookkeeping number for the process. It should be defined by the chemical, the material, the part (or group of parts), and the surface. The process (reference) # should be defined such that there will be no confusion between processes. Again this reference will be used in the other matrices for tracking purposes.

Chemical	Chem # (Reference #)	Process	Proc # (Reference)
Trichloroethane	1	Vapor Degrease (Case Segment)	1-1-1
Trichloroethane	1	Vapor Degrease (Bolts)	1-1-2

Figure 1

• *a manufacturing process number*

This is another reference point for the matrix. The manufacturing process number allows a check on the stage of manufacturing in which this particular process is being done. Again this is an optional part of the matrix. It would be defined as a number (i.e. if it is the second process - it is 2).

• *the number of manufacturing processes*

This is the total number of processes a part goes through as defined by the part specifications (for a refurbished part and for a non-renewable part)

• *the pounds of chemical used in the process (for the specified part) per year*

This category is strictly for informational purposes. It provides a prospective of the amount of the targeted chemicals used.

A blank Matrix A is included in Appendix A.

Matrix B

The technical maturity of the chemicals and processes are evaluated in Matrix B. The existing chemical/process from Matrix A and the developmental chemical/process are evaluated according to the number of parts to be processed (in the program life) and the testing which has been performed on the chemical, process, and processed parts. This matrix might be sent to the environmental, research and development, or manufacturing group for completion. This matrix was designed to accommodate the existing process and

the possible replacement processes, but it can also be used specifically for comparison and evaluation of possible replacement chemicals. The matrix is broken into sections which ask for the identification of the chemical and process along with the corresponding reference numbers for each.

The reference numbers for the existing chemical/process were defined in Matrix A; these same numbers should be used for the chemical/process in Matrix B. For each existing chemical/process there should be a chemical/process replacement. For each "replacement" chemical a number should be assigned to correspond with the chemical it is replacing.

A space is provided to identify the existing (old) technology and the possible replacement technology (new).

The next item to be completed is "Years of Existence." This is the number of years the chemical/process has been available for commercial purchase.

Subsequent items deal with chemical, material, and process testing. In an effort to provide for every type of test, the "type tests" are very general in scope. This matrix is not necessarily complete for full analysis; it is provided to quantify the extent of testing for each chemical/material/process. Some materials and/or processes may not need a particular type (general) of test. For those areas where the test information requested is not applicable, note in the space that it was considered not necessary by placing a check in the corresponding box.

The following items are requested:

• *Toxicity Testing*

New chemicals must pass a series of toxicity tests before they are allowed to be used. By identifying the toxicity testing which has been completed, the new technology can be identified as a cost or scheduling conflict before completing the rest of the matrices.

• *Environmental Testing*

Environmental testing can be used to determine if the chemical/process is "environmentally safe." By identifying if the chemical/process has been tested, one can foresee the possibility of future environmental regulations.

• *Chemical Reactivity Testing*

By identifying the amount of chemical reactivity testing that has been done, one can see the amount of future necessary chemical reactivity testing that might possibility be needed before the chemical can be qualified for use.

• *Age Sensitivity Testing*

This category includes such areas as shelf-life, extensions of shelf life, viscosity changes over time, age sensitivity of the chemical while on the part, handling, etc. The information requested in this category is not restrictive in the nature of type of age testing; but when considering the extent of age testing for an existing chemical, the same type testing should be evaluated for the considered existing technology.

• *Misc. Testing*

This category includes any other type testing required for this chemical/process that cannot be included in one of the other categories. Again, the same consideration should be taken for testing with the existing technology and the replacement technology.

• *Parts to be Processed (Program Life)*

The program design life for the part and the number of expected parts to be produced during that time should be entered in this space. This allows for judgment of the necessity of finding a replacement technology.

A blank Matrix B is included in Appendix A of this report.

Matrix C

Matrix C is a risk assessment matrix which provides a valuable tool for determination of the critical safety and reliability parts and processes. This matrix is designed to allow the risk of failure of the hardware to perform its function, due to the process change, to be calculated numerically.

The existing targeted chemicals, process, and drawing numbers (from Matrix A) and the possible replacement chemicals and processes with appropriate drawing numbers should be filled in first. A space is provided to check which is "existing" technology and which is "new" technology.

The FMEA # is requested for reference purposes. The FMEA provides a ranking of criticality of the part and process which is given a "weight" or numerical value. This number will be assigned a 1, 3, or 9 for Crit 3, 2, and 1 respectively.

Chemical	Process	Proc #	Criticality	Severity Value
TCA	Vapor Degrease	1-1-1	C1	9

Figure 2

The probability of failure value is determined by weighting the factor of safety and the type inspection(s) performed. The scoring of 6-1 will be given to the Inspections in the order listed in the legend below the evaluation matrix (6 being Visual and 1 being Plug or other hardware specific, destructive test). The Safety Factor should be inverted and multiplied by the Inspection value to get the Probability Value. (See Figure 3.)

Chemical	Process	Inspections	Original S.F.	Probability Value
TCA	Vapor Degrease	NS	9	5/9

Figure 3

The risk evaluation (weight) is determined by multiplying the probability value by the severity value. This matrix might be sent to a risk assessment group.

Chemical	Process	Severity Value	Probability Value	Risk (= P*S)
TCA	Vapor Degrease	9	5/9	5

Figure 4

Again, a blank Matrix C is included in Appendix A.

Concerns

The following categories are the concern categories which are listed separately in the QFD matrix. Each concern category is given a separate matrix for simplification and facilitates the use of particular parts of the entire workbook The format in specifying the chemical/process pairs is the same as Matrix B. The code following each concern is specified by three letters (such as NMH) which are defined in the legend below the evaluation matrix (None, Minimal, High). The highest score is a 9 which in this case corresponds to "None". The lowest is 1 which corresponds to "High". If the question is not applicable then place a check mark in that box noting it was recognized as unnecessary. If the criteria described in the explanation can be rewritten to better evaluate the process, then make a note of the change in the explanation and use the updated criteria for **ALL** of the chemical/process pairs that are to be evaluated.

Each new process and chemical will be "scored" for each concern listed in Matrices D through J. Each "score" will be shown as most positive, neutral, or negative (or blank for no relation). Matrices D through J will also allow the concerns to be weighted for importance. These weighted factors will need to be considered in the final prioritization calculations. Additional information such as risk factors for part failure and technical maturity of the chemical and process will be used when trade-offs become necessary. These data will be evaluated using QFD methodology.

Appendix A includes example Matrices for use as guides in completing the prioritization process.

Matrix D

Matrix D addresses the chemical concerns for the existing and replacement technologies. Again this can be used alone or as a part of the QFD matrix. This matrix should give the user a firm understanding of how the chemical acts or reacts during its shelf life or use. An environmental engineering group and/or manufacturing should complete this matrix.

Matrix E

The process concerns deal with the way that a chemical acts or reacts during a process application. An environmental engineering group and/or manufacturing should complete this matrix.

Matrix F

Matrix F considers the regulatory impacts on a chemical/process. When completing this part of the matrix, one should consider the known dangers (i.e. known phase-out and reduction plans) when rating a chemical/process on meeting the laws. The regulatory concerns consider how OSHA requirements, federal, state, local environmental laws and regulations affect chemicals and processes. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

Matrix G

The safety concerns are worker exposure, spill response, fire response, and explosion response. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

Matrix H

The environmental concerns consider how chemicals impact the program environmentally. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

Matrix I

The cost concerns evaluate how cost will deviate with the replacement of current technologies. This matrix might be completed by the project or program office (or their support personnel).

Matrix J

The scheduling concerns delineate how scheduling requirements will be met with respect to Environmental Regulations and NASA program schedules. This matrix might be completed by the project or program office (or their support personnel).

QFD APPLICATION

The QFD matrix will be completed by the project office or program manager. The basic QFD format is shown in Figure 5.

QFD Format

Process Relationships

Concerns	Weighting	Process #1	Process #2	Process #3	Process/Chemical →
Regulatory	20	125	67		
Safety	14	78	101		
Process	12	55	40		
					Concern/Processes Relationships
Trade Offs		·	·		
Risk		·	·		
Technical Maturity		·	·		
Importance Rating		456	300		

Figure 5

The QFD Matrix is quite easy to understand if it is approached one step at a time. In the case of the chemical replacement, first list the customer (NASA or Contractor) concerns vertically on the left. Then list each chemical/process, old and new, horizontally. The relationship of each concern to each chemical/process is then rated on a scale of 1 - weak, 3 - medium, and 9 - strong. Next, a weighting factor is given to each concern. That is, on a scale of 1 to 20 in this case, assign a number rating the *importance* of each concern. To get the overall rating of each chemical/process, multiply the weighting factor times the relationship rating for each process to concern and sum the total down the page.

	Weighting Factor	Chemical/ Process #1	Chemical/ Process #2	Chemical/ Process #3
Concern 1	10	3	9	1
Concern 2	15	1	9	3
Concern 3	12	9	1	9
Overall Rating		153	237	163

Figure 6

Example: Chemical/process #1 would have an overall rating of (10 * 3) + (15*1) + (12*9) = 30 + 15 + 108 = 153. Chemical/process #2 would be (10 * 9) + (15 * 9) + (12 * 1) = 90 + 135 + 12 = 237. Chemical /process #3 would be (10 * 1) + (15 * 3) + (12 * 9) = 10 + 45 + 108 = 163. This methodology would rank #2 as the "better" alternative of the three.

The "roof" at the top of the matrix simply shows how strong the chemicals/processes relate to each other. This knowledge can applied when trade-offs become necessary. In fact, the QFD Matrix can include several different entries that could be included in trade-off studies. The Chemical Replacement Prioritization Methodology applies only a limited use of the QFD capabilities.

Since this methodology is used as a guideline for comparison for replacement technology, it should be noted that there are times when a full QFD evaluation should not be performed. The times that the QFD evaluation is not recommended are:

- when another tool or system is more applicable, such as when decision, risk analysis, or analytical process models are all that are needed
- there is not enough time or resources to do it *RIGHT*
- critical elements of the process are missing (i.e. customer feedback).

In these cases, one should consider using the most relevant matrices to assist in making judgment on replacement technology.

WEIGHTING

For each type of process, the weighting factors will vary (i.e. the weights for precision cleaning may differ from those in foam blowing).

Therefore a QFD weighting application is enclosed as Matrix K. This weighting box allows the concerns to be weighted against each other. The number in the box represents the score of that concern versus each of the other concerns. The more important concerns should be represented by higher numbers. The matrix can be expanded to weight any category or all of the concerns together. For each category, the weights should be normalized by dividing the weight by the # of concerns. A blank weighting worksheet (Matrix K) is included in Appendix A.

SCORING

Depending on the type of application, the scoring will be slightly different. If only part of the matrix packet is used then the weights should be multiplied by the number corresponding to that code. The total of these numbers is the "score" for that process. If the entire matrix packet is to be used as a QFD exercise, then for each of the concern matrices (D-J) the "score" should be determined as before by multiplying the weight by the number corresponding to the code then each concern category should be normalized by dividing by the total number of concerns in that category.

- Matrix A carries no numerical weight.

- Matrix C "scores" should be multiplied by 100 and added to the total from the concerns if using the QFD matrix as a prioritization tool or subtracted from the total if it is used as a replacement technology comparison tool.

- If the matrix packet is to be used as a comparison between alternate replacement chemicals/processes, then the percentage of testing completed as compared to the current technology (from Matrix B) should be determined for each category of tests. The total of these numbers should be added to the accumulated numbers. If the matrix packet is to be used to determine the ranking of "urgency" then this chart could be used as a reference to show the technical maturity of the existing technology. This chart does not necessarily need to be completed if it is to be used for this type of application.

CONCLUSION

Prioritization and Determination for Selection

The objective of this work was the development of a quantitative procedure for determination and ranking of replacement technologies and associated issues. The QFD matrices are designed to produce a numerical "importance" value. If the QFD matrix is completed, the final total will be the importance value. The higher number corresponds to the "higher priority" or "better selection" chemical/process -- depending on the application.

Several agencies have requested copies of this prioritization methodology workbook in its entirety; this includes several NASA offices, NASA contractors, Department of the Navy, Army representatives, university representatives, private consultants, and the US Environmental Protection Agency. At this point the feed back has been very positive from those that have reviewed the document. NASA contractors have actively used parts/variations of this methodology. Thiokol has used this method to determine the type of cleaner and process to be used for cleaning solid rocket motor parts. They also used parts of Matrix A and C to rank the importance (according to risk) of each use of the current cleaner. Martin Marietta has used parts of this methodology for work done in the TPS Materials Research Laboratory at Marshall Space Flight Center. Other feedback has been less specific, however, this publication has been recommended by the Commonwealth of Virginia Department of Environmental Quality and has been made available through the technical assistance library in that area.

MAPTIS (Materials and Processes Technical Information System) is a Marshall information system containing a working prioritization data base. The data base can be found within the NEIS (NASA Environmental Information System), which is a part of MAPTIS. The data base was designed to be "user friendly." It allows the users to select from the concerns listed in matrices D through J, or input another category and the concerns associated with that category. The data base, when told to process, will automatically normalize the weights and do all other necessary math calculations to get the overall score for each chemical/process pair. The data base will also allow the user to printout (on screen or hard copy) the individual scores, the category scores, or the overall scores for each chemical/process. The only matrices not included on this data base are the technical maturity and the risk assessment which are generally used for trade-off comparison and usually need to be done separately for other reasons.

For questions concerning the Prioritization Methodology or to receive a complete copy of this publication, contact:

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Wendy Cruit (205) 544 - 1130

Appendix A

Matrix A - Chemicals and Uses For Prioritization Methodology

Chemical	Chem # (Registry #)	Chem # (Reference #)	Material	Process	Part/Component/Subsystem	Surface	Proc # (Reference)	Proc Step #	Total Process Steps (#)	Reference # (tracable to FMEA)	Amount Used In Process (lb/yr)

Matrix B - Technical Maturity of Substutite For Prioritzation Methodology

Chemical	Chem #	Process	Proc #	New	Old	Years of Existence	Toxicity Testing		Environmental Testing		Chemical Reactivity Testing			Age Sensivity Testing (shelf-life & aging)				Misc. Testing		# of parts to be processed (Program Life) -- old and new
							#	Type	#	Type	#	Results	Type	# Samples	Shelf Life	Type	Ext.	#	Type	

Appendix A

MATRIX C - Risk of System Failure

Chemical	Chem #	Process	Proc #	New	Old	Part/ Component/ Subsystem #	FMEA # (Ref.)	Severity (S)		Probability (P)				Risk (= P*S)
								Criticality	Severity Value	Inspections	Original S.F.	Anticipated S.F.	Probability Value	

	Inspections:		
6	V = Visual	3	W = Witness Panel
5	NS = NDE (UT, X-Ray, ect...)	2	WT = Witness Panel -- Tested
4	LC = LOX Cleanliness (NVR, Other)	1	P = Plug Test

Appendix A
Example Matrices D and E -- Chemical and Process Concerns

Weighting Factors to be Inserted Here →
1 - Less Important 20 - More Important

* NOTE: Either Numbers, Letters, or Symbols can be used to comple the Matrices.

						Chemical Concerns																		*Process Concerns*																									
																								Contaminants Removed		Process Steps		Parts Processed at One Time		Req. Surface Prep.		Bondline Thickness																	
Chemical	Chem #	Process	Proc #	New	Old	# of Sources	Limited Resources for Manufacturing (NMH)	Availability (EMB)	Stability (Storage) (GFP)	Flammability (NMH)	Drying Ability (GFP)	Base Meterial Compatibility (GFP)	Toxicity (NMH)	Flash Point (NMH)	Ease of Maintenance (GFP)	Historical Data Base (CPN)	Desirable Reactivity (GFP)	Undesirable Reactivity (NMH)	Lot-to-Lot Variability (NMH)	Age Sensitivity - Processed Part (NMH)	Shelf Life (EMB)	# Req.	# Produced	#	Δ Increase/Decrease	#	Δ Increase/Decrease Time	Δ Increase/Decrease	# Req.	# Produced	Process Time (Δ)	Process Interaction (#)	Process Interaction (GFP)	Bond Strength Requred (EMB)	Operator Sensitivity (NMH)	Lot-to-Lot Variability (NMH)	General Cleaning Ability(GFP)	Surface Requirement (EMB)	Useful Life of Replacement Processed Parts (EMB)	Damage caused by Process (NMH)
TCA	1	V. D. - Final of Large metal part	1-1-1		X	2	N	B	G	H	G	G	M	H	G	C	/	N	N	N	M	?	-1	1	0	1	0	1m	0	/	/	0	1	G	/	N	M	G	M	M	M
Aqueous Soap	R1	Pressure Spray in Air - Large Metal Part	1-1R1-1	X		1	N	M	G	N	P	G	M	N	G	P	/	M	N	M	M	?	0	3	2	1	0	1m	0	/	/	-1	1	F	/	N	M	G	M	M	M
Terpene	R2	Aggitated Immersion	1-1R2-1	X		1	9	3	9	9	1	9	3	3	9	1	/	3	1	1	3	?	-2	2	1	1	0	1m	0	/	/	-1	1	9	3	9	1	3	3	3	3

9	Exceeds (E)	Good(G)	None (N)	Complete (C)
3	Meets (M)	Fair (F)	Minimal (M)	Partial(P)
1	Below (B)	Poor (P)	High (H)	None (N)

Appendix A

Example of Matrices E - J -- Regulatory, Safety, Environmental, Cost, and Scheduling Concerns

Weighting Factors to be Inserted Here
1 - Less Important 20 - More Important

Chemical	Chem #	Process	Proc #	New	Old	Regulatory Concerns: OSHA Requirements (EMB)	State Environmental Laws (EMB)	Local Environmental Laws (EMB)	Federal Environmental Requirements (EMB)	Future Federal Regulations (EMB)	Safety Concerns: Worker Exposure Limits (NMH)	Spill Response Plans (CPN)	Fire Response Plans (CPN)	Explosion Response Plans (CPN)
Weighting factors														
TCA	1	Vapor Degrease	1-1-1		x	3	1	1	1	1	3	3	3	9
Aqueous Soap	1R	Spray in Air	1-1R1-1	x		3	3	3	9	9	3	3	9	9

Chemical	Environmental Concerns: Clean Air Monitoring (EMB)	Pollution Prevention (CPN)	Toxic Emissions (NMH)	Emissions Control (GFP)	Ozone Depletor Potential (NMH)	Chemical Storage Availability (CPN)	Resource/Ingredient Recovery and Recycling (CPN)	Hazardous Waste Management (EMB)
Weighting factors								
TCA	1	9	9	1	1	9	9	3
Aqueous Soap	9	9	3	9	9	9	3	3

Chemical	Cost Concerns: Labor $ (DNI)	Operations $ (DNI)	Facilities $ (DNI)	Materials $ (DNI)	Chemical $ (DNI)	Other Hardware $ (DNI)	Contracts $ (DNI)	Change of Specifications $ (DNI)	Specification Verification $ (DNI)	Change of Drawings $ (DNI)	Development of Procedure $ (DNI)	Waste Management $ (DNI)	Emissions Control Testing $ (DNI)
Weighting factors													
TCA	3	2	1	3	2	3	2	3	3	3	2	3	3
Aqueous Soap	2	2	2	3	6	3	2	2	1	2	2	3	3

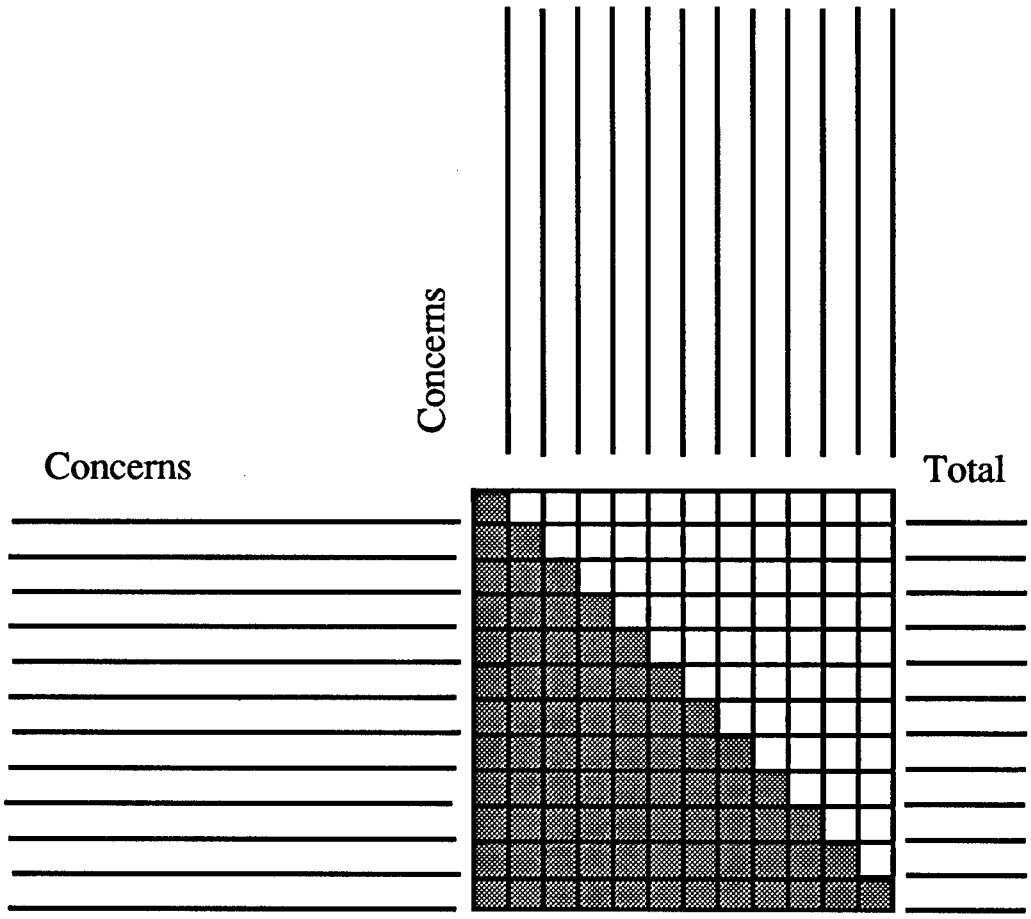
Chemical	Scheduling Concerns – Federal, State, and Local Regulations: Research (EMB)	Trade Studies (EMB)	Modification in Planning (EMB)	Specification Documentation (EMB)	Drawing/Design Changes (EMB)	Production Time (EMB) (New Equip.)	Testing (EMB)	Vendor Selection & Certification (EMB)
Weighting factors								
TCA	9	9	9	3	9	3	3	3
Aqueous Soap	9	9	3	3	3	9	3	3

Chemical	Scheduling Concerns – Present Program Schedule: Research (EMB)	Trade Studies (EMB)	Modification in Planning (EMB)	Specification Documentation (EMB)	Drawing/Design Changes (EMB)	Production Time (EMB) (New Equip.)	Production Time $ (EMB) (Hardware Avail)	Testing (EMB)	Vendor Selection & Certification (EMB)
Weighting factors									
TCA	9	9	9	3	9	9	9	9	9
Aqueous Soap	9	9	1	1	3	3	1	3	3

9	Large Decrease (D)
6	Slight Decrease (D)
3	No Change(N)
2	Slight Increase (I)
1	Large Increase (I)

9	Exceeds (E)	Good(G)	None (N)	Complete (C)
3	Meets (M)	Fair (F)	Minimal (M)	Partial(P)
1	Below (B)	Poor (P)	High (H)	None (N)

Appendix A
Matrix K -- Weighting Worksheet



1 = Less Important
20 = More Important

NOET - Prioritization for Chemical Replacement

COMPLIANCE STRATEGIES

NCMS

313-995-0300

National Center for Manufacturing Sciences

3025 Boardwalk
Ann Arbor, MI
48108-3266

NATIONAL CENTER FOR MANUFACTURING SCIENCES

ENVIRONMENTALLY CONSCIOUS MANUFACTURING

Clare Vinton

The purpose of this presentation is to share the results and some of the thinking of the **Environmentally Conscious Manufacturing - Strategic Initiative Group (ECM-SIG)** at the **National Center for Manufacturing Sciences (NCMS).** NCMS is a consortium of more than 185 North American Manufacturing organizations comprised of about 75% for profit manufacturing companies and about 25% nonprofit organizations that support manufacturing activities. NCMS conducts collaborative R&D programs designed to improve global competitiveness of its members and other North American manufacturers to address common issues that are important to manufacturing industries. NCMS is an industry driven organization whose agenda is established by industry with input from appropriate government agencies.

The technology programs at NCMS are established in Strategic Initiative Groups (SIGs). Each of the SIGs has a Planning Committee that is responsible for the agenda, programs and projects for their respective SIG.

The 6 SIGs are:

Manufacturing Processes and Materials
Production Equipment and Systems
Computer Integrated Operations
Management Practices
Environmentally Conscious Manufacturing
Electronic Manufacturing

The planning committee for the ECM-SIG is comprised of the following people:

- Mike Leake, Texas Instruments Incorporated, Chair
- Angelo Decrisantis, United Technologies Corporation
- Jan Sekutowski, AT&T
- Abdul Abdul, General Motors Corporation
- Jim Anderson, Ford Motor Company
- Paul Arbesman, Allied Signal
- Phil Brown Eastman Kodak
- Karen Salveta, Digital Equipment Corporation
- Vic Schaefer, Cincinnati Milicron
- Dave Sordi, Torrington
- Ralph Worden, Kingsbury Corporation
- Dale Denny, National Defense Center for Environmental Excellence
- Steve Lingle, Environmental Protection Agency
- Pete Ritzcovan, Department of Energy
- Gary Vest, Department of Defense

The programs that the ECM Planning Committee have established and prioritized are:

1. Life Cycle Design for Environmental Compatibility
2. Manufacturing Solvents and Their Substitutes
3. Hazardous Materials Emissions (33/50 List)
4. Environmentally Conscious Manufacturing Packaging Initiatives
5. Emissions from Surface Finishing Operations
6. Sensors for Environmentally Conscious Manufacturing Processes
7. Environmental Practices
8. Remediation of Industrial Wastes
9. Waste Minimization/Energy Conservation Practices
10. Handling and disposal of Metal Working Fluids

In the past industry has tended to focus environmental activities on compliance related issues. Industry needs to become more proactive in the regulatory process to ensure that regulations are based on sound science and not just on emotion and political expediency. The 70s were the decade that focused on treatment technology by scrutinizing a company's gaseous, liquid and solid emissions . The 80s were the decade that included the manufacturing process itself by scrutinizing a company's products especially for recycability. We are now adding the incoming feedstocks and including the scrutiny of a company's raw materials and energy consumption that are used in the manufacturing processes. There are some who think it is not enough to eliminate the emissions of chemicals that have been officially classified as hazardous, we must also eliminate the use of those chemicals.

Pollution Prevention has the support of the majority of environmentalists, government officials, and industry officials and all seem to be committed to the concept. Life Cycle Analysis (LCA) is a way of addressing pollution prevention. LCA addresses environmental implications for all of the phases in the life of a product, during maintenance, use and disposal as well as during manufacture of the product. It is important to include full cost accounting in LCA. We need to be sure that we include all of the environmental costs into the pricing structure so we are making economic decisions not environmental decisions. We should prevent pollution by making it cost more for to do the things that are bad and cost less to do things that are good. During the 19th century, kids were often poisoned from chewing phosphorus matches. When less toxic sulfur matches were invented, they cost more and people did not buy them. Congress showed wisdom, they taxed phosphorus matches so they cost more than sulfur matches and guess what, people stopped buying phosphorus matches and kids ceased to be poisoned as a result of chewing them!

The increasing human population has caused changes to earth's environment, the industrial revolution has accelerated those changes during the last 2 or 3 centuries. Sustainable development can be achieved by establishing a "Closed Industrial Ecology". This Closed Industrial Ecology must learn to use by-products from every industrial process for feedstock for other industrial processes. We must find a use for these precious resources and stop disposing of them as waste. These conservation activities must include energy conservation along with the conservation of other natural resources. We must strive in our Pollution Prevention activities toward the implementation of technologies that maintain an ecological balance, raise the standard of living in developing countries and maintain the quality of life in developed countries. Populution is a human activity that must be addressed.

AIR POLLUTION CONTROL SYSTEM RESEARCH AN ITERATIVE APPROACH TO DEVELOPING AFFORDABLE SYSTEMS

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Abstract

"Air Pollution Control System Research - An Iterative Approach to Developing Affordable Systems," describes a Strategic Environmental Research and Development Program (SERDP) funded project lead jointly by the Marine Corps Multi-Commodity Maintenance Centers, $(MC)^3$, and the Air and Energy Engineering Research Laboratory (AEERL) of the USEPA. The research focuses on paint booth exhaust minimization using recirculation, and on volatile organic compound (VOC) oxidation by the modules of a hybrid air pollution control system. The research team is applying bench, pilot and full scale systems to accomplish the goals of reduced cost and improved effectiveness of air treatment systems for paint booth exhaust.

Introduction

The Marine Corps has taken the lead in R&D for air pollution control systems (APCS) for paint booths, and cleaning/degreasing facilities. The Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$ have teamed with the Air & Energy Engineering Research Lab (AEERL) of the U. S. Environmental Protection Agency, and the Applied Research Laboratory at The Pennsylvania State University (ARL Penn State) to conduct the R&D. Funding has been secured from the Strategic Environmental R&D Program (SERDP). This paper will describe the roles of the team members, the technologies involved, the lab facilities which have been developed, and the iterative approach which is being followed in the execution of the research. Potential benefits to the $(MC)^3$ depots, lower level Marine Corps maintenance activities, other DoD facilities, and to industry will be addressed.

The technologies which are being researched, separately and in combination, include: Paint booth air recirculation; UV oxidation of volatile organic compounds (VOC); ozonated water treatment of VOCs; and carbon bed regeneration. Whenever possible, promising lab results will be quickly duplicated on the pilot scale system, and then on the full-scale field system. This iterative approach will allow for rapid dissemination of the technology improvements as they are developed.

Each team member is playing a key role and each stands to benefit from the research effort. The USMC is purchasing a commercial hybrid APCS and the depot at Barstow, CA will be the first host facility for the full-scale elements of the research; the depot will be the first to benefit as the cost and effectiveness

of the system are iteratively improved. AEERL has done significant research on paint booth recirculation (Darvin, 1993), but at smaller scales than the Barstow depot offers; the program provides the opportunity to prove their technology at full scale in a production environment. ARL Penn State has made research contributions in UV oxidation (Heinsohn, 1993) and carbon bed regeneration (Cannon, et al., 1993); this program has enhanced their facilities and is building on their expertise in State College, and is providing full-scale applications.

The goal of the program is to improve and demonstrate a combination of technologies intended to make VOC treatment both effective and affordable. The U.S. Marine Corps, the other services and industry will each benefit.

Funding

The primary funding for the research described in this paper will be provided by the Strategic Environmental Research and Development Program, which states as one of its purposes: "address environmental matters of concern to the DoD and the DoE through support for basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations." The contributions of each of the four participating agencies will also be substantial, and will be discussed later in the paper. The research will build on paint booth recirculation work accomplished by the Air & Energy Engineering Research Laboratory (AEERL) of the U. S. Environmental Protection Agency, much of which has been funded by the U.S. Air Force, and on UV oxidation research conducted at Penn State which was funded by the Air Emissions Reduction Center (AERC), a consortium of pharmaceutical companies.

Concept of Research

The research is being accomplished on lab scale, pilot scale, and production air pollution control systems (APCS). The production system, to be installed at Marine Corps Logistics Base (MCLB), Barstow, CA, will treat the exhaust from three paint booths which will be modified to recirculate a large percentage of their exhaust. These recirculation systems are, themselves, a critical element in the overall R&D effort. Areas of research relating to the APCS which are thought to hold substantial promise are now, and will continue to be studied on lab scale equipment. Results are being published, presented, and made available to the equipment manufacturer who will provide the full scale system to MCLB Barstow and the pilot scale system to ARL Penn State. The ongoing research has already resulted in design changes relating to UV light selection and spacing and to oxidant generation method. As the acquisition process proceeds, research results will continue to impact the configuration and the performance of the APCS. The pilot scale system has been delivered well prior to the full scale system, permitting trials of promising modifications in time to influence final configuration. Once the Barstow system has been installed, and is operating in concert with the paint booth recirculation systems, problems encountered can be investigated on all three scales. Additionally, new coating materials and equipment can be tested for treatability and functionality before committing them to the production environment. Numerous cycles of R&D, triggered at any of the three scales of equipment are expected. Results will continue to be published throughout the program, with a goal of improving the cost and performance of systems for both DoD and the private sector. The program was designed to provide the most efficient technology transfer possible in a complex technical environment.

The Team Members

Four organizations are key to the conduct of the program. Each is making substantial contributions and each is gaining from participation. The Maintenance Directorate of the Marine Corps Multi- Commodity Maintenance Centers $(MC)^3$ has lead the way in establishing this program. Marine

Corps funds initiated the program and Marine Corps funds will purchase the full scale APCS for installation at Barstow. MCLB Barstow will be the beta site throughout the program. The $(MC)^3$ personnel at Barstow are making the compromises between production and research necessary to assure program success. Participation in the program ensures that the $(MC)^3$ paint facilities will remain compliant with air quality regulations. Participation places the Maintenance Directorate in an R&D leadership position, assuring them their share of both responsibility and voice among the DoD depots.

The AEERL also provided early funding to start the program prior to SERDP funding release. AEERL brings substantial paint booth recirculation technology to bear. Mr. Charles H. Darvin, who has made major contributions to recirculation development, is AEERL's principle investigator on this project. Participation ensures continuing development of this important technology, giving AEERL a most productive avenue on which to fulfill their mission. AEERL is committed to the technology transfer process; they see paint booth recirculation, as well as the APCS development, as excellent candidates.

ARL Penn State also provided kick-off funding and has assembled a very strong team of researchers to advance the work, some of which was ongoing under other programs. New, totally dedicated lab space has been provided and appropriately equipped. ARL is growing their expertise during the program, and will continue to enhance their laboratory facilities, improving the likelihood of attracting additional research funding.

Terr-Aqua Enviro Systems (TAES) has provided the pilot scale APCS and a wealth of engineering experience to accelerate the programs. TAES will gain considerable market place exposure, and has the option to take full advantage of research results to improve their systems. While all research results will move rapidly to the public domain, TAES will be in a position to react most quickly. The program has, with this mechanism, enhanced the likelihood of continuous, successful technology transfer.

Each team member will have made a substantial contribution to make this program a success, and each stand to gain in proportion to its input. The balance achieved in creating this win-win situation may become a model for multi-agency programs in the future.

The Technologies

The marriage of paint booth recirculation and a hybrid APCS is driven by cost and by the needs of DoD depots to use a variety of coating materials. APCS cost is a direct function of volumetric exhaust flowrate, and, within limits, is independent of the concentration of volatile organic compounds in the exhaust stream.

Recirculation/Partitioning

The flow reduction technique defined by recirculation and partitioning is a unique concept that modifies the exhaust stream to permit the lowest possible discharge volume. Recirculation/partitioning makes air emission control more economically feasible by reducing the exhaust volume that must be controlled. A reduction of volumetric exhaust flowrate will result in a corresponding reduction of emissions control equipment acquisition and operating cost.

The concept of air recirculation is used in a number of applications particularly in paint baking ovens (Darvin, 1993). However, the technique of flow partitioning is a new booth design concept which when demonstrated in an operating booth will eliminate the concern of recirculating booth air to a manned spray booth. This issue is unique to the OSHA requirements for manned spray booth operation which defines the level of air flow and pollutant concentration within a booth. The present operating codes have prevented the use of flow reduction schemes in booths which could reduce emissions control cost for spray

painting operations. Recirculation and partitioning will allow compliance with the air flow requirements within the booth while achieving a 50 percent and greater reduction in booth exhaust flow rate. (See Figure 1).

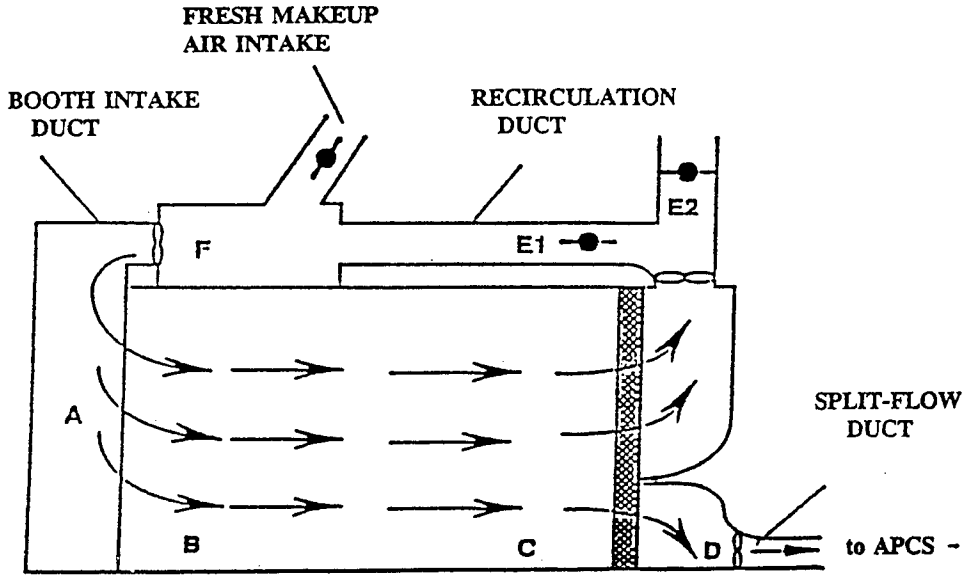

Figure 1. Recirculating/Partitioned Spray Booth

The TAES APCS

The TAES APCS which will be installed at MCLB Barstow (and pilot scale at ARL Penn State) uses a self-contained, self-regenerative multi-stage process. The design captures and oxidizes a broad range of Volatile Organic Compounds (VOCs), including chlorinated and halogenated VOCs. The APCS will reduce VOC emissions in exhaust air streams from paint spray booths, ovens, mixing rooms, conformal coating operations, solvent cleaning and paint removal facilities to below air quality regulation levels while producing no secondary hazardous pollutants.

The APCS consists of the following stages:

- A collection system which will capture and deliver the contaminated air stream to the APCS.
- Pre-filters and secondary filters which remove any airborne particulates which are entrained in the air stream down to approximately one micron. Typical high efficiency particulate arrestor (HEPA) filters are used for this.
- Photolytic-Reactors which initiate photo dissociation and radical oxidation processes. (This device houses special UV lights to initiate oxidation of VOCs).
- Mist Air Dispersion Unit which will "wet" the air stream. This is done so that any sub-micron particulate has the opportunity to go into aqueous phase.

- An Aqua-Reactor which is a counter flow packed bed scrubber with highly oxidant rich water circulating throughout.

- Carbon Beds which capture and treat remaining VOCs are the final step in the treatment train. These carbon beds are regenerated with oxidants for onsite destruction of the VOCs.

The Research

While not necessarily separated in the execution, the research is most clearly described in four areas: Recirculation/Partitioning; UV-Radical Oxidation; Carbon Bed Regeneration; and Miscellaneous.

Recirculation/Partitioning

The recirculation/partitioning portion of the program includes studies to develop, demonstrate and evaluate the emission flow reduction potential of the concept while remaining within the criteria established by OSHA and consensus code organizations. Specific research is being conducted to: (a) define the level of pollutant buildup in the recirculating air stream; (b) to develop booth design, modification specifications, and models; (c) define control cost projections based on flow reduction potential; and (d) predict resulting energy requirements to control the modified booth. The diagram of the recirculation partitioned spray booth concept is represented in Figure 1.

Past EPA studies suggest that pollutants in a horizontal flow spray booth are divided into two concentration regions in which the lower region of the booth exhibits an average concentration for all pollutant species greater than in the upper region of the booth. The result is that the greatest portion of the pollutant generated during painting remains in the lower level of the booth. Based on this finding, separate exhaust streams might be directed from the two regions of the booth: one a pollutant-rich lower stream directed to a control system and the second, a lean upper stream recirculated to the spray booth.

Booth pollutant concentration analysis and booth flow modeling studies are required to evaluate and validate the potential of the recirculation/partitioning concept for Marine Corps painting facilities. The results of these studies confirm the capability of the design concept to remain within the booth concentration limits established by OSHA and other consensus organizations. Specific analysis of metals, isocyanates and total organic volatiles is being conducted. Both pre- and post-booth modification studies will be completed during more than 100 individual experiments completed during each stage of the program. Each experiment will give data points that indicate how and where pollutants accumulate within the flow patterns of the test booths. Modeling of the concentration zones for various pollutants and the flow patterns within the test booths and under varying painting scenarios will be completed. These data and resulting models will allow development of criteria for booth design, modification and operation.

UV-Radical Oxidation

The UV-radical oxidation system manufactured by Terra-Aqua Enviro Systems (TAES) has been permitted and in operation for several years in the South Coast Air District of California. This district is known to have the most stringent air emissions standards in the U.S. The UV-radical oxidation system has rapid transient characteristics, but little has been published describing the chemical reactions that occur in each component and how the chemical kinetics is coupled with the velocity field in the reactor (Heinsohn, 1993). Thus, it is not known what percent destruction occurs in each of the TAES components, or perhaps whether one of the system components can be eliminated.

This area of the research will focus on the photolytic reactor component of the UV-radical oxidation system. The research will:

- Determine the destruction efficiency and exhaust products for a variety of military coatings; and

- Describe how UV-radical oxidation processes destroy VOCs and hazardous air pollutants (HAPs) so that the system's performance can be improved and its cost and size reduced.

Carbon Bed Regeneration

The Terr-Aqua system employs carbon beds as the final step in the treatment train. Granular activated carbon (GAC) adsorption of VOCs has been documented (Cannon, et al., 1993), and GAC adsorption offers a best available technology for capturing VOCs and HAPs. While in service, the GAC will eventually become exhausted (spent) in its capacity to adsorb organic compounds, at which point it can either be regenerated and reused, or landfilled and replaced.

The TAES system employs frequent cycles of VOC loading onto GAC followed by in-situ oxidant regeneration. The frequent cycling precludes the buildup of VOCs on GAC to levels that cause the effluent VOC concentration to exceed standards. The GAC thus serves as a collector for VOCs, which facilitates the necessarily long reaction times for oxidation of the retained VOCs. Thus, although typical air residence times through the activated carbon system may be measured in seconds, the VOC retention and destruction time on the activated carbon surface may be measured in hours. VOCs and HAPs are not the only organic materials affected by oxidation, however: the activated carbon surface itself may also become oxidized, which could potentially cause either favorable or detrimental effects. The intent of the research is to develop the fundamental science that characterizes regeneration so that the process can be enhanced. The technical objectives of this research area are:

- Determine the extent to which oxidants regenerate an activated carbon that has become loaded with volatile organic compounds.

- Determine whether this oxidation adversely or favorable alters the adsorptive properties and pore structure of activated carbon.

- Monitor the influence of several variables on regeneration effectiveness, including regeneration times, oxidant intensity and spacing, temperature, and nature of VOCs that have been adsorbed.

- Provide fundamental insight on techniques for enhancing the oxidation method of regenerating GAC.

Miscellaneous

This is by no means the least important area of the research. As experience is gained on lab scale, pilot scale, and ultimately the production APCS, promising areas of research, offering rapid and/or high return on research effort will become apparent. These opportunities, plus the investigation of problems effecting production at MCLB Barstow, will receive rapid response. Early candidates which may well get considerable attention are:

- The effect of metals contained in various coating materials on the treatment process and disposition of these metals during the process.

- The effects of water temperature and pH on the performance of the aqua reactor.

Issues

Treatment vs. Pollution Prevention

Both President Clinton and Ms. Browner, the Administrator of the USEPA, have issued policy statements which emphasize pollution prevention by source reduction and deemphasize the treatment and control approaches to reducing pollution. This research focuses on treatment. The justification is simply that:

- The military is years away from converting entirely to low or zero solvent based coating materials; and

- Other processes and industries can benefit substantially from the research.

All DoD facilities which paint must soon determine how they will cope with increasing regulatory pressure. Those facilities which are in non-attainment areas must react immediately. This research will serve those needs.

Competition vs. Technology Transfer

The procurement process sometimes moves at speeds which are not only non-responsive to the needs of their customers, but the process frequently insures that the equipment installed is not of the latest technology. In order to ensure that the research is conducted on current technology, and that at least one private supplier of APCS equipment will convert research results to available product, TAES has been included as an active participant in the research. Great care will be taken to ensure that research results which belong in the public domain are made available in a timely manner.

Summary and Goals

A unique and very capable team has been assembled to execute promising research. The marriage of paint booth recirculation technology to a hybrid ultra violet-radical oxidation air pollution control system (APCS) offers promise for an affordable system which will accommodate a wide range of coating materials. The ultimate goals of the research are to bring the cost of paint booth/APCS systems down and their effectiveness up. Success will bring costs within reach of DoD maintenance activities below the depot level, as well as, small and medium businesses which badly need such technologies.

References

1. Cannon, F. S., V. L. Snoeyink, R. G. Lee, G. Dagois, and J. DeWolfe, 1993. "The Effect of Calcium in Field-Spent Granular Activated Carbons on Pore Development during Thermal Regeneration." *Jour AWWA*, 85(3) pp. 76-89.

2. Cannon, F. S., V. L. Snoeyink, R. G. Lee, G. Dagois, and J. DeWolfe. 1993 a. "Effects of Metals on Thermal Regeneration of Granular Activated Carbon." American Waterworks Association Research Foundation, Denver, CO.

3. Heinsohn, R. J., Private Communication, 1993.

Table of Abbreviations

AEERL	Air and Energy Engineering Research Laboratory
APCS	Air Pollution Control System
ARL	Applied Research Laboratory
HAP	Hazardous Air Pollutant
$(MC)^3$	Marine Corps Multi-Commodity Maintenance Centers
MCLB	Marine Corps Logistics Base
SERDP	Strategic Environmental Research and Development Program
TAES	TerrAqua Enviro Systems, Inc.
UV	Ultra Violet
VOC	Volatile Organic Compounds

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THE SEARCH FOR CFC ALTERNATIVES IS OVER?

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ABSTRACT

The Electronics Manufacturing Productivity Facility (EMPF) is a U.S. Navy Center of Excellence tasked to do research in electronics manufacturing. For the past seven years, the EMPF has performed extensive research in various cleaning materials and processes that have recently been made available to printed circuit board assemblers. This paper outlines our research and points out the positive and negative aspects that need to be considered when choosing an alternative process.

INTRODUCTION

The search to find suitable alternatives to chlorofluorocarbon-based (CFC) cleaning solvents is coming to an end. That does not mean the issues are any clearer, nor does it mean the decisions are any easier. It means that we are out of time and a decision, right or wrong, has to be made.

The Electronics Manufacturing Productivity Facility (EMPF), located in Indianapolis, Indiana, is a Navy Center of Excellence tasked to do research in electronics manufacturing. Information learned in our research is disseminated to the electronics manufacturing industry via final reports, technical articles, seminars, and workshops. Part of our charter is to give telephone consulting to those who have problems in specific areas of their assembly process. Many of the telephone inquiries that I have received lately usually begin, "I heard that CFC's are being phased out. Is this true?" Or, "My boss told me to get rid of our CFC's. What other solvent can I put in my vapor degreaser?" "I heard CFC's are being phased out, but I'm just going to have to get a waiver because I still need to clean." There was one caller who proudly stated "I don't know what all the fuss is to get rid of CFC's. I found a solvent that works just fine. Trichloroethane!" It was hard to tell him that he had jumped off a sinking ship into a life raft with a big hole in it.

For those who are still unsure of the situation, here it is in a nutshell. Scientists have claimed that CFC molecules are depleting the Earth's protective ozone layer. In 1987, the Montreal Protocol was signed, calling for a gradual global reduction of all production of CFC's by the year 2000. President Bush accelerated the reduction to include a complete phaseout in the United States by 1995. Shortly after that, the Copenhagen amendment adopted that same phaseout for the rest of the world. DuPont, the world's largest producer of CFC's, has announced it will stop all Class I CFC production by the end of 1994. In an effort to dissuade manufacturers from using CFC's, the Clean Air Act established a labeling law effective May 15, 1993 requiring products made with, or containing, Class I or Class II CFC's be labeled as such. As an added burden, annual tax increases imposed by the federal government are driving the cost of CFC's higher each year.

If you are one of many who are thinking, "No problem - I still have two years," there is more. Consider that even if you had complete control of your budget with unlimited financial resources and were able to order equipment today, you should not expect delivery for 6 to 12 months depending on how many other orders were taken that day. Add to that the acquisition of water treatment systems (both before and after the cleaning process), an air treatment system, installation, process development and training. All of a sudden two years does not seem that long.

Before any of this can happen, of course, you must select from the many cleaning chemistries and alternate fluxing/soldering processes that are available. You could call various vendors and listen to their sales pitches, or sift through junk mail and look for the advertisements with water falls, green grass, sunshine, smiling birds, orange trees and the all too familiar universal symbol for "contains no CFC's". Selecting a substitute that is right for your process is a job in itself and you can't take short-cuts by looking at your neighbor's house to see what they're using. What's right for their process may or may not be right for yours. The cleaning efficiency of a solvent will depend on variables such as flux type, board design, density, component types, throughput, cleaning machine, time, spray nozzle configurations and pressures, to name a few. In addition, environmental laws vary from state-to-state and even between localities within the same state.

CFC ALTERNATIVE TESTING

The EMPF, along with the Institute for Interconnecting and Packaging of Electronic Circuits (IPC), has tested 15 commercially available solvents to date (see table) for use with rosin-based fluxes. Although these solvents have passed a very carefully controlled test, the "best" solvent or even "possible" solvent will vary with your process. You may use this list as a starting point, select a few possibilities, and see what works best for you.

In addition to deciding what works best from a cleaning standpoint, there are other concerns that must be considered. Material compatibility examines how these cleaning materials will react to materials on your product such as part markings, solder mask, laminates and some components. Industrial hygiene and safety addresses odor, flammability, and exposure limits. From an environmental standpoint, is the waste treated as hazardous material or can the solvent be easily treated to drain, recycled or even close-looped? Finally, the cost associated with the new process needs to be considered. Equipment costs, material costs, operational costs, maintenance costs, engineering, labor and training costs. There are also costs associated with support equipment for water, air and waste management.

PHASE 2 APPROVED CFC ALTERNATIVE CLEANING MATERIALS
as of June 1, 1994

Allied Signal Genesolv 2004	Mike Ruckriegel	(201) 455-6751
Alpha Metals 2110	John Stevenson	(201) 434-6778
British Petroleum Prozone	Dave Dodgen	(214) 238-1224
Bush Boake Allen Solvent E212	Richard Lamp	(904) 783-2180
Church & Dwight Armakleen E-2000	Frank Cala	(609) 683-7068
Dr. O.K. Wack Chemi Zestron	Karsten Lessmann	011 49 841-635-0 (Germany)
DuPont Axarel 32	Rich Stewart	(919) 248-5048
DuPont Axarel 38	Rich Stewart	(919) 248-5048
ECD Emulsonator/DuPont Axarel 36	Steve Glass	(503) 659-6100
Exxon Actrel ED11 & Actrel ES	Jim Schreiner	(713) 425-2115
Envirosolv KNI-2000	Steve McCane	(904) 724-1990
Hughes RADS	Rick George	(310) 616-6085
ISP Micropure CDF	Jim Butler	(201) 628-3345
Kyzen Ionox MC	Kyle Doyel	(800) 845-5524
Petroferm Bioact EC7	Craig Hood	(904) 261-8286
Petroferm Bioact EC7R	Craig Hood	(904) 261-8286
Petroferm Bioact EC-Ultra	Craig Hood	(904) 261-8286

In addition to the solvents listed, other cleaning processes are either in process or being planned for the near future.

CLEANING WITH ULTRASONIC ENERGY

Using ultrasonic energy to satisfactorily clean tough situations or improve a less-aggressive solvent's cleaning ability may also be an option. Historically, the military has been against the use of ultrasonics because of some studies performed in the 1950's that showed ultrasonic frequencies were causing fragile wire interconnects between the die and the terminal of microelectronic devices to vibrate enough to fatigue and eventually break. The military has recently changed its stand; however, and the latest revisions to some military specifications now state:

> *"Ultrasonic cleaning is permissible on electronic assemblies with electrical components, provided the contractor has documentation available for review showing that the use of ultrasonics does not damage the mechanical or electrical performance of the product or components being cleaned."*

This change of heart by the military is due to more recent studies conducted by the EMPF and other research laboratories that have given us a better understanding of ultrasonics. At the same time, newer wire bonding techniques have provided a more robust component which is more able to withstand the harsh vibrations of ultrasonic energy. This is not to say ultrasonics is 100% safe. Under proper conditions, ultrasonics can be a useful tool, but fatigue is a part of life with ultrasonics and some components under certain applications will fail. "Test clean" a safe sample of your product in ultrasonics before you invest a large quantity of time or money.

WATER SOLUBLE FLUXES

Another option may be to eliminate rosin-based fluxes all together and use a water soluble flux (WSF). WSF can be cleaned either by using water alone, or water with a detergent/saponifier. WSFs will typically provide excellent solderability and enlarge the soldering process window. The reason they provide such good solderability is because of their corrosivity; however, these corrosive properties can cause problems if cleaning is not properly performed. If a WSF were to get trapped in an area, such as under a tightly spaced component, inside an unsealed component, or up under the insulation of a stranded wire, a failure is likely to occur. Many WSFs contain polyethylene glycols and other polyglycols which are nonionic and hygroscopic, meaning they will absorb moisture from the air and promote electrochemical migration and degradation of electrical performance in the presence of ionic contamination. Since polyglycols are nonionic, they cannot be measured in the commonly used resistivity of solvent extract cleanliness tests such as the Omegameter™ or Ionograph™. Recent revisions to military specifications are allowing the use of WSFs (except on stranded wires and unsealed components) with certain restrictions being placed on those containing polyglycols. These restrictions are currently being reviewed by the Navy.

NO-CLEAN FLUXES

If selecting a cleaning process looks tough and you're thinking about taking the easy way out by going to a "no-clean" flux, it's not that easy. No-clean does not mean you do not have to clean because there is no residue, it means you do not have to clean because the residue is small, and not detrimental to the assembly. No-clean fluxes, also known as low solids, or low residue (LR) fluxes, were formulated to leave a minimum quantity of a benign residue. This residue is not conductive or corrosive; however, it may interfere with the adhesion of the conformal coating. As in choosing a cleaning material, other issues must be considered when selecting and implementing a low residue flux. Material compatibility, environment, industrial hygiene, safety, and cost associated with the new process all need to be considered. Flux application is not as simple as it was with the good old rosin-based fluxes, and the operator must have an intimate knowledge of his soldering process. On the positive side, the military recognizes the potential for using LR fluxes for a broad range of soldering applications,

including soldering of stranded wires and unsealed components. The potential of LR fluxes is reflected in the most recent revisions to military specifications.

In contrast with the WSFs, LR fluxes are not very aggressive, therefore they create a smaller soldering process window. This window can be enlarged by using an inert atmosphere such as nitrogen to reduce oxidation of the base metals. Another process worth considering which also requires nitrogen, uses a dilute adipic acid to precondition the board. The actual soldering takes place in a sealed chamber filled with an inert atmosphere of nitrogen and formic acid. When exposed to the high temperatures associated with wave soldering, the adipic acid evaporates and the formic acid converts to carbon dioxide and water. Only a small amount of noncorrosive residue is left on the assembly.

Manufacturers who are going to LR fluxes must think no-clean ***process*** from incoming component and board cleanliness levels throughout all stages of handling, processing and shipping. Implementing a no-clean process is not as simple as changing the flux and rolling the vapor degreaser out into the back alley for the trash collector. Unfortunately, flux is not the only source of contamination. There are several very ionic, very corrosive materials that are used in the manufacturing of bare boards. An assembler must verify that the bare boards, along with components and other parts to be used on the assembly, are clean upon receiving, then maintain that level of cleanliness throughout the assembly process. Ionic and nonionic residues come from many sources and preventing this contamination from coming into contact with the assembly is hard. Even a bare board that was verified to be clean upon arrival at the assembly facility may still leach ionic materials when exposed to elevated temperatures. Parts are sometimes stored for months at a time in a clean(?) storage area awaiting subsequent operations. Boards are handled and moved from station to station for component insertion and soldering. The cleanliness level of the parts is only as clean as the people handling them, and many people do not realize that not all gloves are free of ionic residue. If the gloves are free of ionic residue, do assemblers contaminate the outside of the gloves when removing them from the bag or when putting them on? Will an assembler use the gloved hand to open a valve, turn an unclean doorknob or satisfy an itch? A no-clean process is possible, but it starts from the bare board and continues until the assembly is complete. There are big companies, with big research departments, with big dollars, that have spent years developing a reliable LR process.

CONCLUSION

Choosing and implementing a process that is right for your particular assembly house takes time, and you have no time-outs left. CFCs will be phased out by the end of 1995. Acquiring CFCs will be harder and more expensive by the end of 1994, and the labeling law is currently in effect.

- Will you use rosin-based, water soluble, or low solids flux?
- Will you solder in air or nitrogen?
- Which solvent is best?
- Which machine is best?
- Which process is best, aqueous or semi-aqueous? Batch or in-line?
- Should you use ultrasonic energy?
- Will you recycle, treat or close-loop your effluent?
- Will you clean or is no-clean the ultimate solution?

A decision has to be made because the search to find suitable alternatives to CFC-based cleaning solvents is coming to an end.

Phase 2 Approved Commercially Available CFC Alternative Cleaning Materials as of 7/94

SOLVENTS

Allied Genesolv 2004 (HCFC)	Mike Ruckriegel	(201) 455-6751

* Advanced Vapor Degreasing (AVD) with Petroferm Solvating Agent 24 & 3M PF-5070 Rinse Agent

Petroferm Solvating Agent 24	Christine Fouts	(904) 261-8286
3M PF-5070 Rinse Agent	Wayland Holloway	(612) 737-3030

SEMI-AQUEOUS SOLVENTS

* Arakawa Pine Alpha ST-100S	Dave Ahlberg	(310) 373-0404
British Petroleum Prozone	Dave Dodgen	(214) 238-1224
Bush Boake Allen E-212	Richard Lamp	(904) 783-2180
Dr. O.K. Wack Zestron FA	Karsten Lessmann	011 49 841-635-0 (Germany)
ECD Emulsonator/DuPont Axarel 36	Pat Barrett	(503) 659-6100
Envirosolv KNI-2000	Steve McCane	(904) 724-1990
Exxon Actrel ED11 & Actrel ES	Jim Schreiner	(713) 425-2115
ISP Micropure CDF	Jim Butler	(201) 628-3345
Kyzen Ionox MC	Kyle Doyel	(800) 845-5524
Petroferm Axarel 32	Jim Scott	(904) 261-8286
Petroferm Axarel 38	Jim Scott	(904) 261-8286
Petroferm Bioact EC7	Craig Hood	(904) 261-8286
Petroferm Bioact EC7R	Craig Hood	(904) 261-8286
Petroferm Bioact EC-Ultra	Craig Hood	(904) 261-8286

AQUEOUS SOLVENTS

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Lonco RADS	Kevin Grossenbacher	(800) 323-9625

**** approval pending***

Major Weapon System Environmental Life-cycle Cost Estimating for Conservation, Cleanup, Compliance and Pollution Prevention (C^3P^2)

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Abstract

The Titan IV Space Launch Vehicle Program is one of many major weapon system programs that have modified acquisition plans and operational procedures to meet new, stringent environmental rules and regulations. The Environmental Protection Agency (EPA) and the Department of Defense (DOD) mandate to reduce the use of ozone depleting chemicals (ODCs) is just one of the regulatory changes that has affected the program. In the last few years, public environmental awareness, coupled with stricter environmental regulations, has created the need for DOD to produce environmental life-cycle cost estimates (ELCCE) for every major weapon system acquisition program. The environmental impact of the weapon system must be assessed and budgeted, considering all costs, from cradle to grave. The Office of the Secretary of Defense (OSD) has proposed that organizations consider Conservation, Cleanup, Compliance and Pollution Prevention (C^3P^2) issues associated with each acquisition program to assess life-cycle impacts and costs.

The Air Force selected the Titan IV system as the pilot program for estimating life-cycle environmental costs. The estimating task required participants to develop an ELCCE methodology, collect data to test the methodology and produce a credible cost estimate within the DOD C^3P^2 definition. The estimating methodology included using the Program Office weapon system description and work breakdown structure together with operational site and manufacturing plant visits to identify environmental cost drivers. The results of the Titan IV ELCCE process are discussed and expanded to demonstrate how they can be applied to satisfy any life-cycle environmental cost estimating requirement.

The requirement to identify environmental life-cycle costs during the program acquisition phase is rapidly emerging as one of the most significant environmental initiatives of our time. The Department of Defense (DOD) has wholeheartedly embraced the concept and not only sees it as a rational means of safeguarding the environment, but as an effective means of reducing pollution-related costs, sustaining military operations and maintaining a "good neighbor" reputation for environmental compliance.

Environmental compliance and pollution prevention have been mandated by the federal government. Executive Order 12873, October 1993, mandating recycling and pollution prevention, added emphasis to environmental programs already underway. The Federal Facility Compliance Act of 1992 enables the EPA and the states to use the full range of enforcement tools they have at their disposal against a federal facility. All environmental areas, air, water, hazardous waste and solid waste are now addressed from the President down to the user level in all manner of regulations.

Each environmental Act or Executive Order that affects DOD has the potential of impacting the cost of developing, procuring, operating or disposing of a major weapon system. The Department of Defense is actively pursuing methods for evaluating environmental life-cycle cost impacts of major weapon systems. This information will then be included as a part of the milestone approval briefings. The major

objective of this effort is to assure that there are no future environmental funding "surprises", particularly for demilitarization and disposal. The acquisition community, in its attempt to put some discipline into the process, wants managers to make the "best" environmental decisions and then estimate C^3P^2 environmental costs to the end of the life-cycle. The estimating methodology must satisfy current Defense Acquisition Board direction yet be easy to modify to incorporate new environmental rules.

The Air Force Titan IV Space Launch program was selected as the first program for estimating life-cycle C^3P^2 environmental costs. The Titan IV missile, used by DOD, NASA and other customers to launch satellites, is currently undergoing a solid rocket motor upgrade, the reason for the latest review cycle. Launches are scheduled through the year 2004 with two options to extend the program: to 2007 and 2014. The environmental life-cycle cost estimate covered the years 1992 to the end of the program, with 1994 as the base year for the estimate.

The identification of life-cycle environmental issues associated with Conservation, Compliance, Cleanup and Pollution Prevention (C^3P^2) were required in order to gather the accurate data necessary to produce an accurate cost estimate. No previous examples were available to use as a model for collecting and organizing the data; therefore, a system of data collection, compilation and cost estimating was devised to meet the requirements. The weapon system life-cycle phases from DOD 5000.4M, *Cost Analysis Guidance Procedures,* were used as the baseline for the life-cycle. These are:

- Research and Development
- Manufacturing
- Maintenance and Logistics
- Operations and Support, including demilitarization and disposal
- Facilities, construction or major modifications
- Personnel and Training

The Titan IV cost estimate was prepared from documentation provided by the system program office and data gathered during visits to the operational launch sites and the prime contractor's manufacturing facility. Five other major element contractors were interviewed by telephone to determine the extent of their compliance, pollution prevention, management and training activities. Data was gathered and grouped according to environmental requirements for the program. This enabled the team to stay focused on Titan IV C^3P^2 life-cycle environmental issues.

There are three basic documents that provide adequate detail to support data gathering and the production of an environmental life-cycle cost estimate. These are the operations concept (plan), the maintenance concept and the Work Breakdown Structure (WBS). Other documents, such as a detailed acquisition plan and test and evaluation plan, provide additional details that improve the estimate. The WBS contains all the major elements, components and subcomponents that make up the total system. This includes management, documentation, training and facilities in addition to the actual hardware. The Operations and Maintenance concepts describe how a weapon system will be employed and maintained. Therefore, they provide the data an analyst needs to establish quantities for each WBS element during the operational and disposal phases of the life-cycle.

The next step was to evaluate selected Titan IV WBS elements against the C^3P^2 environmental categories to determine if there were any environmental data associated with the individual elements. Management, which was included in the WBS, and risk were added to C^3P^2 as important environmental cost categories. A procedure similar to that shown in Figure 1 was used to collect and roll-up costs for components and subcomponents. The sum of all individual costs is the total weapon system environmental cost.

Once the methodology was in place, data gathering and cost estimating were straight forward and followed standard procedures. The findings for each C^3P^2 environmental category required personnel to examine environmental regulations as they applied to the WBS elements and activities; that is, the Clean Air Act, Clean Water Act, Federal Facilities Compliance Act, and so forth. The relationships shown in Figure 1 were used to simplify the data collection process. The methodology or process was developed to handle the different types of waste streams associated with manufacturing, operations and demilitarization

and disposal. A summary for each phase of the life-cycle, Design and Acquisition, Operations and Maintenance and Demilitarization and Disposal is provided below.

Compliance data for each principal cost area were gathered from operational launch sites and major component manufactures.

- **Air**. Air regulations and procedures impacting Titan IV environmental cost were: New Rule Development, Permit Application, Emission Calculations, Negotiations with Regulatory Agencies, Recordkeeping, Title V Operating Permit and Title III Maximum Achievable Control Technology. The majority of cost for air compliance was attributed to manpower and permits. Some manufacturers were incurring operational costs for air handling equipment and in limited cases were programming capital outlays for new equipment to meet EPA requirements. The cost of replacing ODCs and other toxic chemical cleaners was captured under pollution prevention.
- **Wastewater.** Wastewater activities at the operational locations were instituted to control the disposal of deluge water remaining in the launch pad flame bucket after each Titan IV launch. At the manufacturing plants, wastewater management was instituted to dispose of contaminated water produced in various operations, such as chemical milling, and to manage storm water runoff. Environmental activities included Sample Coordination, Sample Analysis, Waste Characterization, Labeling, Waste Minimization Activities, Transportation to a Treatment Plant and management recordkeeping operations.
- **Solid Waste Management.** This was judged an operational cost for Titan IV and no life-cycle cost was assessed.
- **Hazardous Materials.** Hazardous materials management was limited to the personnel required to control, inventory and file reports. These costs were included in Management.
- **Hazardous Waste Management.** Hazardous waste management included those activities associated with generating, treatment, storage, waste minimization, recycling and discharge of hazardous waste. Cost drivers were the management time spent reviewing applicable regulations, time to review operational processes and identify hazardous waste generation sources (inventory), the cost of temporary storage facilities, waste characterization, sampling and analysis, labeling, transportation and disposal. The manufacturing facilities incur the largest portion of hazardous waste management costs, primarily for disposal.
- **Noise.** A study to determine the effect of missile launch noise on California marine mammals was the only noise compliance issue associated with the program and was included in the estimate.
- **Special Compliance Reporting.** Compliance reporting costs were captured in the Management Costs.

Pollution Prevention for Titan IV was being practiced by all organizations involved in the program. Recycling and materials substitution programs were in place at all locations queried. In some cases, there were significant cost dividends. Costs were not grouped by category for this evaluation as shown in figure 1, but rather were associated with the appropriate Titan IV WBS element. One exception that was listed separately was a pelletized carbon dioxide degreasing system that was being tested as a replacement for a liquid ODC wipe down process.

Conservation activities have been included as a part of the Titan IV program for many years. Costs associated with preservation of the natural habitat, cultural and archeological resources were consolidated with management data. There are approximately two environmental impact studies and environmental assessments performed per year for the program that were documented in the life-cycle estimate.

Clean-up, or restoration, is accomplished as required during the operational phase of the life-cycle and thoroughly at the end of the program. If pollution prevention and spill control programs have been effective, there will be little clean-up required. The Titan IV program was initiated before today's strict environmental rules were passed and there are environmental hazards that were created early-on in the program that have been, or will have to be, remediated before the program is phased out. Some

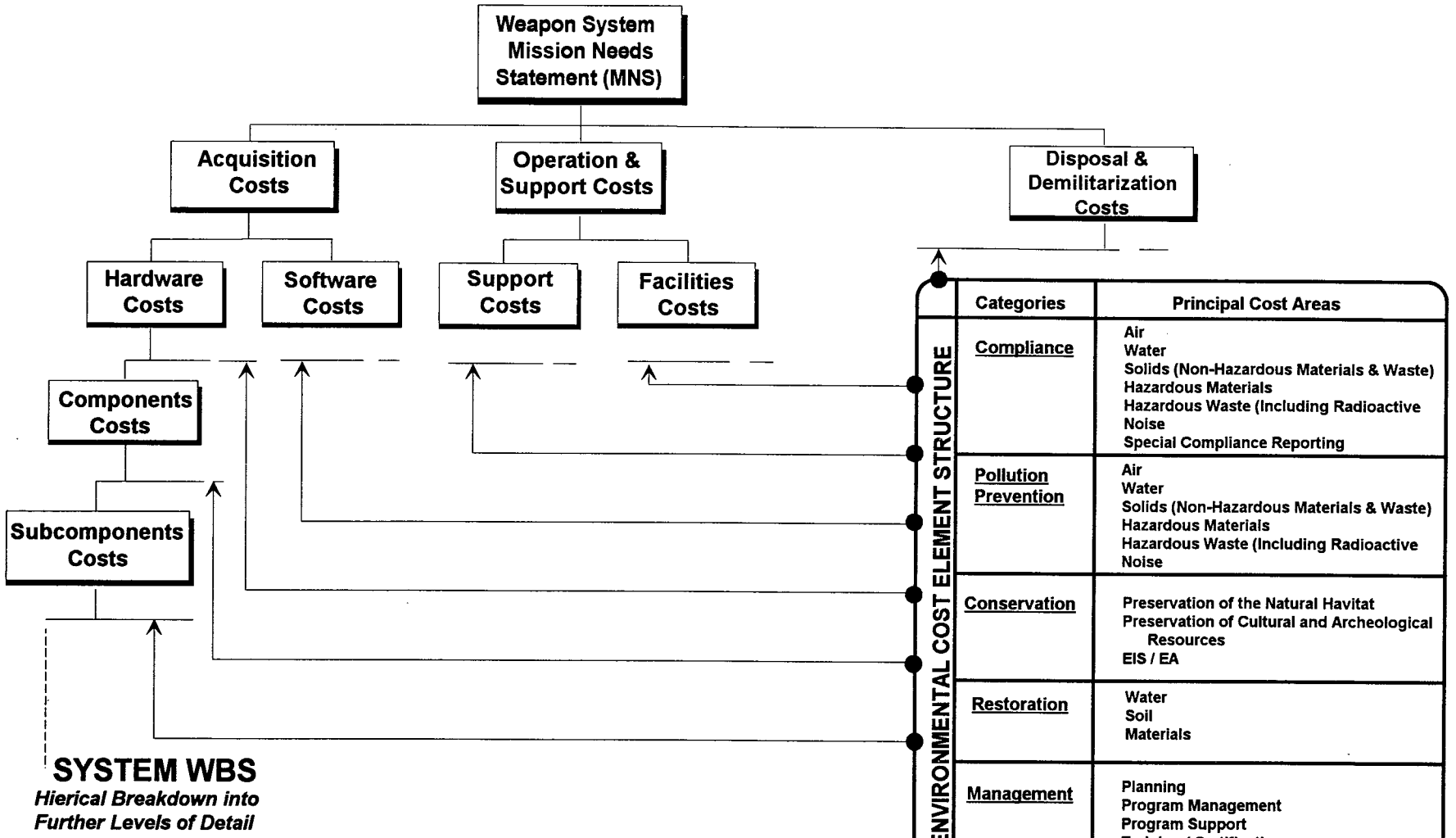

Figure 1.

Integration of an Environmental Cost Element Structure with the Work Breakdown Structure

manufacturers have installed monitoring wells around their facilities to evaluate ground water pollution in order to take appropriate action. Lead has been detected near one launch site and may have to be cleaned up at the end of the program. The extent of clean-up overall was unknown and estimates were not available. As a result, these estimates were incorporated into the "Risk" estimate.

Management included all of the people activities that could be directly attributed to complying with EPA environmental requirements. Environmental test and evaluation was incorporated into this cost estimating category along with Planning, Program Management, Program Support and Training.

Risk was the estimate of the unknown environmental life-cycle requirements. Where impending changes were identifiable, such as the Maximum Achievable Control Technology enacted in Title III of the Clean Air Act Amendment, a reasonable risk estimate could be made. The environmental rules that are known to be in work but have not been published yet were harder to estimate. Demilitarization and disposal requirements at the end of the program were difficult to quantify. If the expectations of the operations concept are met, all systems will be launched into space. The plans did treat the more hazardous elements, such as the solid propellant boosters that may be converted into mining explosive at phase out. Based on prior experience, risk was estimated to be between 8 and 12 percent of the total environmental cost estimate.

After the individual WBS element estimates were completed the cost was summarized (rolled-up) to produce a single value life-cycle environmental cost estimate for Titan IV. The data showed that cost drivers for operational launch sites and manufacturing facilities were about the same, the only difference being cost magnitude.

A workshop was convened after the Titan IV environmental life-cycle cost estimate was published to evaluate the methodology that was used and to recommend methods for improving and automating the process. The workshop organized the Titan IV methodology and expanded on the data collection procedures by defining the components of environmental cost. The conceptual data collection process and cost estimating methodology is that presented in Figure 1. Environmental life-cycle costs are impacted from the inception of the program as first described in the weapon system requirements document or statement of need. When the requirement is approved by OSD and development begins, the need to evaluate trade-offs and assess environmental life-cycle cost also begins.

The workshop limited the life-cycle to three phases: acquisition, operation and support and disposal and demilitarization. The acquisition phase includes design, development, manufacturing, test and evaluation and system delivery. Operations and support includes daily operations and training, logistics support and maintenance activities. Demilitarization and disposal are the final steps required to remove the weapon system from the Air Force inventory and make all parts safe for disposal or recycling.

Conclusions drawn from the Titan IV effort are that it is difficult to separate out environmental life-cycle costs from other research and development, acquisition and operational costs. Currently the cost of environmental compliance is included in the program as a cost of doing business. However, when weapon systems are modified, as the Titan IV was, the environmental impact of the change must be evaluated. If there are environmental costs added to the program as a result of the change, they must be identified and included in the program to assure adequate funding.

Another result of the Titan IV effort was the recognition that demilitarization and disposal costs have not been adequately accounted for in the phase out of prior weapon systems. Environmental compliance costs associated with demilitarization and disposal must be evaluated separately to submit adequate funding requests for this life-cycle phase. Every weapon system will have some final disposition charges and recycling paybacks that must be introduced into the life-cycle estimate as early as possible in the life-cycle.

Future development plans will build on the Titan IV estimating experience with a technical plan and cost guide being developed. These will build on MIL-STD-881B, Work Breakdown Structure, incorporate data from aircraft and missile cost handbooks, and use existing models for environmental containment costs. Relevant parts of existing environmental cost estimating models will be integrated to build an automated cost analysis tool. The design is based on proven model building methodology with easy incorporation of environmental rule and legislative changes.

The methodology and environmental life-cycle cost estimating procedures used for the Titan IV Space Launch system are not specific to DOD weapon systems. It will work for any system that has well defined components and goes through life cycle phases. It can be used to assess the environmental cost requirements for building and operating automobiles, large equipment, commercial airlines and the like. When the automated environmental life-cycle cost estimating model is in place, the time required to produce an estimate is expected to decrease while the accuracy increases.

Evaluating the Cost Effectiveness of Environmental Projects: Case Studies in Aerospace and Defense

by
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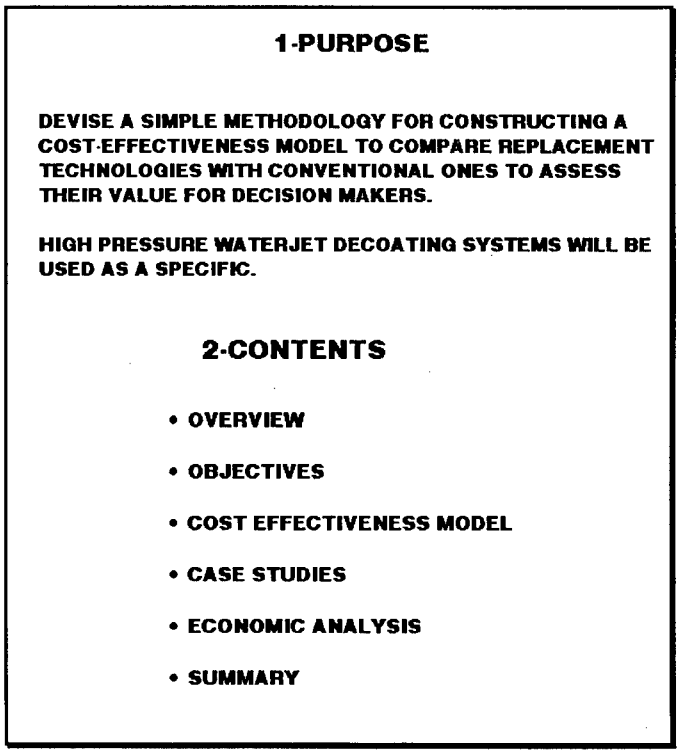
Abstract

Using the replacement technology of high pressure waterjet decoating systems as an example, a simple methodology is presented for developing a cost effectiveness model. The model uses a four-step process to formulate an economic justification designed for presentation to decision makers as an assessment of the value of the replacement technology over conventional methods. Three case studies from major U. S. and international airlines are used to illustrate the methodology and resulting model. Tax and depreciation impacts are also presented as potential additions to the model.

Introduction (Charts 1 & 2)

The purpose of this paper is to present a simple methodology for constructing a cost effectiveness model designed to compare, in economic terms, the value of a potential replacement technology with conventional methods. The replacement technology of high pressure waterjet decoating will be used as an example because it is rapidly gaining acceptance as a cost-effective alternative to chemical stripping, abrasive grit blasting, machining, and hand sanding. Since the current major user of waterjet decoating systems is the aviation industry, the case studies will be drawn from data collected by major airlines.



Although waterjet decoating systems will be used as the example replacement technology, the methodology developed is applicable to any situation where a sound, economic basis is needed for comparing two technologies capable of performing the same tasks.

Overview (Chart 3)

Waterjet coating removal system do provide a good example for cost effectiveness modeling because they offer an alternative to a number of both labor intensive and potentially environmentally hazardous methods now in common use in many industries. The major attractions of waterjet decoating are high coating removal rates, low potential for damage to the substrate material, and environmental safety since the only waste products from the process are the coatings removed. All processing water is normally collected, filtered, reclaimed, and reused in the high pressure pumps.

3-OVERVIEW

- **Waterjet coating removal is a rapidly emerging niche area of waterjet machining technology.**
- **Waterjet Systems is a technology spin-off company based on transfer of waterjet decoating expertise from NASA.**
- **High pressure waterjet technology is an environmentally sound alternative to conventional waste-generating technologies of:**
  ...Gritblasting.
  ...Chemical immersion/stripping.
  ...Machining.
  ...Hand sanding.
- **The only waste products are the coatings removed. All process water is recovered, reconditioned and reused.**

Objectives (Chart 4)

Although the focus of this paper is economic justification because of today's priority on enhancing productivity in our highly competitive global environment, a total assessment that includes both tangible and intangible benefits should be presented to decision makers as measure of the total value of a replacement technology.

4-OBJECTIVES

- **THE OBJECTIVES OF THE COST EFFECTIVENESS MODEL WILL BE TWOFOLD:**
  1-Assess the value of a replacement technology as an alternative process.
  2-Provide a sound, economic basis for justifying to decision-makers the capital funds needed to purchase the replacement.
- **THE END RESULT WILL BE SIMPLE MODEL WITH A FRAMEWORK SUITABLE FOR A WIDE VARIETY OF PROJECTS THAT CONTRAST ONE TECHNOLOGY TO ANOTHER.**

Cost Effectiveness Model (Chart 5)

This is the four-step methodology used to develop a cost-effectiveness model. In step one, not all the elements listed can contribute to the economic analysis; however, some may be very important in assessing the total value of the alternative. In the aviation industry, for example, the intangible factor of passenger safety can override all economic factors in a decision.

5-COST EFFECTIVENESS MODEL

- **ESTABLISH CURRENT METHOD BASELINE:**
  - **...Costs.**
  - **...Turn-time.**
  - **...Material.**
  - **...Intangibles.**
- **DEVELOP POTENTIAL BASELINE FOR NEW METHOD USING SAME CRITERIA.**
- **QUANTIFY DIFFERENCES TO ASSESS VALUE OF NEW METHOD OVER CURRENT ONE.**
- **CONVERT DATA TO MEANINGFUL ANALYSES FOR DECISION MAKERS:**
  - **...Payback period.**
  - **...Return on Investment (ROI).**
  - **...Internal Rate of Return (IRR).**

Step two can be difficult unless data are available on the replacement technology. There is danger, for example, in comparing actual data from the workplace with "paper data" generated with only cursory testing. The credibility of the entire analysis is based on the validity of the data used.

Step four is the most important, because the results of the model must be presented to decision makers in a form they can easily understand. Customarily, all such economic analyses use a common measure of economic value - payback period, for example - so that one capital investment can be compared to another and prioritized to compete for limited capital funds. The process varies from one company to another, and may vary for different types of equipment as well.

Benefits Analysis - Tangible vs. Intangible (Chart 6)

The compilation of tangible and intangible benefits is generalized for replacement technologies; however, some benefits listed as intangible could be quantified and used in the economic analysis, if needed. For our waterjet example, it is possible to replace girt blasting booths, chemical treatment tanks, and some machining lathes with a single waterjet system. The savings in replacing these three systems, therefore, could be

6-BENEFITS ANALYSIS - TANGIBLE VS. INTANGIBLE

TANGIBLE	INTANGIBLE
• LABOR HOUR (MANPOWER) SAVINGS	• BETTER COMPANY IMAGE
• REDUCED WASTE DISPOSAL COSTS	• BETTER WORKPLACE & COMMUNITY ENVIRONMENT
• MATERIAL COSTS	• PROCESS REPLACEMENT
• OPPORTUNITY COSTS	• REDUCED COMPLIANCE DOCUMENTATION

quantified but the mechanics are complex because of complicating factors such as equipment age, removal costs, salvage value, etc.

On the tangible benefits side, material costs represent the savings in processing costs. In our waterjet example, these savings would include the cost of grit, chemical replenishment, machining tools, etc. Our case study analysis, for simplicity, will focus on labor cost savings.

Case Study #1 - Major U. S. Airline (Chart 7)

These are representative comparison data from an airline that uses high pressure waterjet equipment to process a large variety of jet engine parts. The current labor costs are compared with waterjet processing costs to compute the per part labor savings as well as the annual hourly savings expected for each specific part.

7-CASE STUDY #1 - MAJOR U. S. AIRLINE

PART IDENT.	CURRENT (HR)	WATERJET (HR)	SAVINGS (HR)	PARTS/YR	SAV./YR (HR)
JT8 BURNER CAN	2.16	0.5	1.66	3,000	4,980
JT8 1ST STAGE STATOR CASE	46	0.5	45.5	463	21,066.5
JT8 FWD FAN CASE	5.4	0.5	4.9	370	1,813
JT8 REAR FAN CASE	1.2	0.3	0.9	370	333
JT8 DIFFUSER CASE	4	0.5	3.5	370	1,295
JT8 FWD TURBINE CASE	6	0.5	5.5	370	2,035
JT8REAR TURBINE CASE	5	0.5	4.5	370	1,665
JT8 ALUM. 2ND STG STATOR CASE	2	0.5	1.5	370	555
JT8 2ND STG COMP. STATOR CASE	2	0.5	1.5	370	555
JT8 4TH STG LPT AIR SEAL RING	2	0.5	1.5	370	555
JT8 13TH STG AIR SEAL RING	2	0.5	1.5	370	555
JT8 2ND STG AIR SEAL RING	2	0.5	1.5	370	555
JT8 #5 BEARING HOUSING	4	0.25	3.75	370	1,387.5
JT9 REAR COMPRESSOR INLET CASE	3.2	0.5	2.7	370	999
JT8 FAN FWD STATOR CASE	5	0.5	4.5	370	1,665
GE OUTER COMBUSTOR LINER	3	1	2	251	502
GE INNER COMBUSTOR LINER	3	1	2	251	502
GE COMBUSTOR ASSEMBLIES	3	0.5	2.5	251	627.5
GE FRONT STATOR CASE	2	0.75	1.25	251	313.75
GE REAR STATOR CASE	6	3	3	251	753
GE 3-9 STG COMPRESSOR SPOOL	4	1.5	2.5	251	627.5
GE11-13 STG COMPRESSOR SPOOL	3	0.5	2.5	251	627.5
GE 14-16 STGCOMPRESSOR SPOOL	3	0.5	2.5	251	627.5
GE 1ST STG HPT SUPPORT	2	0.5	1.5	251	376.5
GE 2ND STG HPT SUPPORT	2	0.5	1.5	251	376.5
GE 1ST STGNOZZLE IMPING. RING	2	0.5	1.5	251	376.5
GE #4 BEARING SEAL	2	0.5	1.5	251	376.5
GE 2ND STG NOZZLE	4	0.25	3.75	251	941.25
GE 1ST STG COMPRESSOR HUB	2	0.5	1.5	251	376.5
GE TURBINE MID FRAME	2	1	1	251	251

Economic Analysis - Payback Period (Chart 12)

The chart shows a 5-year analysis of the cost factors involved with the new waterjet equipment. An original investment of $800,000 is assumed with an annual maintenance cost of approximately 5% of the purchase price for both parts and labor. An average hourly wate (fully burdened with benefits, etc.) of $20 per hour was assumed. This will be varied, since $20 per hour may not be representative of other companies.

12-ECONOMIC ANALYSIS • PAYBACK PERIOD

	YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5
MHRS SAVED	25,000	25,000	25,000	25,000	25,000
AVG. HRLY WAGE	$20	$20	$20	$20	$20
LABOR SAVINGS	$500,000	$500,000	$500,000	$500,000	$500,000
MAINT. COST	($40,000)	($40,000)	($40,000)	($40,000)	($40,000)
WTRJET EQUIP.	($800,000)	0	0	0	0
YRLY SAVINGS	($340,000)	$460,000	$460,000	$460,000	$460,000
CUM. SAVINGS (AFTER PAYBACK)	($340,000)	$120,000	$580,000	$1,040,000	$1,500,000

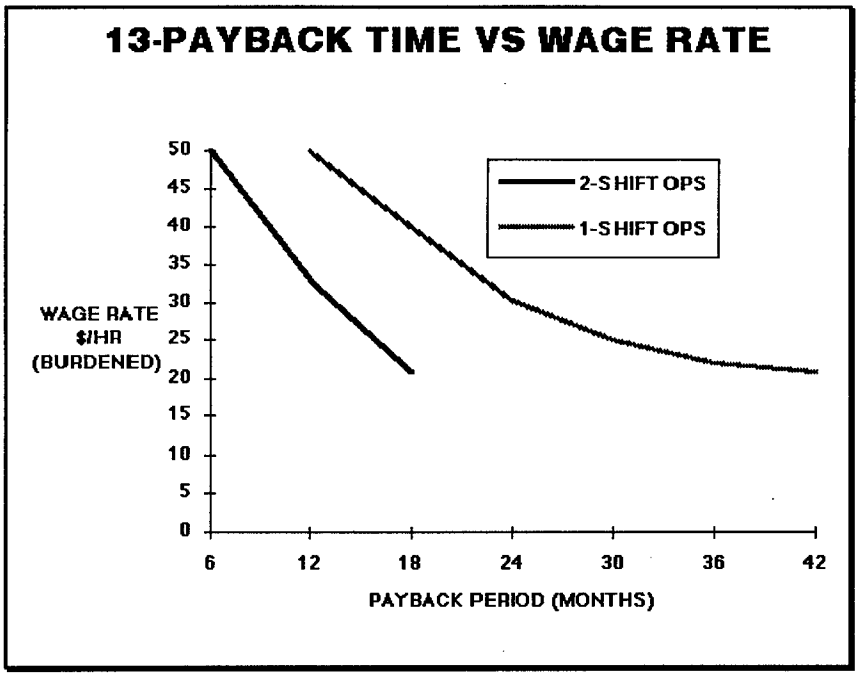
ASSUMPTIONS:
1 · DOUBLE-SHIFT OPERATION
2 · MAINT. COST = 5% OF PURCHASE PRICE
3 · TAX IMPACTS NOT INCLUDED:
a · DEPRECIATION (+)
b · SAVINGS ARE TAXABLE (–)

The yearly labor savings of $500,000 are reduced each year by maintenance costs and, in the initial 2 years, by the cost of the capital equipment itself. For this particular labor cost, the equipment is paid for in 18 months of operation and, by the end of the 5-year period, has earned $1.5 million.

To reduce complexity, several factors such as tax impacts are not included. Depreciation, for example, would provide a tax benefit for several years. On the other hand, the labor savings would accrue to the bottom line and be taxed as additional profits. The value of the out-year dollar savings should also be reduced by inflation since they will be worth less when finally received.

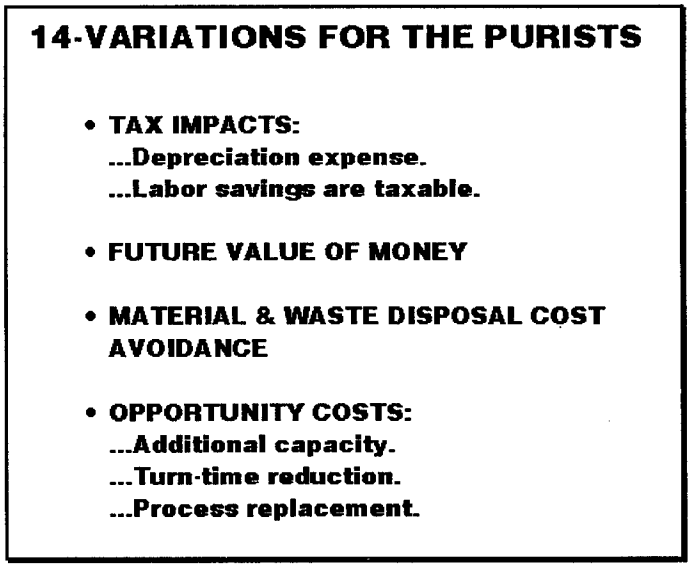
Payback Time vs. Wage Rate (Chart 13)

The two curves shown allow for calculations of the payback period (for single and double-shift operation) as a function of burdened labor wage rates. For the more typical $35 per hour wage rate in the aerospace/aviation business, a waterjet investment could be paid back in less then one year in double-shift operations, as shown.



Variations for the Purist (Chart 14)

There are a number of complicating factors that can be added to the analysis, a few of which are listed. Tax considerations, for example, can work in different ways. For tax purposes, the capital expenditure can be depreciated over a number of years to provide a tax credit. On the other hand, the money saved using the equipment increases profits which are, in turn, taxed. The future value of many can also be a consideration, since savings received in the outyears will be worth less than those saved in the



current year because of inflation. Opportunity costs can also be significant in some cases. In our waterjet example, we were able to save 4.8 man-hours, on average, for every part processed. This can translate to additional throughput capacity for the facility allowing them to accept third-party work and further increase profits.

Summary (Chart 15)

In summary, we have described a relatively simple methodology for developing a cost effectiveness analysis that can be used to compare a replacement technology with a conventional one. The end result of the work is an economic basis for justifying the use of a replacement technology based on tangible benefits. To assess the value of the replacement technology requires consideration of intangible benefits as well.

15-SUMMARY

- **FRAMEWORK FOR PERFORMING ELEMENTARY COST EFFECTIVENESS ANALYSES IS APPLICABLE TO MOST TECHNOLOGY-REPLACEMENT ALTERNATIVES.**
- **FOUR-STEP PROCESS:**
  1-Establish current procedure baseline.
  2-Develop replacement technology baseline.
  3-Quantify differences.
  4-Convert to meaningful analyses.
- **METHODOLOGY WILL BE ROBUST ENOUGH TO ALLOW FOR ADDITION OF MORE COMPLEX FACTORS.**

THE OAK RIDGE REFRIGERANT MANAGEMENT PROGRAM

by

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Abstract

For many years, chlorofluorocarbons (CFCs) have been used by the Department of Energy's (DOE) Oak Ridge Y-12 Plant in air conditioning and process refrigeration systems. However, Title VI of the Clean Air Act Amendments (CAAA) and Executive Order 12843 (Procurement Requirements and Policies for Federal Agencies for Ozone Depleting Substances) signed by President Clinton require, as policy, that all federal agencies maximize their use of safe, alternate refrigerants and minimize, where economically practical, the use of Class 1 refrigerants. Unfortunately, many government facilities and industrial plants have no plan or strategy in place to make this changeover, even though their air conditioning and process refrigeration equipment may not be sustainable after CFC production ends December 31, 1995.

The Y-12 Plant in Oak Ridge, Tennessee, has taken an aggressive approach to complying with the CAAA and is working with private industry and other government agencies to solve tough manufacturing and application problems associated with CFC and hydrochlorofluorocarbon (HCFC) alternatives. Y-12 was the first DOE Defense Program (DP) facility to develop a long-range Stratospheric Ozone Protection Plan for refrigerant management for compliance with the CAAA. It was also the first DOE DP facility to complete detailed engineering studies on retrofitting and replacing all air conditioning and process refrigeration equipment to enable operation with alternate refrigerants. The management plan and engineering studies are models for use by other government agencies, manufacturing plants, and private industry.

This presentation identifies some of the hidden pitfalls to be encountered in the accelerated phase-out schedule of CFCs and explains how to overcome and prevent these problems. In addition, it outlines the general issues that must be considered when addressing the phase-out of ozone depleting substances and gives some "lessons learned" by Y-12 from its Refrigerant Management Program. Discussion topics include requirements for developing a refrigerant management plan and establishing priorities for cost-effective compliance with the CAAA, as well as ways in which employees can be empowered to develop a comprehensive refrigerant management plan. The result of this employee empowerment was a cooperative labor-management effort that is beneficial for Y-12, DOE, and the environment.

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*Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

Introduction

For many years chlorofluorocarbons (CFCs) have been used in air conditioning and refrigeration systems designed for long-term use. Title VI of the Clean Air Act Amendments (CAAA) provided regulations to reduce and prevent damage to the earth's protective ozone layer. In 1987, 24 industrial countries met in Montreal, Canada, to mandate regulations governing the production of CFCs. They set a goal of achieving a 50% reduction of 1986 production levels by the year 2000 (see Fig. 1). In 1990, the same countries represented at Montreal met again, declaring a complete CFC phase-out by the year 2000. The Clean Air Act was passed by Congress in October 1990, establishing a schedule for U.S. companies to comply with the new phase-out dates. The Montreal Protocol and the Clean Air Act were revised in 1992 because CFCs escaping to the atmosphere were contributing to the destruction of the stratospheric ozone layer at an increasing rate. Then-President George Bush mandated an accelerated schedule for the production phase-out of all ozone depleting substances by December 31, 1995.

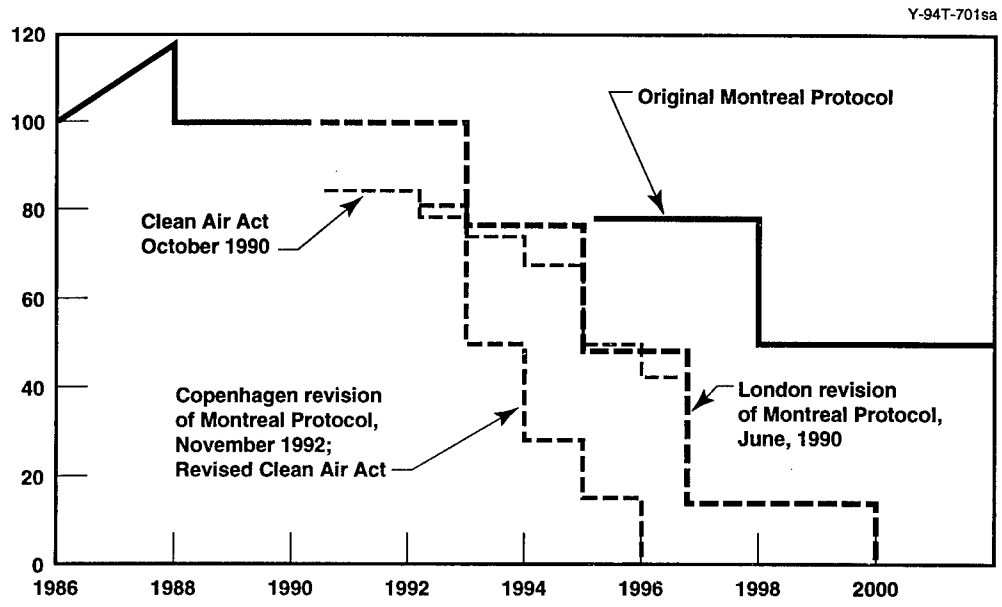

Fig.1. Percentage of 1986 CFC production.

The U.S. is the largest consumer and producer of CFCs in the world (see Fig. 2). Air conditioning and refrigeration account for approximately one-third of the U.S. yearly consumption (see Fig. 3). President Bill Clinton has advocated development of "green technologies" and has developed an early phase-out schedule for hydrochlorofluorocarbons (HCFCs). In his first State of the Union address in February 1993, the President outlined new environmental technology initiatives to accelerate environmental protection. The Senate has recently passed the National Environmental Technology Act, a part of the Administration's broad new technology policy outlined in "Technology for America's Economic Growth: A New Direction to Build Economic Strength." One of Vice President Al Gore's Reinventing Government proposals is the Clean Industry Initiative to promote the development of environmentally friendly refrigerants. The Vice President has also written a book that includes chapters devoted to the cause-and-effect relationship between ozone depletion and global warming.

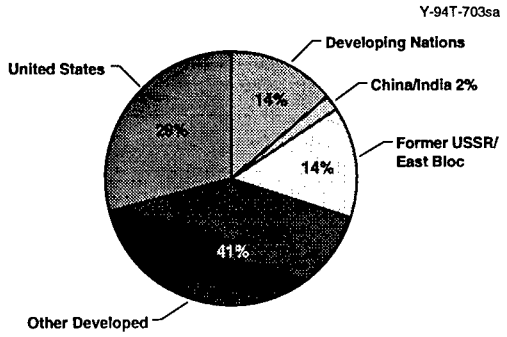

Fig. 2. Approximate consumption of CFCs by country and region.

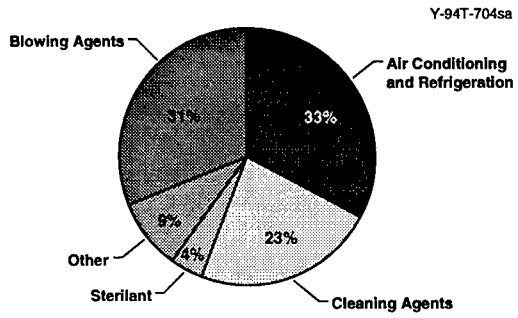

Fig. 3. Estimated United States End Uses of CFCs.

DuPont, the largest producer of CFCs in the world, will stop production of all CFCs in 1994. Halons are scheduled to be phased out by 1994. Production of all other Class 1 CFCs will stop December 31, 1995. In addition, the Environmental Protection Agency (EPA) proposes reducing the production limit of CFCs such that 1995 production can be only 15% of the 1986 level. DuPont had planned to stop CFC production in 1994; however, the EPA asked DuPont to continue production of CFC-12 through 1995 to supply the automotive market. The cost of converting equipment to non-CFCs is staggering, and the cost impact could slow down economic growth in the next 4–5 years if not managed properly. Forecasters believe that in 1996 the United States will still have the following equipment running on CFCs:

- 160 million refrigerators,
- 125 million motor vehicle air conditioners (MVACS),
- 5 million commercial refrigeration systems, and
- over 58,000 large commercial and industrial chillers.

This equipment is valued at over $125 billion. The switchover to non-CFC refrigerants must be carefully managed to prevent an extra economic burden from falling on individuals, companies, and the entire U.S. economy. The EPA estimates the 1996 demand for CFCs will be approximately 48 million pounds; however, no supply will be available. Manufacturers have already said they will be unable to meet the near-term demand for new units and retrofit equipment or to provide sufficient supplies of CFC alternatives to meet the demand. To compound the problem, the alternative refrigerants now being introduced into the market are only interim replacements that will also be phased out in the future.

Conservation measures (recycle and recovery), conversion, and compliance with the CAAA have been slow in coming. The EPA, the Air-Conditioning and Refrigeration Institute (ARI), and the American Society of Heating, Refrigeration and Air-Conditioning Engineers (ASHRAE) have all issued warnings about potential shortfalls of CFCs. A leading refrigerant manufacturer predicts "near chaos" unless more equipment owners start planning and engineering before production is halted in 1995. Rising prices, a "black market," and cooling outages seem inevitable. One expert forecast that "some equipment owners will have stocks of CFCs to see them through, but thousands of building owners, tens of thousands of businesses and industrial companies, and millions of homeowners and auto owners will have no stocks of CFCs." Chiller manufacturers also warn: "Do nothing and you may soon have a chiller (or air conditioning equipment) with no refrigerant." These warnings are ominous and should be taken seriously if we are to maintain our current life style and quality of life. In Economics 101, it is taught that a dollar spent today will cost less than a dollar spent tomorrow. This axiom is still true, and companies that convert to non-CFC alternatives today will not spend as much or be caught in the last-minute panic the experts warn against.

A misconception exists in government and private industry that choosing an alternative refrigerant is a risky proposition. Officials in these areas think that, if they wait long enough, a low-cost "drop-in" replacement will be invented to rescue them and make the problem go away. All alternative refrigerants

have undergone extensive testing for toxicity, fire protection, personal exposure limits, and almost every other health/safety issue before being approved for testing and evaluation by the EPA.

The new alternatives do have some limitations but are considered safe if handled properly; however, they may be slightly less efficient than the refrigerants they replace. This efficiency loss will generally not affect operations because most systems have been over-designed with built-in excess capacity to allow for future expansion. In some cases, the new refrigerant (e.g., HFC-134a) is actually more efficient than the old refrigerant if a complete retrofit is performed on the chiller. The good news is that EPA's Significant New Alternative Program (SNAP) has helped develop and test over 100 new alternative refrigerants. The bad news is that they have found no "drop-in" energy-efficient replacements that simply require draining the old refrigerant and filling a system with a new refrigerant.

Even with alternative refrigerants, equipment room ventilation still must be modified to comply with the new ASHRAE Standards 15 and 34 adopted by most code authorities. Installation of oxygen depletion and halocarbon refrigerant sensors may also be required. Some service organizations will not work in a facility until the sensors have been installed. The current HCFC-123 (CFC-11 replacement) threshold limit value (TLV) of 10 ppm is being re-evaluated by the American Council of Government Industrial Hygienists (ACGIH) and could be raised to 30–100 ppm. Some alternate refrigerants being tested have flammability problems and low flash points, but they will probably never be approved by the EPA, Factory Mutual, National Fire Protection Association, or the ACGIH for manufacture and sale to the general public.

Industry estimates indicate that almost all government agencies and private businesses think a refrigerant management plan is necessary and a good idea, but just over 50% have such a plan! Unfortunately, the government has no national plan or strategy in place. Heating, ventilation, and air conditioning (HVAC) system owners and building managers should not expect any relief or last-minute reprieve from the government. Such amenities as air conditioning and refrigeration, commonly taken for granted, may not be sustainable when CFC production is halted and no new materials are available to replace them.

What Have We Done?

The Department of Energy's (DOE) Y-12 Plant has taken an aggressive approach to comply with the CAAA and was the first Defense Program (DP) facility to develop a long-range Stratospheric Ozone Protection Plan. This plan provides administrative controls to minimize plant emissions of ozone depleting substances, maximize the use of ozone-friendly alternatives, and achieve cost-effective compliance with EPA's CAAA requirements. The plan is a model for government agencies, manufacturing plants, and private industry facilities.

As part of the plan, recycle and recovery programs were implemented several years ago. The "lessons learned" are available to other organizations upon request. Y-12 was also the first DOE DP facility to request line-item funding for retrofitting and replacing all air conditioning and refrigeration equipment to achieve compliance with the CAAA. The necessary detailed engineering studies were completed for converting all HVAC systems, chillers, and refrigeration equipment to operate with alternate refrigerants. Oak Ridge has maintained efficiencies and capacities to minimize any upstream power plant emissions. Where practical, some equipment will be retrofitted to reduce project costs and the impact on the government's shrinking budget. Several interim capital construction projects are currently in progress to install both high-efficiency purge units and pressurization/leak detection units on low-pressure chillers.

Personnel training and refrigerant recycling were identified early as the easiest and least expensive methods for implementing CAAA compliance efforts. In the early 1990s, the Y-12 Plant procured several portable refrigerant recycle units to purify refrigerant in direct-expansion (Dx) air conditioners and MVACs. Several hand-held leak detection units were also procured to find equipment leaks and implement a leak detection program. With only minimal investment (about $4,000–$6,000 each for the recyclers and only $300–$400 for the hand-held detectors), reduced emissions were noticed immediately. These units were so successful that additional larger, EPA-approved, portable recycle units were procured for use on all chillers and large building air conditioning systems. The combination of recycling and leak detection

programs reduced Y-12 CFC emissions by more than 58% from 1992 to 1993. Simultaneously, in-house training programs were developed, and an interactive television hook-up was recently initiated with local community colleges to train students about the CAAA and certify technicians in the various EPA refrigeration classifications. Automotive mechanics were certified by the EPA for work on MVACs, and refrigeration mechanics were certified in all four EPA refrigeration categories. Other training programs were developed to include courses on the proper operation of most recycle/recovery equipment and a management awareness course for engineers, HVAC system owners, and building managers.

In addition, several inexpensive administrative controls were implemented to help reduce emissions and comply with the CAAA. Engineering procedures and specifications were revised to prevent procurement of equipment that uses CFCs. A procedure was initiated that required the review/approval of all purchase requisitions for CFCs and HCFCs. Procedures were also developed for the removal and storage of refrigerants from equipment and appliances before disposal, and plans were initiated for procurement of storage and recovery tanks to stockpile excess refrigerants. Specifications for fleet vehicles were modified so that the air conditioning systems would be compatible with or operate using alternate refrigerants. In a large plant such as Y-12, communications and old habits were the hardest barriers to overcome. Employee training and administrative controls made an immediate impact on awareness of the problem—reducing CFC emissions—and employees were empowered to correct problems.

Equipment and Strategy Used

A task team, drawn from several divisions within the Y-12 Plant, was charged with establishing a strategy and guidelines for an economical conversion to alternative refrigerants. Additional tasks included setting priorities for worker health and safety considerations, energy efficiency, considerations for long-term operation, development of short-term and long-term strategies for compliance, and development of criteria for evaluating existing equipment. Input was requested from almost every division, including accounting; development; engineering; utility operations; fire protection; health, safety, environment and accountability; industrial hygiene; health physics; and the refrigeration mechanics' union. This diversity was necessary and very important because the retrofit/replacement of equipment for use of alternate refrigerants turned out to be more complex than anyone ever envisioned. Industrial hygiene concerns about ventilation and union concerns about worker health and safety when working with or around the new refrigerants were only some of the issues to be resolved. The resulting criteria were used to formulate a $13.6 million FY 1996 Line Item Project for retrofitting and replacing all HVAC systems and chillers in the Y-12 Plant. The team developed the following strategy and criteria for converting to alternative refrigerants:

1. Retrofit or replace only equipment containing a charge of 10 lb or greater. A study determined that the retrofit costs for equipment with a charge less than 10 lb would exceed the replacement costs and value of the equipment. For economic reasons, it was decided that equipment with less than a 10-lb charge should not be retrofitted or converted to the new alternative refrigerants. This smaller equipment (generally 5 tons or less) will be handled on a case-by-case basis. In general, it will be left in service until the end of its service life or until leaks develop, at which time it will be either shut down or replaced.

2. Equipment over twenty years old, and critical equipment less than twenty years old but with a bad leak-rate history, would be replaced. Leak rates and efficiency are the biggest factors in determining replacement—not age or maintenance history. Coincidentally, the oldest equipment generally has the highest leak rates. Most equipment over twenty years old is inefficient with efficiency ratings greater than 1.0 kW per ton. Most new chillers with alternative refrigerants have efficiencies of 0.60 kW per ton or less.

3. Equipment less than twenty years old without bad leaks would be retrofitted to use new, alternate refrigerants. Some CFC-11 hermetic chillers will lose about 2%–5% efficiency and 10%–15% capacity in converting to HCFC-123. Retrofitting must include new O-rings and gaskets. The hermetic motor must be replaced so the winding insulation will be compatible with the refrigerant. The impellers will need reworking to minimize losses in efficiency and capacity. Conversion from CFC-12 to HFC-134a is somewhat easier and could result in a slight efficiency gain. Conversion to HFC-134a requires flushing

of the lubrication system several times and switching to a polyolester lubricant instead of the mineral oil previously used. In order to increase operating pressures, gears must be replaced on chillers, and the pulleys and belts must be changed on Dx units.

4. Equipment with HCFC-22 and MVACs would not be retrofitted or converted. Small, through-the-wall air conditioning equipment, freezers, water fountains, and refrigerators will remain in use until their service life is over or they incur leaks, at which time they will be either shut down or replaced.

5. Where practical, all environmental chambers and all process and walk-in coolers with a refrigeration system containing 10 lb or more of refrigerant would be retrofitted. Coolers and environmental chambers with less than a 10-lb charge would remain in place until they reach the end of their service life or develop leaks, at which time they will be either shut down or replaced. Coolers and environmental chambers are a special problem because many are custom built. Some of the cabinets must be torn apart to install new compressors. After the market was researched, no stock, off-the-shelf units appeared to be available that would exactly fit the openings and meet operating requirements. Most new coolers and chambers would have to be specially designed and built, which is expensive. It is difficult to justify installing a new unit unless it directly supports a process or production system.

6. Shut down the oldest equipment with the worst leaks, excess capacity, and lowest utilization. The air conditioning and refrigeration mechanics generally know which equipment has the worst leak rates. Implementation of a centralized, PC-based refrigerant tracking system can identify and quantify leak rates. Such a tracking system costs only $350–$450, and it is invaluable for auditing and tracking refrigerant usage by individual pieces of equipment. In addition, building and chiller load profiles should be analyzed, incorporating planned expansions and future uses. Existing capacities need to be evaluated to determine if the equipment is actually required or if it should be shut-down.

7. Chill water lines should be extended to replace building air conditioning units where economically practical.

8. Monitors should be installed in each equipment room and chiller building, and the ventilation systems should be modified to comply with ASHRAE Standards 15 and 34.

Refrigeration Equipment

Equipment to be retrofitted or replaced having a charge greater than 10 lb of refrigerant fell into three basic categories:

I **Chillers** – CFC-11, CFC-12, and HCFC-22
II **Direct Expansion (Dx) Air Conditioners** – CFC-12 and HCFC-22
III **Coolers and Environmental Chambers** – CFC-12, CFC-502, CFC-503, and HCFC-22

In Category I, Y-12 plans to replace six hermetic chillers and two open-drive chillers with a total cooling capacity of 4,525 tons. The equipment ranges from an old 200-ton unit up to 1,100-ton units and includes two low-temperature machines. Nineteen chillers with a cooling capacity of 20,300 tons will be retrofitted to operate on the new alternate refrigerants. Due to downsizing, several areas within the plant were shut down, and nine old chillers were taken out of service.

In Category II, three Dx building air conditioners will be replaced with units that operate on HCFC-22. Two Dx units will be replaced with chilled water handlers, and three CFC-12 Dx units will be retrofitted to operate on HCFC-22.

In Category III, 15 environmental chambers, 4 walk-in coolers, and 1 process cooler will be converted from CFC-12 to HCFC-22. Two process coolers will be converted to HFC-134a, and seven environmental chambers will be converted from CFC-502/503 to a non-CFC refrigerant (possibly DuPont Suva HP-62).

Preliminary estimates indicate retrofitting and replacing the equipment in Categories I, II, and III will produce an annual savings of approximately 2,658,000 kilowatt hours of electricity and $125,500 when completed. This savings will be achieved with no loss in capacity. The converted equipment will emit considerably less refrigerant to the atmosphere, and, as a result, less refrigerant will be procured for replacement. It is estimated that future refrigerant procurement costs could be reduced for an added savings of $50,000-$60,00 per year. The impact on stratospheric ozone depletion due to the retrofit and replacement program will be even more dramatic (See Table 1). Preliminary calculations indicate ozone depletion from emissions would be reduced approximately 99.69% after the retrofit and replacement project is completed. The combined energy savings and environmental improvement make this a win-win situation.

Equipment with less than 10 lb of refrigerant were the most difficult to locate and identify and the most time consuming to inventory. Some task team members were shocked to see how many appliances and small through-the-wall units were involved. This equipment included 165 refrigerators and freezers; 132 ice machines, drinking fountains, and water coolers; and 1,375 small air conditioners and through-the-wall units. These units are relatively inexpensive and will be replaced or shut down at the end of their service life or when leaks occur.

Y-94T-726kg

1992 Ozone Depletion From Emissions

Refrigerant Type	Emissions in Pounds	X	ODP Number	=	Ozone Depletion Factor
CFC-11	10,000	X	1.0	=	10,000
CFC-12	90	X	0.95	=	86
HCFC-22	3,025	X	0.05	=	151
CFC-113	200	X	1.07	=	214
CFC-114	5,100	X	0.8	=	4,080
CFC-502	30	X	0.2	=	6
TOTAL					14,537
Estimated Ozone Depletion After Retrofit and Replacement					
HCFC-123	1,000	X	0.02	=	20
HFC-134a	90	X	0.0	=	0
HP-62	30	X	0.0	=	0
HCFC-22	500	X	0.05	=	25
TOTAL					45 (99.69% reduction)

Table 1. Impact on Ozone Depletion.

Lessons Learned

The following summary of the lessons learned by the Y-12 Plant may be used to help a company or government agency make the tough decisions about converting to alternate refrigerants:

1. Formulate a task team from various departments and service organizations and obtain management support for its findings.

2. Develop a schedule and establish a budget to support the task team findings.

3. Involve the equipment manufacturer in planning at the earliest stage and consult with a service contractor or consulting engineer to work closely with the manufacturer.

4. Focus on life-cycle operating costs, equipment availability, and energy efficiencies based on integrated part-load values and applied part-load values rather than refrigerant choices.

5. Participate with the contractor and manufacturer to determine when and how to convert.

6. Develop a management awareness training course and worker certification program and include the hourly employees or maintenance contractor as part of the team.

7. Initiate a leak detection and a recycle/recovery program and contain, contain, contain.

8. Develop an inventory of all air conditioning and refrigeration equipment and refrigerant stocks.

9. Plan to phase in, over a period of several years, replacement and conversion for large complexes using multiple chillers and building air conditioning equipment where replacement costs can be high and not easily funded in one lump sum.

10. Do not wait until December 31, 1995, to start a program and make decisions about converting.

What Should The Conversion Plan Include?

Some basic criteria must be included in any conversion and retrofit plan as good management practices and to help make it succeed. These criteria will provide management control over the implementation process and help ensure fiscal responsibility. In addition to incorporating the lessons learned at Y-12, a plan should include:

- A long-term phase-out schedule for CFCs and a budget for the conversion plan.
- A designated CFC Manager (or CFC Czar) in upper management who will champion the plan and help in the budgetary process.
- Procurement of recycle/recovery equipment and immediate implementation of a leak detection program—recycle, conserve, conserve.
- Tracking of refrigerant usage and procurement at a central location where information can be readily accessed.
- An inventory of all equipment and refrigerant stock and setting of priorities for converting equipment.
- Development of written policies and defined procedures for procurement, handling, storage, and use of refrigerants.
- Evaluation of equipment life, performance, and efficiency, and an analysis of existing needs and future requirements.
- An engineered solution to retrofit or replace equipment, determined with more than one manufacturer's recommendation.
- Clearly defined monitoring, health and safety, reclamation, and disposal procedures so everyone involved has a clear understanding about who is responsible, what should be done, and how to do it.
- Maximization of equipment retrofitting to conserve cash flow and assurance that equipment room ventilation meets ASHRAE standards.

Prepsolv™: The Optimum Alternative to 1,1,1-Trichloroethane and Methyl Ethyl Ketone for Hand-Wipe Cleaning of Aerospace Materials

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Glidsafe® Terpene Cleaners and Solvents
Glidco Organics Corp.
P.O. Box 389, Jacksonville, FL 32201-0389
(904) 768-5800

Including data and case study by:
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Introduction

Throughout the DOD and commercial manufacturing community, engineers are aggressively screening alternative solvents before the Clean Air Act mandated phase-out of methyl chloroform. Although virtually hundreds of products are being considered, the "short list" appears to include only the following:

- Terpenes (usually terpene hydrocarbons)
- Propylene glycol ethers and their esters (e.g. PTB, DPM, PM acetate)
- NMP and BLO (GBL)
- Esters (e.g. butyl butyrate, methyl lactate)
- Halogenated solvents (e.g. parachlorobenzotrifluoride)
- Mineral spirits and paraffinic solvents

And although the criteria for acceptance is different for each user and each application, the following subset is generally common to all:

- Acceptable solvency for specific soils
- Ease of use
- Compatibility with contact materials
- Readily available
- Ability to clean to established specifications
- Low toxicity and ecotoxicity
- Acceptable odor
- Good storage stability
- Affordable and cost effective
- Regulatory acceptance (no ODP, low GWP, not considered a HAP)

The advantages and disadvantages of the various alternatives has been debated within the industry and there are misconceptions regarding the various alternatives. Extensive testing has shown that terpene hydrocarbons are among the most effective cleaning agents for dissolving and removing difficult surface contaminants. In addition, terpenes are desirable because they are safe (low toxicity) and biodegradable.

However, terpenes are so highly biodegradable that this has been a limitation as well as an asset. In the presence of air certain terpenes break down, forming much less volatile compounds that do not evaporate like the terpene solvents themselves. These residues can be left behind during the cleaning process unless another solvent, like alcohol, is used to rinse residues away. Unfortunately, the need to rinse makes cleaning large surfaces, like airplane wings and rocket motors, very difficult. And this has made the use of terpenes for hand-wipe cleaning virtually impossible.

Engineers at Hercules Aerospace, a rocket motor manufacturer in Utah, have worked closely with chemists at Glidco Organics to study the feasibility of using terpenes for zero-residue wipe cleaning. The result of this work is a technological breakthrough, in which the barrier to ultra-low non-volatile residue formation has been broken. After 2 years of development and testing, SCM Glidco Organics has announced the availability of Glidsafe® Prepsolv™: a state-of-the-art ultra-low residue terpene wipe cleaning agent that does not require rinsing. Prepsolv™ can successfully be used in simple hand-wipe cleaning processes without fear of leaving surface residues. Industry testing has confirmed that Prepsolv™ is not only highly effective, but can even be less expensive to use than traditional cleaning solvents like methyl chloroform.

This paper addresses the features and benefits of Prepsolv™, and presents performance and material compatibility data that characterizes this unique cleaning agent.

Since its commercialization, Hercules Aerospace has chosen Prepsolv™ as the optimum cleaning agent to replace ozone-depleting solvents in their weapons factory in Magna, UT. Likewise, Boeing has approved Prepsolv™ for cleaning components in the manufacture of commercial aircraft at their facilities in Seattle, WA and Wichita, KS. Additional approvals are forthcoming for this uniquely safe and effective solvent.

Solvency

Terpene hydrocarbons, because of their chemical structure, are highly effective in dissolving aliphatic and cyclic lubricating oils, greases, waxes, tape residues, silicone fluids, and similar soils likely to be found in the manufacturing industries. In those cases where they are not effective alone, they form the base for mixtures that closely approach the solvency of methyl chloroform (1,1,1-trichloroethane) and methyl ethyl ketone (traditional aerospace industry wipe solvents). Solubility parameters are a reasonable predictor of solvent performance, and although they do not take molecular size into consideration, they are certainly the most useful theoretical tool for solvent selection[1]:

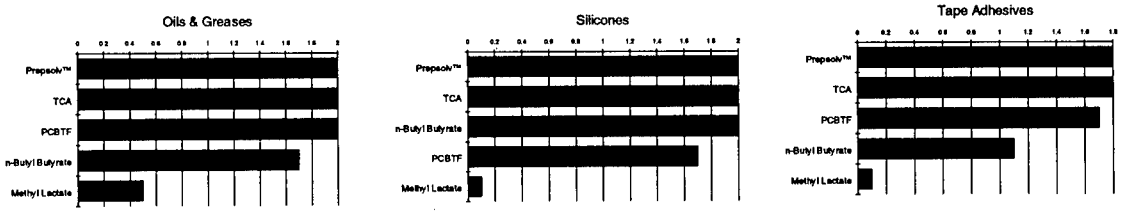
Hansen Solubility Parameter Comparison[2]

Target Solvents	δ_D (Non-Polar)	δ_P (Polar)	δ_H (Hydrogen Bonding)
Methyl chloroform (1,1,1-trichloroethane)	8.3	2.1	1.0
Methylene chloride	8.9	3.1	3.0
Acetone	7.6	5.1	3.4
Methyl ethyl ketone (MEK)	7.8	4.4	2.5
Alternative Pure Solvents			
Glidsafe® Prepsolv™ (Terpene hydrocarbon[3])	8.6	1.0	1.0
Stoddard solvent / mineral spirits	7.7	0.0	0.0
n-Methyl Pyrrolidone (Arco NMP)	8.8	6.0	3.5
n-Butyl butyrate[4]	7.9	2.0	3.6
Methyl lactate[4]	7.8	3.8	6.9
Propylene glycol t-butyl ether (Arco PTB)	7.3	2.1	6.0
Terpene alcohols (Glidco Glidsol® 90)	6.8	3.9	5.0
Water	7.6	7.8	20.7
Blended Solvent Systems			
Glidsafe® UTS-4B (Glidco Organics)	8.5	1.5	2.2
DS-104 (General Dynamics/Dynamold Solvents)	7.8	5.9	5.5

As can be seen, terpenes fall near methyl chloroform in solubility space. This property makes terpene solvents direct substitutes for 1,1,1 in many applications.

Tests performed at Hercules Aerospace Company confirm that solvent solubility can be reasonably predicted by solubility parameter modeling. The following graphical data shows that Glidsafe® Prepsolv™ is the most effective solvent against non-polar soils.

Solvent Solubility Test Results Against Various Soils[5]



Non-Volatile Residue

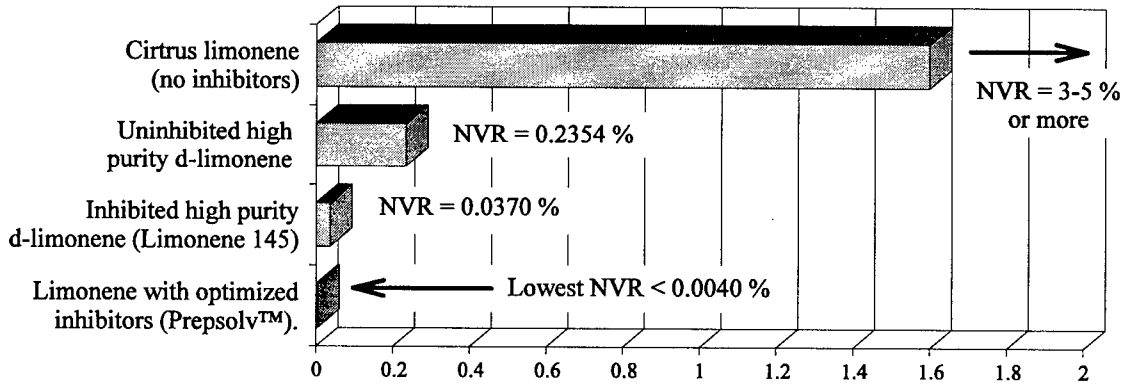
Traditional terpene solvents are not ideal wipe cleaning agents. In fact, many terpene solvents are actually poor choices for wipe cleaning because of their tendency to oxidize and polymerize, creating non-volatile organic surface residue (NVR). This polymeric residue is sometimes more difficult to remove than the original soil. The tendency has caused some researchers to conclude that terpenes are often not appropriate candidates for wipe cleaning solvents.

Antioxidants and inhibitors are added to terpenes much the same way that stabilizers have traditionally been added to chlorinated solvents. However, traditional development of terpene antioxidant and inhibitor technology was almost exclusively performed by the flavor and fragrance industry. Their needs and selection criteria were quite different from those of the aerospace industry, and their recommended inhibitors and antioxidant systems are not appropriate for precision cleaning applications.

A variety of commercially available terpene solvents were tested for NVR per ASTM D1353 (205°F in air). By this test, even the highest purity solvents left unacceptably high levels of surface residue (see graph on following page).

However, this problem has been solved. Hercules Aerospace and Glidco Organics initiated a development project to screen terpene systems and inhibitors to optimize a system that would adequately protect the terpenes from oxidation and polymerization, while not contributing themselves to surface residue. The resulting blend of terpenes and inhibitors leaves *virtually zero* NVR. This blend is available as Glidsafe® Prepsolv™. As you can see, proper choice of terpene solvent and inhibitor technology results in a truly "clean" terpene wipe solvent. It is no longer correct to assume or conclude that terpene solvents cannot be used as precision wipe cleaning agents.

Measured Non-Volatile Residue per ASTM D-1353 (weight %)



Inhalation Hazard and Workplace Safety

Because terpenes have low vapor pressure, they have low inhalation hazard. The ratio of the saturated vapor concentration of a solvent to its TLV is called the Inhalation Hazard Index (IHI) and is an indication of the relative danger from vapor exposure. The higher the ratio, the higher the vapor concentrations become in the workplace, and the quicker the TLV concentration is approached. Lower IHI ratios indicate that vapor concentrations will only slowly approach the TLV, which means that these solvents are safer to use in the workplace. High ratios indicate increased potential health risk. The following table compares the vapor pressure and Inhalation Hazard Index for common solvents. Note that Glidsafe® Prepsolv™ has the lowest IHI value and therefore is safest to use in the workplace:

Inhalation Hazard Index for Industrial Solvents[6]

	VAPOR PRESSURE (MMHG @ 20°C)	TLV-TWA (PPM)	INHALATION HAZARD INDEX @ 20°C
Glidsafe® Prepsolv™	1.6	100[7]	21.2
Stoddard Solvent / Mineral Spirits	2	100	26.3
2-Butoxyethanol (EB)	0.88	25	46.3
Perchloroethylene	13	50	342
Parachlorobenzotrifluoride (PCBTF)	5.3	20	349
1,1,1-Trichloroethane	100	350	376
Methyl Ethyl Ketone (MEK)	85	200	559
Trichloroethylene	59	50	1552
Methylene Chloride	340	50	8940

Vapor Pressure

Terpenes have relatively low vapor pressure. Low vapor pressure solvents have a number of advantages in wipe cleaning including:

- Reduced VOC emissions;
- Increased cleaning efficiency as a result of solvents remaining on the cloth longer before evaporation;
- Reduced evaporative losses translating into increased economy. Most experience indicates that terpene solvents are consumed at roughly 15-20% the rate compared to methyl chloroform in wipe cleaning.

In use, solvents are "consumed" not only by evaporation, but by disposal of unused material on cloths. In fact, disposal of unused material accounts for a major portion of the consumption. The evaporative losses alone from terpenes and conventional solvents have been compared in the lab:

Solvent Vapor Pressures and Estimated Evaporative Losses

	VAPOR PRESSURE (MMHG @ 20°C)	EVAPORATIVE LOSSES (LB/HR/SF @ 20°C)
Glidsafe® Prepsolv™	1.6	0.01
Methyl Ethyl Ketone	85	0.28
Methyl Chloroform	100	0.40

Regulatory Status of Prepsolv™

Terpenes like Prepsolv™ are non-toxic, biodegradable, and contain no reportable components. They are non-chlorinated, and therefore do not affect the Earth's Ozone Layer and are not regulated as a result of the Montreal Protocol. In addition, they are not classified as Hazardous Air Pollutants by the 1990 Clean Air Act Amendments. Furthermore, the U.S. EPA has endorsed terpenes as replacements for ozone-depleting solvents like 1,1,1-trichloroethane and CFC-113.

Water Solubility

As "zero discharge cleaning" becomes a goal, it is necessary to consider routes for release of solvents into the workplace and environment. Just as low vapor pressure restricts air emissions of terpenes, low water solubility can restrict release into water systems. This is not a strong consideration in wipe cleaning, but a consideration for solvent selection in general.

Terpene hydrocarbons are virtually insoluble in water. This is very different from alternatives like glycol ethers and NMP which are readily soluble in water. As water regulations tighten, this will become more and more important, and cleaning agents which can easily be separated from wastewater will become more desirable.

Relative Water Solubility of Terpenes vs. Other Solvents

	APPROX. SOLUBILITY IN WATER (WT % @ 20°C)
Glidsafe® Prepsolv™	0.02
Propylene Glycol Tert Butyl Ether (PTB)	14.5
2-Butoxyethanol (EB)	T
n-Methyl Pyrrolidone (NMP)	T

Material Compatibility

Glidsafe® Prepsolv™, being a blend of terpene hydrocarbons, is a non-polar, pH neutral, non-corrosive solvent. As such, it does not produce corrosion in any metals tested to date.

Metals Compatibility Data per SMI Testing

TEST	SPEC	RESULT
Hydrogen Embrittlement	ASTM F519	Conform (Type 1C)
Sandwich Corrosion	ASTM F1110	Conform
Titanium Stress Test	ASTM F945	Conform (AMS 4911)

Testing by Hercules Aerospace has confirmed that "no signs of corrosion or material degradation were noted in the immersion test" with the metals tested:

- Anodized 6061 Aluminum)
- Aluminum 1100
- Lead Alloy (FLSC)
- Aluminum 7075
- Cadmium Plated 4140 Steel
- Aluminum 6061
- 304 Stainless Steel

Conclusions

A terpene-based wipe cleaning agent is now available called Glidsafe® Prepsolv™ that combines the advantages of high solvency, environmental acceptability, regulatory compliance, low toxicity, with ultra-low non-volatile residue. All these advantages combine to suggest that this innovative material be considered as an alternative cleaning agent for replacing ozone-depleting and toxic solvents in hand-wipe cleaning.

No single solvent is likely to be a universal replacement for 111 and MEK. However, the state-of-the-art in terpene wipe-cleaning agents is advancing to the point that most all of the limitations of early terpene products no longer exist. Certainly, fear of non-volatile residue is no longer a reason to avoid consideration of terpenes for hand-wipe cleaning of aerospace materials.

Prepsolv™ Status Update - July '94

The latest NVR testing by Hercules Aerospace (June '94) documents in their final project report that Prepsolv™ leaves no visible or measurable NVR on evaporation.

Glidsafe® Prepsolv™ is now approved by Boeing per specification BAC 5750 for use in commercial aircraft fabrication and maintenance cleaning, and is preferred by Hercules Aerospace for cleaning during rocket motor fabrication and finishing as indicated below.

The following are excerpts from Hercules final report: "Test Report, 1,1,1 trichloroethane Replacement For Use in Cold Wipe Applications, June 1994".

CONCLUSIONS

The only solvent that produced any signs of corrosive attack on the alloys testes in immersion or galvanic couple testing was WS5B. No signs of corrosion were noted with any of the other candidate solvents. Testing performed for non-metallic surfaces showed that all solvents except DS104 performed equal to TCA. Laboratory input and actual use in operating areas reduced the viability of using IBIB due to its strong odor. Based on the material testing performed in test Series 2 Prepsolv, Iso-butyl Isobutyrate (IBIB), and Oxsol 100 perform as well as TCA on non-metallic surfaces in finishing operations. DS104 is not a top candidate because the tensile testing results showed significantly lower max. Stress values than TCA. In addition, input received from McDonnell Douglas suggest that other candidates would be more favorable due to the moderately strong odor of DS104.

Bonding tests showed that Prepsolv and WS5B were the best performers. RTV premold to aluminum bond compatibility was unfavorable using Prepsolv™, yet the surface preparation results for the same bond were different, but not unfavorable. Oxsol 100 and DS104 were the worst performers for bonding operations.

The overall performance of each of the solvents tested for finishing operations, based on meeting the established criteria, from best to worst are:

1. Prepsolv
2. WS5B
3. IBIB
4. Oxsol 100
5. DS104

RECOMMENDATIONS

Prepsolv should be qualified as the primary solvent for use in finishing operations because it is the best overall performer based on the laboratory testing which correlated very close to TCA. Although WS5B, IBIB, and Oxsol 100 did not perform overall as well as Prepsolv, the data generated should be considered valid in implementing the tested solvents for the appropriate operations in the event Prepsolv is not available in the future or does not remove abnormal soils.

Prepsolv can be handled safely in the finishing area with no additional protection required by the operators.

Case Study - John A. Purvis and Wade W. Moran, Hercules Aerospace Solvent Selection

Solvent Selection At Hercules Aerospace

Hercules Aerospace Corporation's Bacchus plant in Magna, Utah produces solid propellant rocket motors. Methyl chloroform, an ozone depleting compound, is used in a large number of manufacturing operations for these systems, mainly as a "wipe solvent" for cosmetic cleaning and for preparation of surfaces prior to bonding with adhesives or coatings. In this application, the solvent is applied to a clean cloth, which is then wiped on the surfaces to be cleaned. Remaining solvent is allowed to dry prior to bonding the components.

As an active participant in the Chemical Manufacturer's Association *Responsible Care®* program and to comply with legislation, Hercules is actively involved in eliminating ozone-depleting chemicals and minimizing use of hazardous air pollutants. In this effort, Hercules has achieved favorable results in selecting alternate solvents.

Of course, no single solvent identified can be used for all purposes. Rocket motor designs incorporate many different materials (aluminum, steel, graphite composite, elastomers, cork) and a large number of adhesive bonds utilizing a variety of adhesives. In addition, over 60 different "soils" are involved in the processes ranging from fugitive oils and greases and mold releases to epoxies, cyanoacrylates and urethanes in various states of cure. The solvents must remove these soils, but must not damage the substrates, react adversely with materials such as the propellant, nor weaken previously made bonds. One solvent blend developed was found superior to methyl chloroform for solvency power for the many soils but was incompatible with several of the substrates, requiring the identification of compatible, but less versatile solvents. Terpenes were found to be excellent solvents for oils, greases, certain resins, rubbers and tape residue (all major soils) but were reputed to be prone to oxidation and high in non-volatile residue. Hercules pursued the issue with Glidco Organics, a major manufacturer of both citrus and pine terpenes. The problem was eventually resolved by use of a refined citrus terpene and optimization of the antioxidant package. The resultant solvent is stable and has no significant non-volatile residue as measured gravimetrically or by infrared spectroscopy.

Hercules' strategy included thorough research of industry efforts and a careful examination of the process to determine if soils could be isolated, if steps could be re-ordered, or if soils needed to be removed from surfaces. If cleaning was required, mechanical and aqueous cleaning methods were considered. Where organic solvents were considered necessary, most important was the use of firm solvent selection criteria, *solubility parameter* technology and economical laboratory screening tests. Solvents identified for future qualification have been reduced from over 100 to 7 systems. These include parachlorobenzotrifluoride (PCBTF), an ester, a propylene glycol ether, a propylene glycol ether acetate, a lactate, a terpene (d-limonene) and blends of these materials.

Solvent Selection Criteria

Given the enormous number of solvents on the market, a set of firm criteria were developed. The solvent must be effective in removing the various soils. Solvents that have any known ozone-depleting potential, are hazardous air pollutants or are overly toxic were avoided. The inhalation hazard index (IHI) was used for comparison rather that the threshold limit value (TLV). Use of the TLV for comparison is often done but is normally misleading because of vapor pressure differences. The IHI takes into account the TLV and the vapor pressure. The higher the IHI, the more hazardous the material. For example, while d-limonene has a lower TLV than methyl chloroform, its IHI is less because of lower volatility. The IHI = $10^6*(P_V/P)/TLV$ where P_V is the vapor pressure and P the atmospheric pressure.

A flashpoint above 38°C (100°F) is required but volatility is also critical so components can be bonded soon after surface cleaning to prevent surface recontamination and minimize flowtime. Any solvents that contained measurable non-volatile residue with an ambient drying were not considered. Good stability in storage, a tolerable odor and compatibility with contact materials are also important attributes.

Given the costs incurred in qualifying new solvents and the importance of system reliability and consistency, the use of unknown or single-source formulations was avoided - a future formulation change or non-availability could not be tolerated. This criteria required selection of pure materials, which was beneficial in other ways. First, guarantee of supply is virtually assured since materials are typically available from a number of sources. Duplication of testing was also avoided since many proprietary tradename cleaners are similar in formulation. Toxicity information and solubility data are available and cost is less.

Use of Solubility Parameters to Select and Blend Solvents

The solubility parameter system is a practical and quantitative guide for selecting solvent candidates and for estimating the properties of a blended solvent. The system is well documented and accepted throughout the industry. Solubility parameters takes the like-dissolves-like logic by evaluating the mixing compatibility of materials by describing and quantifying the cohesive energy forces holding materials together (cohesive energy density). During dissolution, the intermolecular bonds of materials A and B are broken while new bonds between the different materials are formed. If A-A, B-B, and A-B bonds are similar, little energy is needed to replace the broken A-A and B-B bonds with the A-B bonds. But if the A-A bond is much stronger than the A-B and B-B bonds, breaking the A-A bond will be thermodynamically unfavorable[8] Solubility parameters can determine which situation will be favorable.

The Hildebrand parameter (δ) is the most commonly used and can be estimated for any material easily with a few physical constants. Hansen later modified the parameter to differentiate the contributions of dispersive (London) forces (δ_d), hydrogen bonding (δ_h), and polar forces (δ_p) through a semi-empirical process. These are in effect simultaneously, and can be resolved into a vector which describes the total Hansen solubility parameter, δ_t ($\delta_t^2 = \delta_p^2 + \delta_h^2 + \delta_d^2$). Hoy later modified the Hansen system by incorporating more theoretical considerations and provided the primary system used in our studies. References are readily available that provide detailed descriptions and also values for many solvents and other materials. A graphical representation of Hoy system δ_p vs. δ_h was found to be useful in the Hercules effort and is provided showing the dispersive parameter in parentheses. Note that these Hoy parameters differ in value from the Hansen parameters[9,10]

Hercules uses solubility parameter data in several ways. First, duplication of testing of similar solvents is easily avoided. For instance, NMP and BLO are very similar in all parameters, and therefore need not both be tested. Also, given the solubility parameter of a particular soil, it is easy to determine which solvents would function well. For soils with no solubility parameter data available, laboratory solubility tests can be run with a variety of different but known solvents to characterize the soil. The best solvent for the job can also be identified. Graphical examples of soil "mapping" are provided. To develop a more versatile solvent system, the solubility parameter data are also useful for predicting solvent blend properties that exhibit intermediate solubility parameters which can work for different soil types. The best hydrocarbon soil cleaners all share the attribute of having very low hydrogen bonding, while the solvents best for paints and

adhesives tended to be moderate H bond with high polarity. d-Limonene, which was already quite versatile due to its moderate solubility parameter and Hoy polarity, was found to be a very useful base for blends which could also effectively remove the higher parameter soils such as paints, primers and epoxies. The solvent solubility parameter graph illustrates why d-limonene is in a position to form a wide variety of versatile cleaners by blending with various oxygenated solvents to get a parameter specific to one's needs.

Solvent Screening Testing

While solubility parameter technology is a useful system for solvent selection, it should only be used as a guide. Verification in the laboratory for solvency with the identified soils, and compatibility with the expected substrates is essential.

Solubility was tested in one of two methods. In one test, 0.1 gram of the soil was placed in a test tube with 4 ml solvent and agitated at 200 rpm for 5 and 40 seconds with the solubility and residue judged at the end of each interval (similar to ASTM D-3132). The second method consisted of coating a metal plate with the soil which was cured or "staged" for a certain amount of time and then cleaned with a solvent saturated wipe. Effectiveness in either case was judged by the speed in which the soil went into solution or could be visually removed from the plate. The general scoring is similar to the ASTM method with finer resolution provided by adjusting the numbers up or down by 0.3.

Solubility tests were very quick to perform and proved to be very useful in screening out mediocre candidates and helped characterize the soils for further testing.

Solubility Test Results - Relative Performance[11]

	Soil Group					
	E	**P**	**S**	**U**	**T**	**O**
1,1,1 TCA	1.8	1.7	2.0	1.4	1.8	2.0
Limonene (Prepsolv™)	0.7	1.4	2.0	0.9	1.8	2.0
PCBTF	1.5	1.6	1.7	1.9	1.7	2.0
Aliphatic/Terpene	NT	NT	1.7	NT	NT	1.7
n-Butyl Butyrate	1.4	1.9	2.0	1.4	1.1	1.7
Methyl Lactate	1.5	0.9	0.0	1.5	0.1	0.5
50/50 BLO/NMP	1.5	1.6	NT	1.7	0.0	NT
60/40 Limonene/NMP	1.8	2.0	1.5	1.9	1.1	1.9
90/10 PNB/PM	1.2	NT	0.9	1.2	NT	1.6

E = Epoxies (9 types) **U** = Urethanes (2 types) **P** = Paints/Primers (5 types)
T = Tape Adhesives (7 types) **S** = Silicones (2 types) **O** = Oils/Greases (3 composites)

0 = Insoluble with no solution or suspension and a large amount of residue.
1 = Partially soluble with a hazy or cloudy solution and/or varying amounts of residue.
2 = Completely soluble with a fully clear solution with no residue.
NT =Not tested.

Non-volatile residue (NVR) was also a value measured in the laboratory, being of concern for bond surface preparation. A solvent that leaves a low surface energy or low cohesive strength residue has the potential to produce a poor bond. NVR is measured in several ways. One method is ASTM 1353-90, where 100 ml of the solvent is evaporated to dryness on a steam table and then placed in a 205°F oven for a time. This test proved most of the solvents to be very clean. Some, however, had a significant amount of residue at the end of testing which was not expected from results of ambient dry observations. There was concern that the high temperature of the test may oxidize/polymerize some of the solvents, especially those with unsaturated sites, such as the terpenes. An alternate method was developed to help determine if the residue could be attributed to temperature/oxidation effects during testing. Approximately 0.1 g. of the solvents were placed on Germanium ATR crystals and evaporated at 205°F, 105°F, and 105°F in a vacuum. The ATR crystals were then analyzed by infrared spectroscopy, providing a semi-quantitative measurement of the amount of residue.

NON-VOLATILE RESIDUE ANALYSIS RESULTS

	ASTM D1353 Wt% NVR	105°F FTIR Absorbance[12]	Amb. FTIR Absorbance	ATR NVR Analysis
1,1,1 TCA	0.0000	0.00	0.00	-
Stoddard 140	0.0095	0.05	-	Hydrocarbon
Aliphatic/Terpene blend	0.0063	0.06	-	Ester
Limonene 145	0.0370	0.06	-	Ester/alc/AO
Limonene 145 w/o anti-ox	0.2354	0.00	0.00	-
Prepsolv™	0.0040[13]	0.00	0.00	-
NMP	0.0240	0.11	-	Ester/alc.
n-Butyl Butyrate	0.0046	0.04	-	Ester

Ambient testing of Glidco Limonene 145 and ATR/FTIR analysis showed that the bulk of the residue was attributable to the test environment, but residual anti-oxidant was present and led to study of a clean anti-oxidant package for bond surface preparation.

The potential for bond degradation from NVR was tested by treating smooth machined aluminum plates with various solvents before epoxy bonding. This configuration was estimated to be more sensitive to contamination than any bondline in our processes. 4-8 RMS milled 6061 plates were cleaned with toluene/ethyl acetate and rinsed with clean acetone and exposed to two treatments of streaming solvent over the plate and forcing off the excess with an inert aerosol dust chaser leaving only a thin film of solvent. The plates were then dried for 1.5 hours at ambient and placed in a desiccator overnight before bonding to grit blasted, stainless steel buttons with 3M EC2216 epoxy. The buttons were then pulled in tensile at 0.2 ipm. No degradation of the bondline was seen with the Glidco Limonene 145, Prepsolv™, or PCBTF compared to the methyl chloroform control.

The most critical bonds in the rocket motor are rubber-to-rubber, rubber-to-steel and rubber-to-composite. Therefore, compatibility of the solvents with the rubber is of great importance. The solvent affinity for the rubber and drying rate was tested simultaneously by exposing the rubber by a 30 second soak (simulating an accidental spill) and by a triple wipe with a solvent soaked cloth. The samples were dried at ambient lab conditions and gravimetrically tested over 5 days. Surprisingly, even methyl chloroform remained in the rubber for over 4 days due to its initial high absorption into the rubber. Apparently, a high evaporation rate is of little help since, once in the rubber, solvent transfer is diffusion limited. Effect on rubber mechanical properties were also measured. While solvents that soaked into the rubber had an immediate affect, in all cases the rubber returned to normal once dry.

Future Efforts

While Hercules' program to select solvents is explained, the criticality of rocket motor missions and designs demands rigorous qualification of any replacement solvent prior to its use in a production environment.

Qualification testing is currently in progress and will, in detail, examine the effect of selected solvents on material properties, corrosive effects, compatibility with bond lines and the effect of the solvents on long term properties of the motor.

Footnotes

[1] *Hansen solubility parameters differ from the Hoy solubility parameters in the Hercules case study.*

[2] *Source: Texaco Solvents Data, 1992 unless otherwise noted.*

[3] *John Van Dyk, Van Dyk Associates.*

[4] *Estimated from homolog data.*

[5] *Data per Purvis and Moran, Hercules Aerospace Case Study.*

[6] *Data for methyl lactate, n-butyl butyrate, n-methyl pyrrolidone, and gamma-butyrolactone not available.*

[7] *TLV/TWA not established for most terpenes. Assume 100, the established TLV for turpentine.*

[8] *Gardon, J.L., "Cohesive Energy Density", Ency. of Polymer Sci. and Tech, Vol. 3.*

[9] *Hansen, C., J. Paint Tech., Feb. 1967.*

[10] *Hoy, K.L., "Tables of Solubility Parameters", (Union Carbide).*

[11] *Shaded values indicate good performance relative to methyl chloroform.*

[12] *Absorbance for functional group of solvent or oxidation product.*

[13] *FTIR analysis showed only a trace of oxidation product. Most of the NVR was labware contamination (silicone). New sample used for ATR tests.*

ENVIRONMENTALLY SAFE FUELS, FIRE SUPPRESSANTS, REFRIGERANTS, AND INSULATIONS

A Water Blown Urethane Insulation for Use in Cryogenic Environments

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Abstract

Thermal Protection Systems (TPS) of NASA's Space Shuttle External Tank include polyurethane and polyisocyanurate modified polyurethane foam insulations. These insulations, currently foamed with CFC 11 blowing agent, serve to maintain cryogenic propellant quality, maintain the external tank structural temperature limits, and minimize the formation of ice and frost that could potentially damage the ceramic insulation on the space shuttle orbiter. During flight the external tank insulations are exposed to mechanical, thermal and acoustical stresses. TPS must pass cryogenic flexure and substrate adhesion tests at -253°C, aerothermal and radiant heating tests at fluxes up to approximately 14 kilowatts per square meter, and thermal conductivity tests at cryogenic and elevated temperatures.

Due to environmental concerns, the polyurethane insulation industry and the External Tank Project are tasked with replacing CFC 11. The flight qualification of foam insulations employing HCFC 141b as a foaming agent is currently in progress; HCFC 141b blown insulations are scheduled for production implementation in 1995. Realizing that the second generation HCFC blowing agents are an interim solution, the evaluation of third generation blowing agents with zero ozone depletion potential is underway. NASA's TPS Materials Research Laboratory is evaluating third generation blowing agents in cryogenic insulations for the External Tank; one option being investigated is the use of water as a foaming agent. A dimensionally stable insulation with low friability, good adhesion to cryogenic substrates, and acceptable thermal conductivity has been developed with low viscosity materials that are easily processed in molding applications. The development criteria, statistical experimental approach, and resulting foam properties will be presented.

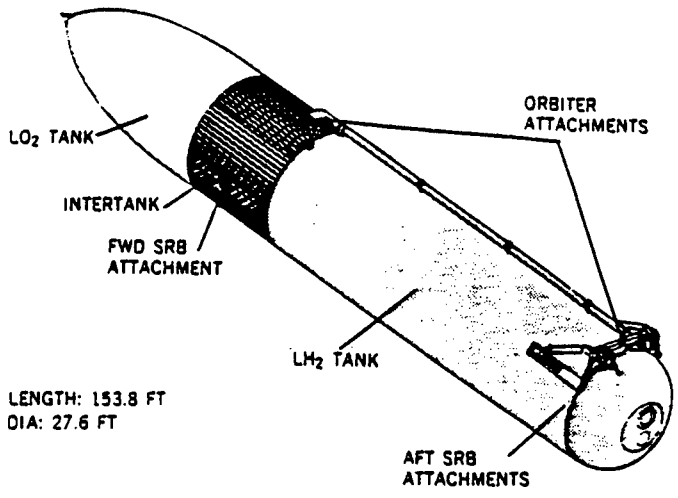
Introduction

The purpose of this study was to evaluate the use of water blown polyurethane based insulations in cryogenic environments. Success criteria included the following insulation properties: low friability, good adhesion, cryogenic strain compatibility, dimensional stability, high closed cell content, and acceptable thermal conductivity. Emphasis was placed on adhesion to an epoxy primed aluminum substrate and on flexibility at cryogenic temperatures.

External Tank Insulations

The External Tank serves as a cryogenic propellant tank and also as a structural backbone for the Space Shuttle system. Figure 1 shows the main components of the External Tank; they are a forward liquid oxygen tank, an intertank, and the aft liquid hydrogen tank. Thermal Protection Systems (TPS) of the External Tank include high density silicon based ablative resins, polyisocyanurate spray on foam insulations, and both sprayable and moldable polyurethane insulations. The TPS serves to prevent the formation of ice and frost on the tank surface, maintain structural temperature limits, and maintain propellant quality. The polyurethane pour foam was selected as the first target application for the water blown insulation.

Figure 1. External Tank Structure



Industry Studies

Over the past few years, several papers have been presented on the development of rigid foams blown with carbon dioxide from the water-isocyanate reaction. The industry has found this technically challenging and economically inviting. Issues associated with these water blown foams include: increased thermal conductivity, high open cell content, accelerated foam aging, poor dimensional stability, high friability, and poor adhesion [1,2]. The primary concern lies with the high diffusion rates of carbon dioxide in the polymer matrix of the foam. The rapid diffusion of carbon dioxide out and the slower ingress of air components leads to foam shrinkage and higher thermal conductivities [3,4]. The thermal conductivities of these gases are presented in Table 1. Processing of water blown foams is more difficult because of the inherently higher viscosities of the polyol components. Several have found that molding of these foams is complicated by poor flowability and high molding pressures [5-7]. Nevertheless, systems have been developed for use in appliances, vending machines, water heaters, supermarket display cases, and picnic coolers.

Table 1. Thermal Conductivity of Cell Gases

Gas	K (BTU.in/ft².h.°F)
Nitrogen	0.168
Air	0.168
Oxygen	0.170
Carbon Dioxide	0.102
Trichlorofluoromethane	0.068

Experimental

Developmental Approach

The polymer structure was modified to incorporate higher molecular weight polyols that could compensate for the high crosslink density associated with water blown foams without sacrificing dimensional stability. The experimental sequence was initiated by screening several polyols for their effect on foam friability, substrate adhesion, and closed cell content. The polyols evaluated are presented in Table 2. Six polyols were then selected for further study. A statistically based experiment was designed to evaluate these polyols and determine the optimum ratio required to achieve a dimensionally stable foam with cryogenic compatibility. Thirty foam formulations were blended, foamed, and tested with varying levels of each of the six polyols. Three replicate formulations were included in the experiment to allow estimation of the replicate standard deviation of the foam properties. In each of the

experimental formulations, isocyanate index was held constant at 150, while surfactant and water levels were held constant at 2 and 1.25% of the total formulation respectively. Data was analyzed and fitted with quadratic models. These empirically based models were then used to evaluate the trade-offs in material properties associated with various polyol ratios.

Table 2. Polyols Evaluated

Polyol #	OH Equivalent Weight
1	246
2	180
3	170
4	119
5	156
6	167
7	200
8	106
9	94
10	330

Foam Preparation

Foams were prepared by preblending the polyol component, and then combining stoichiometric weights of polyol and polymeric isocyanate for mixing. The room temperature liquid components were hand mixed for 8 seconds at 12,000 rpm with a Premier Mill Laboratory Dispersator. The reacting mixture was then poured into paper cups for manual reactivity measurement, or separately into a Timetech reactivity unit for automatic data acquisition of foam exotherm temperature, foam gelation pressure, and foam rise height. The catalyst levels for each of the thirty formulations was adjusted to maintain a constant reactivity for all systems.

Initial polyol screening tests were conducted with room temperature, free rise box pours. Test panels for the polyol optimization experiment were made in 10"x20"x3" molds. Four room temperature molds containing an epoxy primed aluminum substrate were poured for each of the thirty formulations. Panels were cured a minimum of one hour at room temperature before demolding. An additional 2 week aging period was allowed before test samples were cut and prepared from the panels.

Foam Properties

Table 3 lists the tests conducted on the foam insulations. Emphasis was placed on the results of the adhesion and cryogenic flexure tests. Bond tensile samples were tested at -196°, 21°, and 93°C to measure substrate adhesion. Four point flexure samples were tested at -196°C. Tensile and flexure tests are currently being run at -253°C.

Table 3. Test Methods

Foam Property	Method	Units
Bond Adhesion (1)	ASTM D 1623	psi
Compression	ASTM D 1621	psi
Density	ASTM D 1622	pcf
Friability	ASTM C 421	%mass loss
Closed Cell Content	ASTM D 2856	% closed cells
Thermal Conductivity	ASTM C 177	BTU.in/ft².h.°F
Oxygen Index	ASTM D 2863	%oxygen
4-Point Flexure	In-House Test	psi

Note: (1) Adhesion to epoxy primed 2219 aluminum alloy

Results

The results of the polyol screening tests are presented in Table 4. The results show a broad range of foam properties with bond tension values ranging from 20 to over 100 psi in room temperature tests. Elongation measured in the bond tension tests was used as an indicator of four point flexibility. Based on

these test results, Polyols 1 through 6 were selected for further study. Table 5 presents the levels at which the polyols were evaluated in the experiment.

Table 4. Results of Polyol Screening

Polyol #	21°C Bond Tension	% Elongation	Compression	% Closed Cells	Friability	Oxygen Index
1	20	18	5	80.7	3.84	21.0
2	79	10	31	91.5	1.34	20.9
3	79	9	31	92.2	0.38	20.8
4	107	11	34	92.6	1.45	21.0
5	78	10	48	93.8	0.39	19.8
6	44	9	33	93.2	1.37	20.9
7	64	9	27	92.2	0.23	20.5
8	38	8	41	93.1	1.27	21.0

Table 5. Experimental Variables

Variable	Range
Polyol 1	0 to 30 % of Polyol Blend
Polyol 2	0 to 100% of Polyol Blend
Polyol 3	0 to 100% of Polyol Blend
Polyol 4	0 to 100% of Polyol Blend
Polyol 5	0 to 100% of Polyol Blend
Polyol 6	0 to 100% of Polyol Blend

The thirty formulations evaluated in this experiment had the following constant variables: isocyanate index of 150, common surfactant, and 1.25% water in the total formulation. Material properties varied considerably with the change in polyols. Several of the test panels debonded from the aluminum substrate with demolding, while others had good substrate adhesion.

Results of the mechanical and physical testing were reduced and analyzed with Echip™ software to determine the effects of the various polyol ratios on foam properties. The R-square values, indicating how well the empirical models fit the experimental data, are presented in Table 6. Polyol 1 was found to have the greatest effect on the foam flow in the molds, and based on the empirical models also contributed to cryogenic bond tensile strength and four point flexibility. Polyols 3 and 6 contributed to dimensional stability and improved oxygen index. The optimum formulation having the best combination of properties, substrate adhesion greater than 50 psi and cryogenic flexibility, was obtained with the polyol blend consisting of 20% Polyol 1, 50% Polyol 3 and 30% Polyol 6.

Table 6. Degree of Fit of Empirical Models

Property Modeled	R-square value
Bond Tension, 21°C	0.827
Bond Tension, 93°C	0.741
Bond Tension, -196°C	0.861
4-point Flexure, Stress at failure	0.814
4-point Flexure, Strain at failure	0.878

Figures 2 to 4 are two dimensional contour plots illustrating the effects of polyol ratio on substrate adhesion at various temperatures. These plots show the detrimental effects of Polyol 1 when used at levels greater than 30% of the polyol blend. Figures 5 and 6 show the maximum stress and strain in a four point flexure test are obtained with Polyol 1 added at approximately 25% of the polyol blend.

An evaluation of a phosphorous based flame retardant in the water blown foam was conducted. Table 7 presents the effects of the non-reactive flame retardant on the foam properties of gel time, density, and oxygen index. The flame retardant was added to the foam system at levels ranging from zero to twenty-five percent of the total formulation. Based on this limited data, a flame retardant level of 12% was selected.

Table 7. Effects of Added Flame Retardant

% FR	Gel (sec)	Density	Oxygen Index
0	43	2.5	<20.9
4	52	2.5	23.0
7	53	2.5	24.0
10	56	2.5	25.0
15	57	2.5	26.1
20	58	2.6	26.9
25	62	2.8	27.3

These oxygen index values are not intended to reflect hazards presented by this or any other material under actual fire conditions.

As a result of this study, a water blown molding insulation has been developed with acceptable mechanical properties at cryogenic temperatures. Table 8 presents data for this insulation, System A, and a comparable insulation, System B, that is co-blown with CFC 11 and water. The reaction profile of System A is illustrated in Figure 7 which shows the rise in foam exotherm temperature with time.

Table 8. Properties of the Water Blown Insulation

Foam Property	System A Water Blown	System B Control (1)
Density		
Free Rise	2.3	2.5
Molded	2.6	3.0
Bond Adhesion (2)		
-196°C	63	38
21°C	83	64
93°C	49	33
Compression	28	30
Friability	1	26
Closed Cell Content	93	87
Thermal Conductivity	0.20	0.17
Oxygen Index	25	23

Note:
1. CFC 11 and water co-blown
2. Adhesion to epoxy primed 2219 aluminum alloy

Conclusions

The development of a water blown insulation for use in cryogenic environments required the development of a polymer network with reduced crosslink density to obtain a low friability insulation with good adhesion to epoxy primed aluminum substrates. This development work completed with a molding system will serve as a platform for further development of a sprayable, water blown foam insulation. Statistically designed experiments have been employed in the evaluation of a catalyst package for accelerated reactivity suitable in spray formulations, and are currently being used in a processing sensitivity study to evaluate the parameters of substrate temperature, relative humidity, and component temperature on foam properties. As industry continues to develop low viscosity and low permeability polyols, improved surfactants and catalysts, the use of rigid water blown foams in a variety of applications will grow.

Acknowledgments

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References

1. Moore, S. E. Dimensionally Stable All Carbon Dioxide Blown Foam at 1.60 pcf Density. Proceedings of The 34th Annual Polyurethane Technical/Marketing Conference; 1992 October 21-24; New Orleans, LA: SPI 135-140.
2. Mirasol, S.; Bhattacharjee, D.; Moreno, O. Carbon Dioxide Blown Dimensionally Stable Rigid Polyurethane Foam for Entry Door Applications. Proceedings of The 34th Annual Polyurethane Technical/Marketing Conference; 1992 October 21-24; New Orleans, LA: SPI 390-395.
3. Yamato, L. T.; Schiff, D. E.; Bhattacharjee, D.; Dressel, D.; Galbreath, D. E.; McAdams, H. P. Novel Spray Foam Polyols with Improved Performance. Proceedings of The 34th Annual Polyurethane Technical/Marketing Conference; 1992 October 21-24; New Orleans, LA: SPI 410-421.
4. Moore, D. R.; Kaplan, W. A.; Tabor, R. L. Low Permeability Polyols for Rigid Foam Applications. Proceedings of the Polyurethanes World Congress; 1993 October 10-13; Vancouver, B.C. Canada: SPI 439-444.
5. Stewart, R. D. Second Generation Carbon Dioxide Blown Systems. Proceedings of the Polyurethanes World Congress; 1993 October 10-13; Vancouver, B.C. Canada: SPI 40-45.
6. Dedeaux, D. W.; Rister, E. L.; Zimmerman, R. L.; Kohoutek, F. C. Texacat® Catalysts in Water-Blown Rigid Foam. Proceedings of the 34th Annual Polyurethane Technical/Marketing Conference; 1992 October 21-24; New Orleans, LA: SPI 341-347.
7. Christman, D. L.; Reichel, C. J. Water-Blown Rigid Foams. Proceedings of the Polyurethanes World Congress; 1993 October 10-13; Vancouver, B.C. Canada: SPI 405-410.

Evaluation of HFC 245ca and HFC 236ea as Foam Blowing Agents

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ABSTRACT

Hydrochlorofluorocarbon (HCFC) 141b has been selected as the interim blowing agent for use in urethane insulations on NASA's Space Shuttle External Tank. Due to the expected limited commercial lifetime of this material, research efforts at the NASA Thermal Protection Systems Materials Research Laboratory at the Marshall Space Flight Center are now being devoted to the identification and development of alternatives with zero ozone depletion potential. Physical blowing agents identified to date have included hydrocarbons, fluorocarbons, hydrofluoroethers, and more predominantly, hydrofluorocarbons (HFCs). The majority of the HFC evaluations in industry have focused on the more readily available, low boiling candidates such as HFC 134a. Higher boiling HFC candidates that could be handled at ambient conditions and use current processing equipment would be more desirable.

This paper will describe results from a research program of two such candidate HFCs performed as a cooperative effort between Martin Marietta Manned Space Systems, the U.S. Environmental Protection Agency, and Oak Ridge National Laboratories. The purpose of this effort was to perform a cursory evaluation of the developmental HFCs 245ca and 236ea as blowing agents in urethane based insulations. These two materials were selected from screening tests of 37 C_2, C_3, and C_4 isomers based on physical properties, atmospheric lifetime, flammability, estimated toxicity, difficulty of synthesis, suitability for dual use as a refrigerant, and other factors. Solubility of the two materials in typical foam components was tested, pour foaming trials were performed, and preliminary data were gathered regarding foam insulation performance.

INTRODUCTION

Hydrochlorofluorocarbon (HCFC)-141b has been widely adopted as the interim blowing agent of choice in rigid foam insulations. Even though this material has an Ozone Depletion Potential (ODP) approximately 85% lower than the chlorofluorocarbon (CFC)-11 it is targeted to replace, HCFC-141b is also planned to be phased out in favor of alternatives with zero ODP. Current regulatory timelines, per the U.S. Environmental Protection Agency Phase-out of Ozone Depleting Substances[1], call for phaseout of HCFC-141b, beginning in the year 2002. This situation poses a significant challenge to the polyurethane insulation industry since there are no readily available non-flammable, liquid alternatives which could easily replace the HCFC-141b. This, combined with the fact that the transition from CFC-11 to "near drop-in" HCFC-141b, has taken well over 5 years, indicates that development and commercialization of a suitable zero ODP physical blowing agent is already on a critical schedule.

There is a need for industry to identify and provide a concerted effort toward development of acceptable foam blowing agent(s) that will meet all environmental goals and provide permanent solutions to the blowing agent issue. Alternatives such as hydrocarbons, low boiling HFCs, and water/carbon dioxide have been shown to be suitable for some applications. For other applications, a non-flammable, liquid, physical blowing agent is more desirable. One source of potential zero ozone depleting blowing agents in this category is the new experimental chemicals being developed as proposed refrigerant alternatives. Several such chemicals have been proposed by the Environmental Protection Agency (EPA) Air and Energy Engineering Research Laboratory (AEERL) as alternatives to CFC refrigerants based on having

properties similar to those of CFC refrigerants. One of them, 1,1,2,2,3-pentafluoropropane (HFC-245ca), is being considered as a CFC-11 alternative for chillers, and another, HFC-236ea (1,1,1,2,3,3-hexafluoropropane), has been the subject of more extensive theoretical and experimental evaluation as a CFC-114 alternative for shipboard cooling. Both HFC-245ca and HFC-236ea have desirable properties for use as foam blowing agents.

This paper presents results of a cooperative effort between the U.S. EPA, Oak Ridge National Laboratory, and Martin Marietta Manned Space Systems to evaluate HFC-245ca and HFC-236ea as blowing agents for rigid polyurethane insulation foams, and to perform cursory accelerated aging evaluations of hand poured samples. A third chemical, HFC-245fa, was also considered in this program, but was not evaluated experimentally due to difficulties in obtaining sufficient quantities for evaluation.

PROPERTIES OF HFC-245ca and HFC-236ea

Beyerlein et al. presented a technical paper[2] listing the thermophysical properties of a number of new chemicals, including HFC-245ca and HFC-236ea. Additional properties of these materials supporting their potential use as blowing agents were provided by Smith.[3] In addition to these data, Knopeck et al.[4] reported both physical property data and results of foaming trials of four candidate zero ODP HFCs, including HFC-245ca and HFC-236ea. A comparison of some relevant properties of HFC-245ca and HFC-236ea with CFC-11 and HCFC-141b is presented in Table 1.

Table 1. Blowing Agent Physical Property Comparison

Property	CFC-11	HCFC-141b	HFC-245ca	HFC-236ea
Molecular Weight	137	117	134	152
Boiling Point, °C	23.8	32.1	24.4	6.2
Ozone Depletion Potential	1	0.12	0	0
Atmospheric Lifetime, yrs	60	10	6.4	6.2
Vapor Thermal Conductivity, Btu-in/hr-ft^2-°F	0.057	0.072	0.095	0.100
Heat of Vaporization, Btu/lb-mol	10,700	11,200	12,563	11,537
Flammability	none	slight	none	none

FORMULATION APPROACH

Because HFC-245ca and HFC-236ea are not commercially available, experimental samples are relatively expensive. The high cost of the samples limited the scope of this effort to cursory formulation, development, and testing of manually poured foam panels. Based on our experience with HCFC-141b, where substitution based on molecular weight ratios did not prove optimum, our initial approach was to evaluate the experimental blowing agents in an existing formulation at a 1:1 substitution for CFC-11. This existing formulation is a hand pourable formulation based on a sucrose initiated polyol that exhibits good adhesion from cryogenic temperatures (-423 °F) to approximately 300 °F. Initial trials with this formulation blown with HFC-236ea resulted in poor foam cell structure, and further attempts to characterize the blowing agents using this formulation were abandoned. A more basic, urethane type system was then formulated to serve as a control formulation to provide a simple comparison of blowing agent effects. The A component of the control formulation was polymeric methylene diphenyldiisocyanate (MDI) with a functionality of 2.7 and viscosity of ~ 180cp). The basic formulation of the B component for the control is outlined in Table 2.

Table 2. B Component Formulation

Constituent	Material	% of Formulation
Polyol 1	Aromatic amine	62.7
Polyol 2	Low molecular wt. triol	2
Polyol 3	High molecular wt. triol	4
Catalyst	DMCHA	0.4
Surfactant	Silicone glycol copolymer	2
Blowing Agent	-----	28.9

To blend the B component, a master batch containing everything but the blowing agent was prepared. This master batch was then split into three equal portions, one for each blowing agent. CFC-11 and HFC-245ca were added at 72°F. The HFC-236ea cylinder was cooled to 35° F before addition to the 72° F master batch. Cooling the master batch to 35° F before HFC-236ea addition was also attempted, but the high viscosity of the polyol at that temperature made it difficult to achieve a uniform blend. The previously described method turned out to be suitable because the HFC-236ea did not exhibit an appreciable evaporation rate, when left undisturbed, after being blended with the polyol components.

Both the HFC-245ca and HFC-236ea blended quite readily with mechanical agitation. Samples of the B component with blowing agent were left in glass bottles for a period of 3 months. The HFC-236ea blend showed no signs of separation after this period. The HFC-245ca blend exhibited slight separation at 3 months, but was easily redispersed with agitation.

REACTIVITY EFFECTS

Cup reactivities were performed with the control formulation. The reactivity of the HFC-245ca was performed with the A and B components at 72°F. The initial attempt to evaluate HFC-236ea reactivity at ambient temperature resulted in frothing of the B component and loss of blowing agent. In order to preclude blowing agent loss in the HFC-236ea formulation, the A component was maintained at 72°F and the B component was cooled to 35°F. Control reactivities were performed with the CFC-11 formulation at both of these initial component temperatures. Results of these cup tests are summarized in Table 3.

Table 3. Cup Reactivities

Property	CFC-11	HFC-245ca	CFC-11	HFC-236ea
A/B Temperature,°F	72/72	72/72	72/35	72/35*
Cream time, sec.	18	16	31	17
Gel time, sec.	63	72	98	130
Tack-free time, sec.	90	103	143	158
Rise time, sec.	130	140	186	180
Density, lb/ft^3	1.9	1.7	1.9	1.8

*Initial B component temperature was 35°F to preclude blowing agent loss. No catalyst adjustment was made to normalize reactivity.

These results show that the HFC-245ca has very similar reactivity characteristics to the CFC-11 control. The gel, tack-free, and rise times were approximately 8 to 14 % longer with the HFC-245ca than with the

CFC-11. It is expected that this is due merely to differences in the heat of vaporization in these materials, which could be easily accommodated by adjustments in catalyst level and/or component temperature. As anticipated, the HFC-236ea reactivity with an initial B temperature of 35°F was significantly slower than the CFC-11 with both components at 72 °F. However, when the reactivity of the CFC-11 system was evaluated with the A component at 72° F and the B component at 35°F, the cream time of the HFC-236ea system was shorter than the CFC-11, while the gel and tack-free times were longer than the CFC-11 blown sample. The shorter cream time was expected due to the difference in boiling points of the two materials. The extended gel and tack-free times of the HFC-236ea are suspected to be partially attributable to the high solubility of the HFC-236ea.

Automated reactivity measurements were also made with the three blowing agents. Plots of foam reaction temperature and reaction height are presented in Figures 1 and 2, respectively. A comparison of the reaction temperatures of CFC-11 and HFC-245ca with the A and B component temperatures initially at 73°F shows that, after initiation of the reaction, the HFC-245ca exotherm begins to lag that of CFC-11. Comparison of CFC-11 and HFC-236ea with initial A and B component temperatures of 70°F and 35°F, respectively, shows the same characteristic. This is expected due to the difference in heat of vaporization of the two blowing agents, and should be resolvable with a more optimized catalyst system. In Figure 2, the foam reaction height profiles of CFC-11 and HFC-245ca with A and B temperatures initially at 73°F, show very similar trends. Comparison of CFC-11 and HFC-236ea with A and B temperatures of 70°F and 35°F, respectively, shows that the HFC-236ea begins to rise earlier and maintains a fairly constant rate of rise. The faster initial rise of the HFC-236ea blown foam is expected due to the low boiling point of the material.

FOAM PROPERTIES

Free Rise Foam Characteristics

Free rise samples of each foam were tested for various physical and mechanical properties, and results are presented in Table 4.

Table 4. Free Rise Foam Properties

Property	CFC-11	HFC-245ca	HFC-236ea
Density, lb/ft^3	1.69	1.59	1.73
Compressive Strength, parallel to rise, lb/in^2	24	28	22
Compressive Strength, perpendicular to rise, lb/in^2	8	8	11
Flatwise Tensile Strength, parallel to rise, lb/in^2	61	66	61
Flatwise Tensile Strength, perpendicular to rise, lb/in^2	28	25	35
Friability, % mass loss	4.1	2.5	1.5

These values indicate that foams with approximately equivalent properties can be prepared using the three different blowing agents.

Micrographs of free rise foam samples were prepared as a preliminary comparison of foam cell structure. These micrographs, presented in Figures 3 through 5, show that the HFC-245ca had a cell size and cell size distribution similar to CFC-11, and the HFC-236ea exhibited a slightly finer, more uniform cell structure.

Case Study #2 - Major International Airline (Chart 8)

This airline processes a smaller variety of parts, but overall, these parts are more labor intensive than in Case #1.

8-CASE STUDY #2 - MAJOR INTERNATIONAL AIRLINE

PART IDENT.	CURRENT (HR)	WATERJET (HR)	SAVINGS (HR)
BOOSTER SHROUD	10	0.7	9.3
HPC DISK	5	0.1	4.9
SPOOL	122	0.8	121.2
HPC STATOR CASE	144	0.8	143.2
TURBINE MID-FRAME	5.5	0.7	4.8
COMPRESSOR REAR FRAME	4	0.8	3.2
SUMP	3	0.7	2.3
THERMAL SHIELD	24	0.8	23.2
LOW-PRESS. TURBINE CASE	4	1.0	3.0

Case Study #3 - Major U. S. Airline (Chart 9)

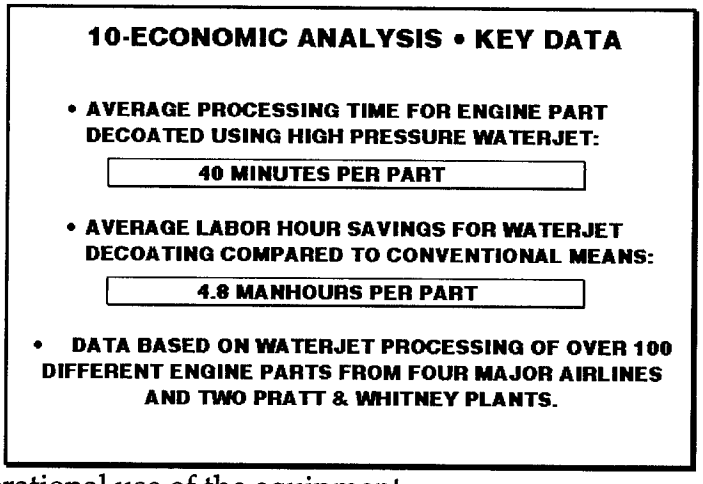
Our third airline justified the waterjet investment based on processing only inlet fan cases. The environmental concerns associated with the conventional method combined with the high labor costs combined to provide the needed justification. A variety of other parts are also being processed since the backlog of inlet fan cases no longer exists.

9-CASE STUDY #3 - MAJOR U. S. AIRLINE

PART IDENT.	CURRENT (HR)	WATERJET (HR)	SAVINGS (HR)
INLET FAN CASE	22	2	20
MISC. PARTS (AVG.)	--	--	5

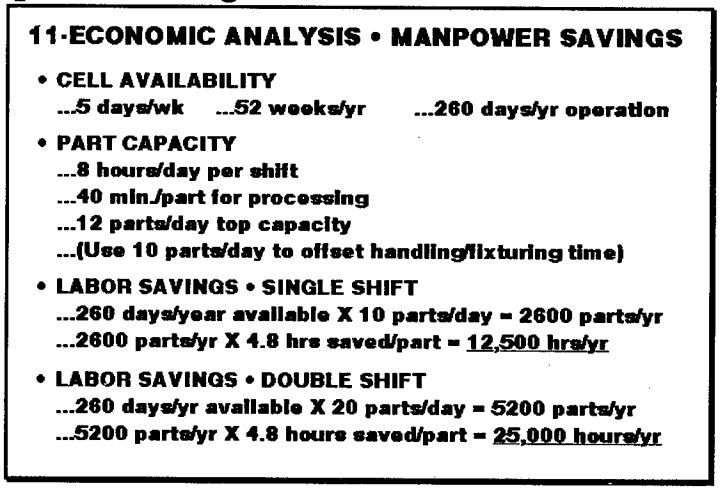
Economic Analysis - Key Data (Chart 10)

If the data from the three case studies shown are combined with data from another airline and two engine part manufacturing plants, the key data shown here are representative of the replacement technology. These key data are critical in the analysis because they establish the expected part capacity of the equipment and the expected labor savings as a function of the operational use of the equipment.



Economic Analysis - Manpower Savings (Chart 11)

These calculations are necessary to establish the baseline and savings then possible with the new waterjet equipment. Note that although 12 parts per shift is the potential maximum throughput, only 10 parts per shift was used to allow for "friction," such as part change, fixturing, and unexpected maintenance. Normal preventive maintenance is performed on an idle shift.



The key findings are a labor savings of 25,000 labor hours per year per double-shift operation and 12,500 labor hours for single-shift operation.

Figure 1.

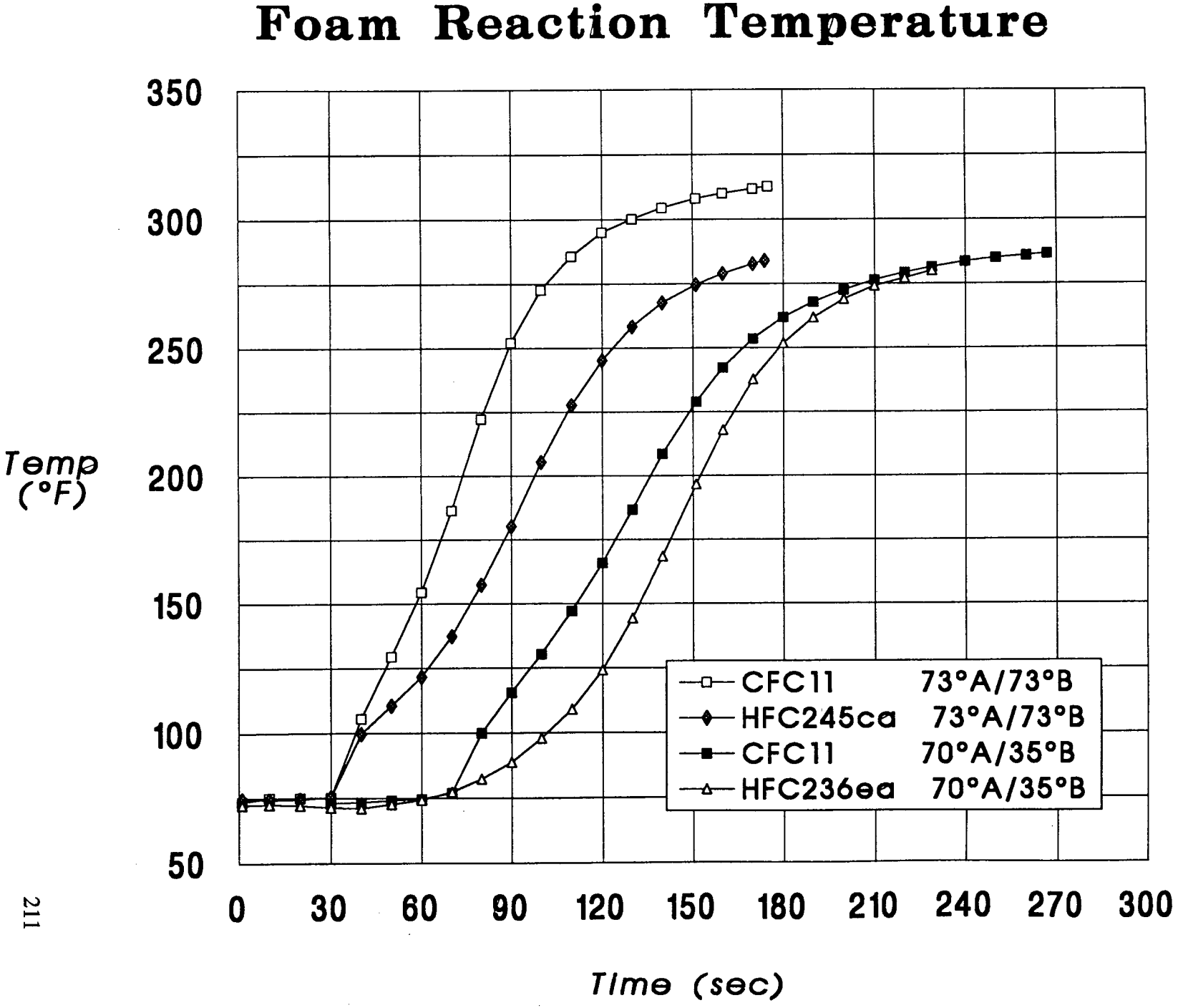

Foam Reaction Temperature
350
300
250
200
150
100
50
Temp (°F)
0
30
60
90
120
150
180
210
240
270
300
Time (sec)
CFC11 73°A/73°B
HFC245ca 73°A/73°B
CFC11 70°A/35°B
HFC236ea 70°A/35°B

Figure 2.

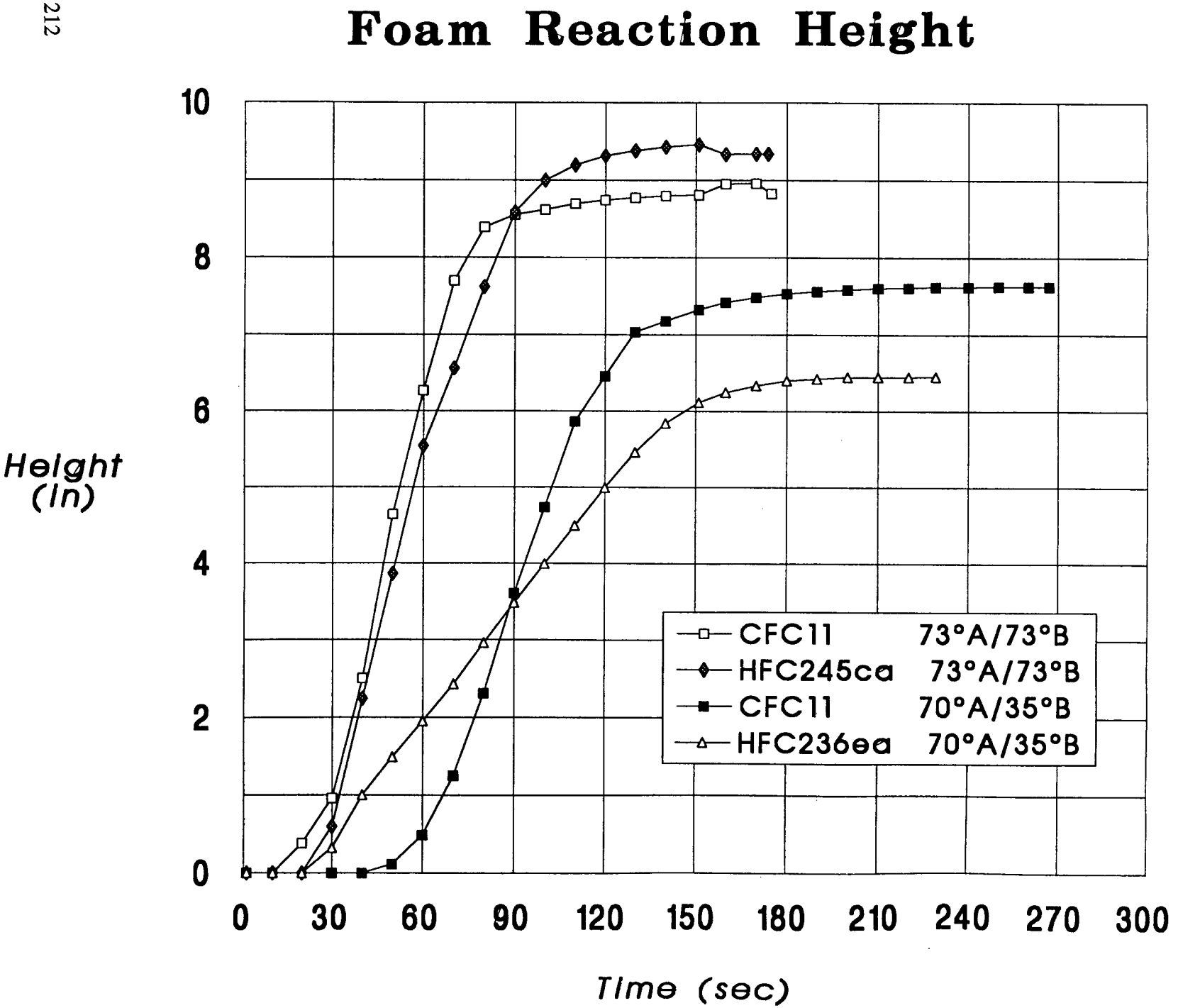

Foam Reaction Height
Height (In)
10
8
6
4
2
0
0
30
60
90
120
150
180
210
240
270
300
Time (sec)
CFC11 73°A/73°B
HFC245ca 73°A/73°B
CFC11 70°A/35°B
HFC236ea 70°A/35°B

Figure 3. CFC-11 foam cell structure

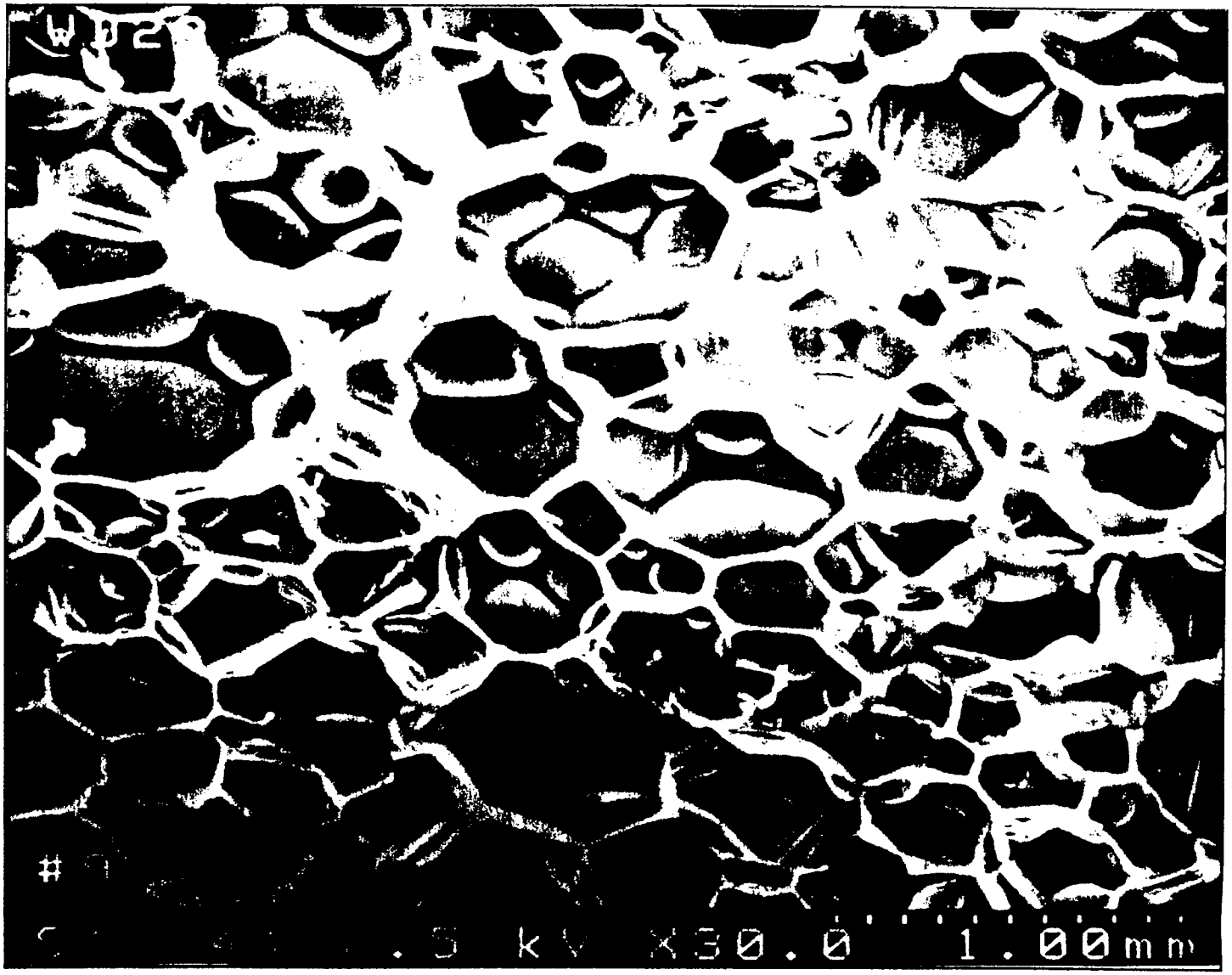
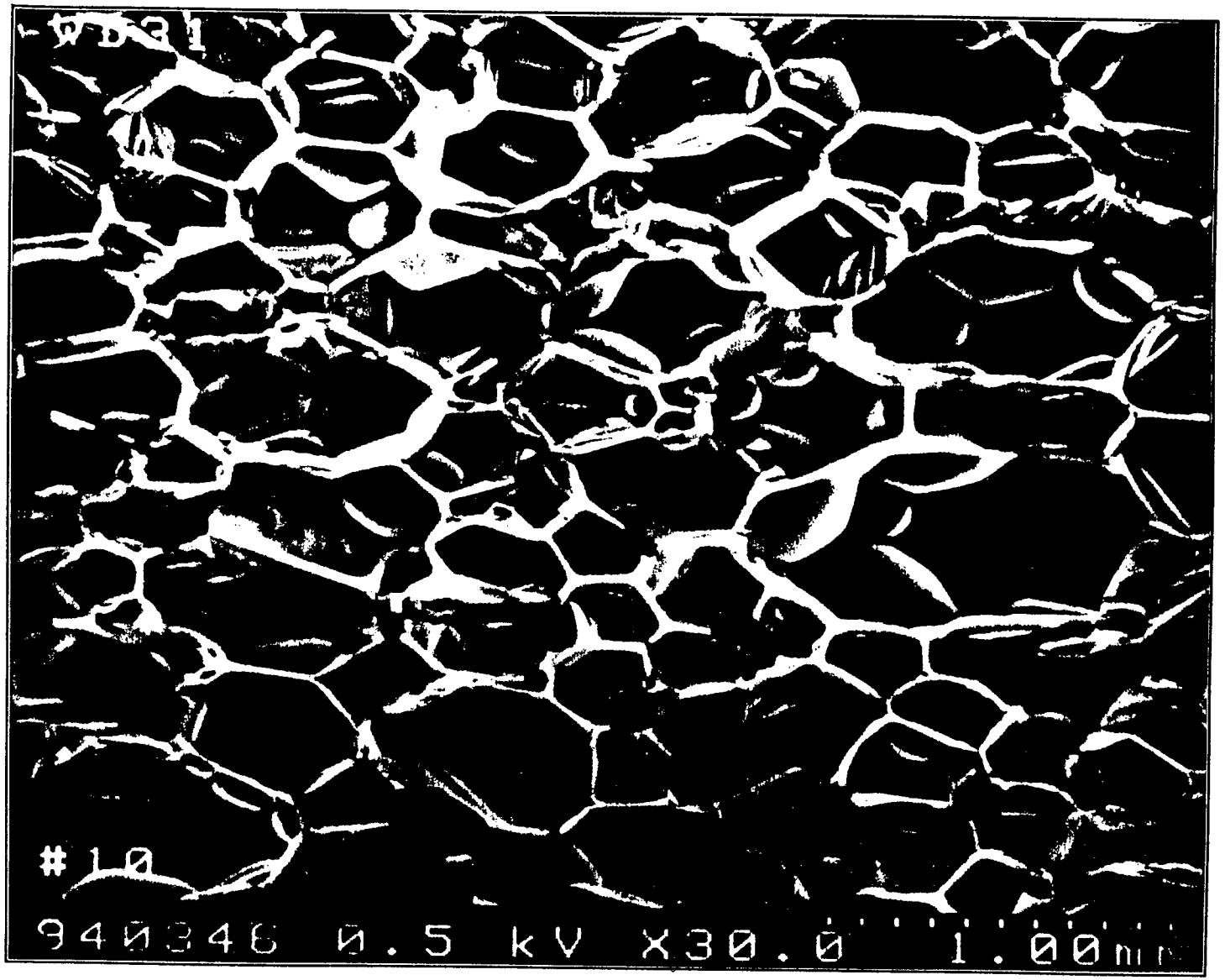


Figure 4. HFC-245ca foam cell structure



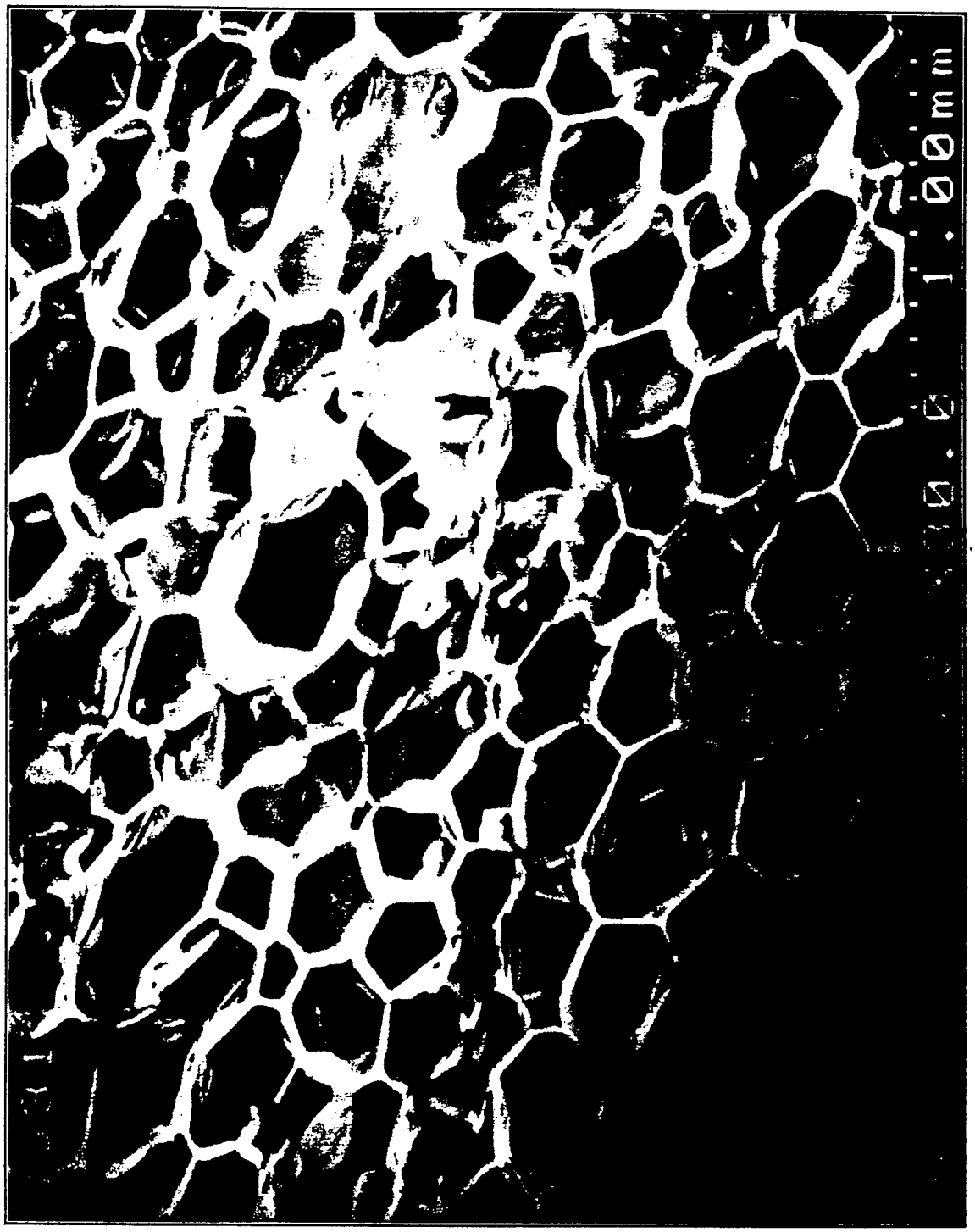


Figure 5. HFC-236ea foam cell structure

Closed Mold Foam Properties

Closed mold test panels were also prepared with each of the three foam systems. These test panels consisted of a 14x24x2 in. mold into which a 0.125 in. thick aluminum test panel was placed for evaluation of foam adhesion characteristics. Mold/panel temperatures of 72°F and 115°F were evaluated. Table 5 presents the results of the panels prepared with a mold and panel temperature of 72°F.

Table 5. Closed Mold Foam Properties, 72°F Mold and Panel Temperature

Property	CFC-11	HFC-245ca	HFC-236 ea
Core Density, lb/ft^3	2.10	1.95	2.12
Compressive Strength, lb/in^2	17	15	21
Bond Tensile Strength* (ambient), lb/in^2	42	46	40
Bond Tensile Strength (-320°F), lb/in^2	42	37	13
Bond Tensile Strength (200°F), lb/in^2	27	28	17
Flatwise Tensile Strength ** (ambient), lb/in^2	39	44	47
Friability, % mass loss	2.5	1.7	1.8

* Test of foam adhesion to aluminum substrate
** Cohesive strength of the foam, parallel to rise

The cohesive strength of the three materials was comparable, with the HFC-245ca and HFC-236ea actually exhibiting slightly higher values than the CFC-11 control. Bond adhesion values to an aluminum substrate were also comparable when tested at ambient temperature; however, the HFC-245ca exhibited a coarse, high density layer approximately 1/8-in. thick adjacent to the aluminum substrate. Approximately 65% of the specimens failed in this region. Almost all of the HFC-236ea foam ambient tensile specimens failed at the substrate interface, leaving a thin polymer residue on the substrate surface. This characteristic is probably due to the short cream time and resulting poor wetting of the substrate with this lower boiling blowing agent. Further formulation development could probably overcome this issue. When tested at low (-320°F) and elevated (200°F) temperatures, the bond adhesion of the HFC-245ca compared favorably to CFC-11, while the HFC-236ea foam suffered a significant loss of adhesion.

Because the HFC-245ca foam samples prepared at 72°F mold and panel temperature exhibited a coarse, high density layer adjacent to the substrate, it was suspected that the heat sink effect of the aluminum panel contributed to this high density layer. Increased mold and panel temperature panels were prepared in an attempt to resolve this issue. Results of the testing performed at 115°F mold and panel temperature, presented in Table 6, did not support this hypothesis. Bond adhesion of all three foams was significantly lower than those prepared at 72°F mold and panel temperature. The flatwise tensile strength of the CFC-11 and the HFC-245ca prepared at 115°F was comparable to the values obtained from panels prepared at 72°F. The HFC-236ea, however, suffered a significant loss of both flatwise tensile strength and bond adhesion. Apparent closed cell content of these foam samples was also determined. The CFC-11 and HFC-245ca, while somewhat lower than optimum, were comparable at approximately 88%. The closed cell content of the HFC-236ea foam could not be determined due to drift in the air pycnometer. This would indicate that this foam has very permeable cell walls or widely distributed ruptured cells/open cell structure. More development work to optimize both the formulation and the application process could help overcome these issues.

Table 6. Closed Mold Foam Properties, 115°F Mold and Panel Temperature

Property	CFC-11	HFC-245ca	HFC-236ea
Density, lb/ ft^3	1.9	1.8	1.8
Compressive Strength, lb/in^2	17	19	21
Bond Tensile Strength* (ambient), lb/in^2	13	14	30
Flatwise Tensile Strength, lb/in^2	44	47	28
Closed Cell Content, %	88	88	ND**
Limiting Oxygen Index, % O_2	21	19	19

* Test of foam adhesion to aluminum substrate
** No data

THERMAL AND AGING CHARACTERISTICS

Thermal conductivity of molded panels (k) was also determined, both in the laboratory and independently by Oak Ridge National Laboratory (ORNL).

Thermal conductivity of molded foam samples was performed in the foam laboratory using an Anacon TCA 8 thermal conductivity analyzer. Results of this testing are presented in Figure 6. These data indicate that both the HFC-245ca and the HFC-236ea had initial thermal conductivities approximately 24% higher than CFC-11 (0.149 Btu-in/hr-ft^2-°F versus 0.120 Btu-in/hr-ft^2-°F). In these samples, the HFC-245ca appeared to be aging at a similar rate to CFC-11 while the HFC-236ea appeared to age much faster.

Molded panels were supplied to ORNL for determination of apparent thermal conductivity and a preliminary assessment of aging characteristics. For determination of apparent thermal conductivity and accelerated aging, the technique used by ORNL involves determination of thermal conductivity of a single full thickness test panel and, separately, determination of thermal conductivity of a stack of thin (3/8-in.) core slices from four panels. These test values are typically plotted as natural logarithm of 100 times the conductivity (1n 100k) versus the square root of the aging time divided by the foam thickness. This results in linear regions with respect to foam age that can be useful in forecasting long term performance. In the model ORNL has developed, the full thickness test panel results typically compare closely to the thin slice results.

Test results from the foam panels prepared for this study are shown in Figures 7 through 9. Each graph shows results of both the full thickness panel tests and the stacked thin slice tests. The full thickness and stacked thin slice values tracked very well for both the HFC-245ca and HFC-236ea, but the CFC-11 full thickness panel results did not compare well to the thin slice results. Inspection of the CFC-11 full thickness panel revealed that it had a coarse, non-uniform cell structure and was probably not representative of actual material performance. This observation is being confirmed with additional testing. Thus, for the CFC-11, the thin slice data are believed to be a better basis for comparison. With this disparity in mind, a cursory relative comparison of the trend between the CFC-11 thin slices and the HFC-245ca and HFC-236ea data can be made.

The thin sliced CFC-11 panels had an initial thermal conductivity of 0.1251 Btu-in/hr-ft^2°F, increasing to 0.1583 Btu-in/hr-ft^2°F after 64 days of aging. The HFC-245ca thick panel exhibited an initial k-value of 0.1453 Btu-in/hr-ft^2°F, which increased to 0.1522 Btu-in/hr-ft^2°F after 43 days of aging. The initial k-value of the thick HFC-245ca panel and the thin sliced panels differed by 2%. Overall, the HFC-245ca foam aging trend appeared to parallel that of the CFC-11 foam, but with values averaging 20% higher than those of the CFC-11 foam.

Figure 6.

Thermal Conductivity vs Foam Age

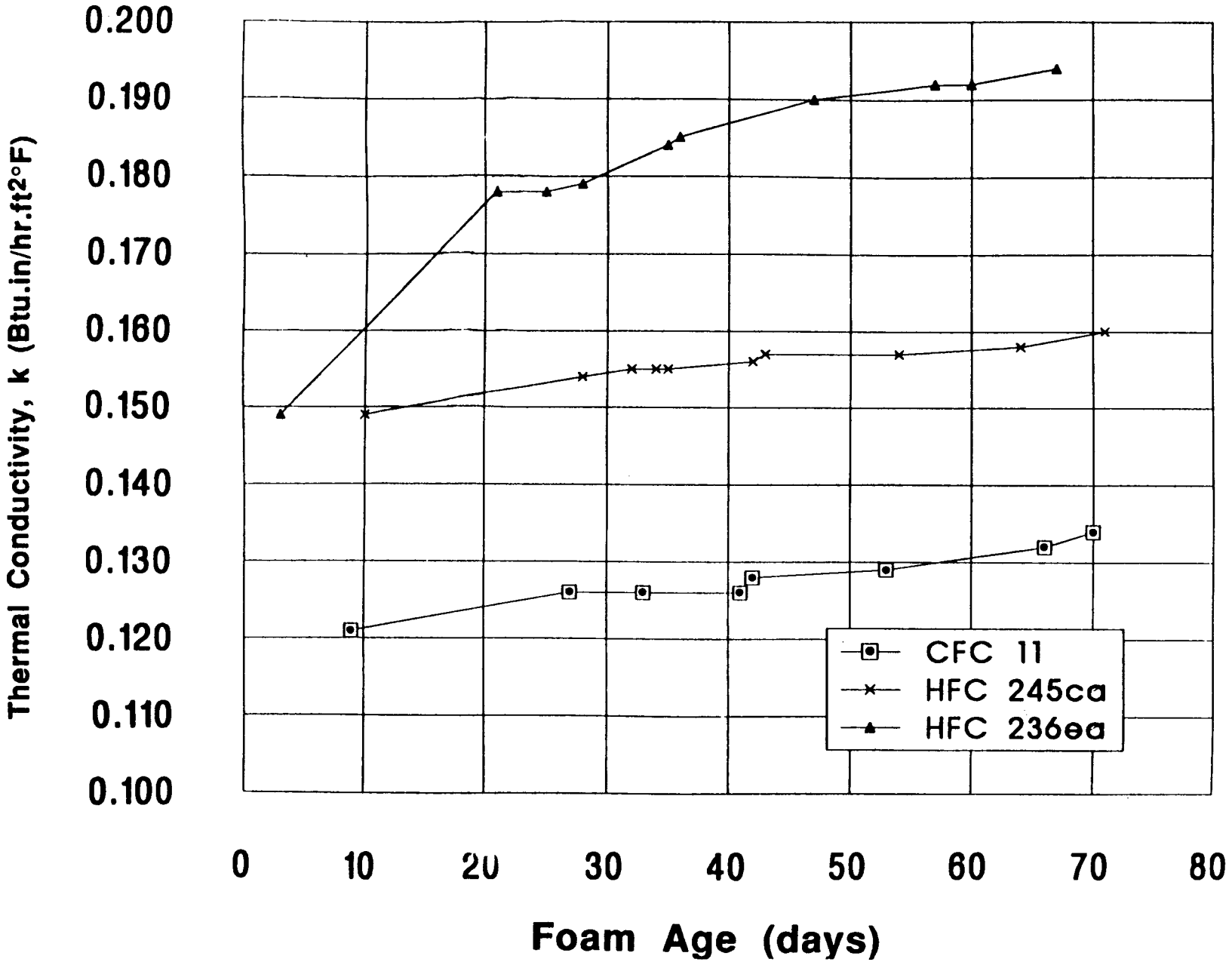


Figure 7. CFC-11 Foam Aging Trend.

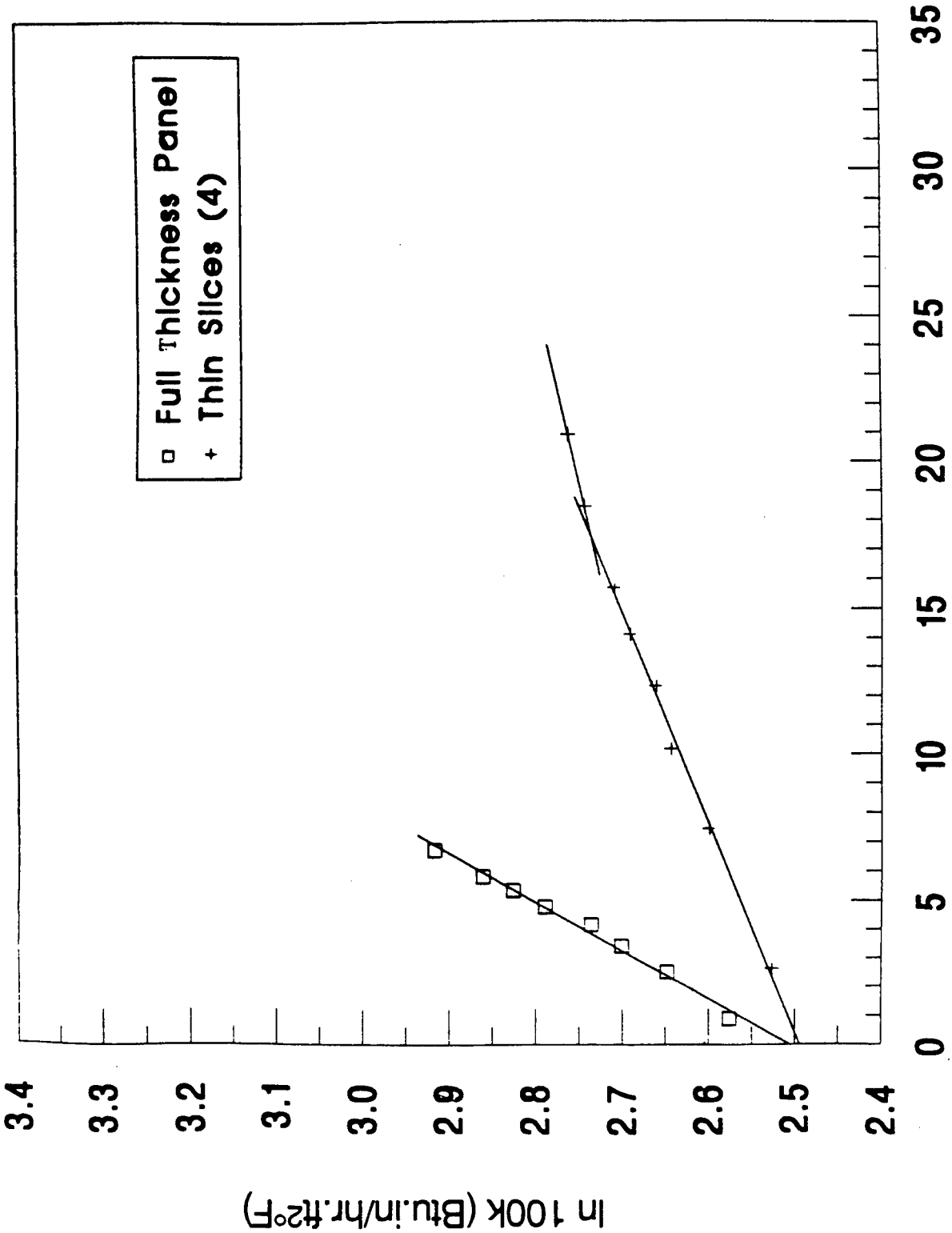
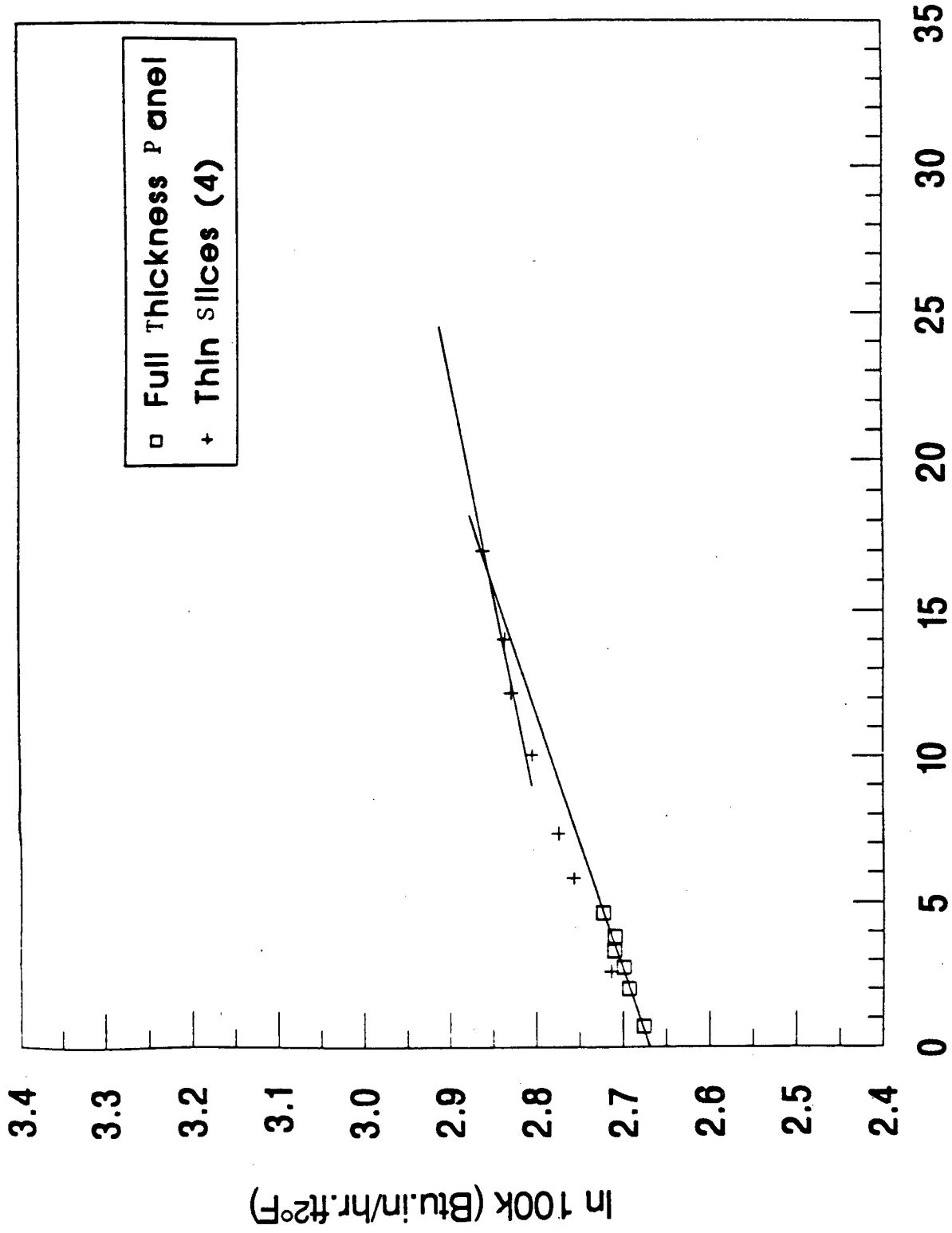


Figure 8. HFC-245ca Foam Aging Trend.



3. Smith, N. D., "New Chemical Alternatives for CFCs and HCFCs," EPA-600/F-92-012, March 1992.

4. Knopeck, G.M., R. C. Parker, R. G. Richard, and I. R. Shankland, "Evaluation of Next Generation Blowing Agents," *Polyurethanes World Congress 1993*, p. 465.

CONVERSION TABLE

British	Multiplied By	Yields Metric
°F	5/9 (°F-32)	°C
in.	0.0254	cm
lb/ft^3	16.02	kg/m^3
lb/in^2	0.0703	g/cm^2
Btu/lb-mol	2.325	J/g-mol
Btu-in/hr-ft^2-°F	0.1442	W-cm/m^2- °C

BIOGRAPHIES

Ron Graves is a research staff member in the Materials Thermal Analyses Group at the Oak Ridge National Laboratory working in the field of energy conservation materials. He attended the University of Tennessee prior to joining ORNL in 1958. He is a member of the American Society for Testing and Materials and is a Fellow in the International Thermal Conductivity Conference. Ron has done research on building insulations for about 16 years and is author or coauthor on numerous papers and reports on the testing and properties of thermal insulations.

Robert V. Hendriks received his B.S. degree in Pulp and Paper Technology from N.C. State University, M.S. degree in Chemical Engineering from Clemson University, and M.B.A. degree from Duke University. He is a Senior Research Engineer with the Environmental Protection Agency, Air and Energy Engineering Research Laboratory in Research Triangle Park, N.C. His current responsibilities involve development of environmentally acceptable alternative refrigerants and foam blowing agents.

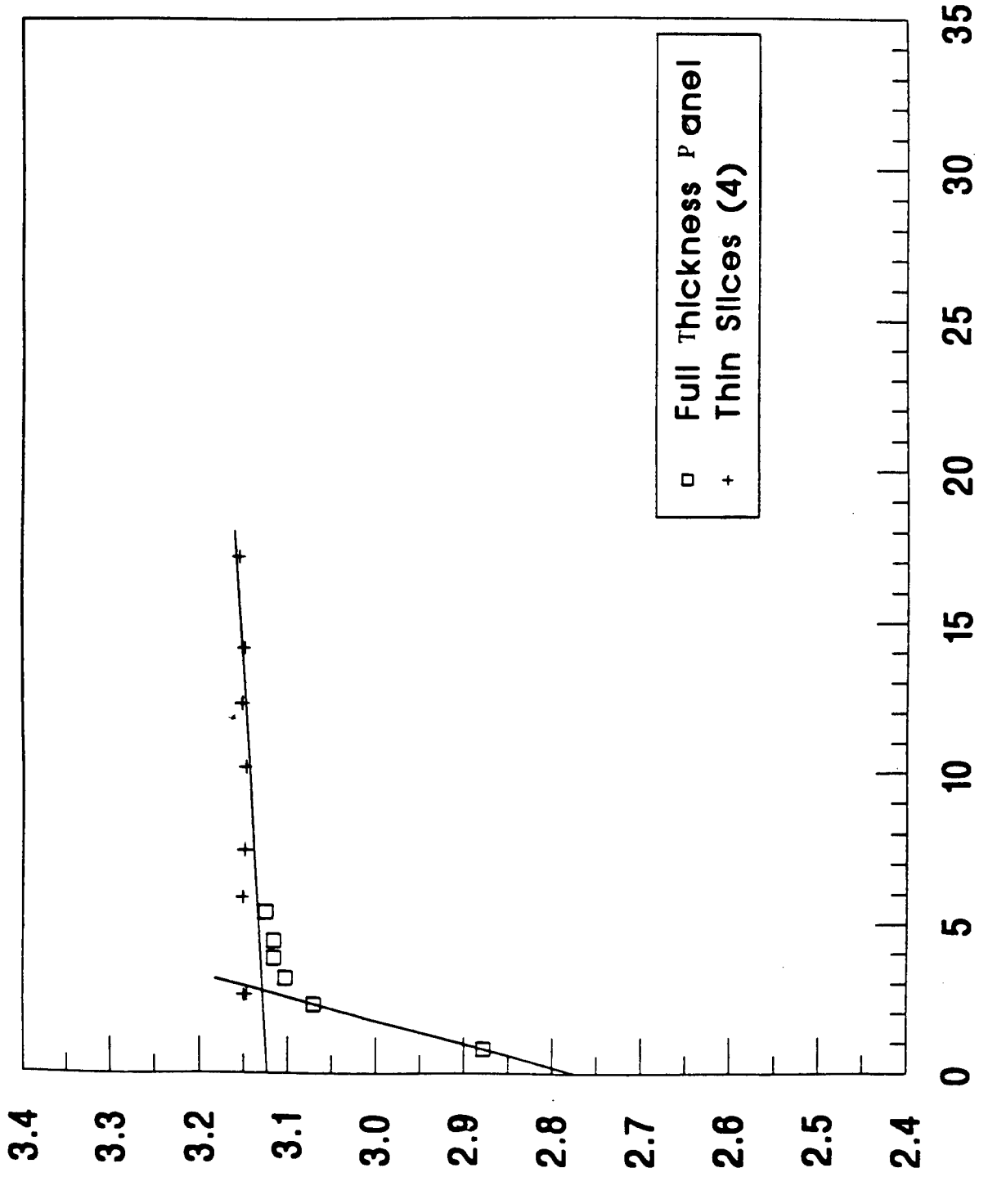
Tom Kollie is the Group Leader of the Materials Thermal Analyses Group at the Oak Ridge National Laboratory. The Group measures and analyzes heat transport in materials. Tom received his M.S. and Ph.D. degrees in Metallurgical Engineering from the University of Tennessee in 1965 and 1969, respectively, and a B.S. in Ceramic Engineering from the Georgia Institute of Technology in 1959. He is a member of ASTM and ASM International. For the past 35 years, Tom has performed research and development on physical properties of materials, thermometry, alloy development, and advanced thermal insulations.

Matthew Liu is a staff Material Scientist with Martin Marietta in New Orleans, Louisiana, where he has been employed since 1975. His educational background is in Polymer Science from the University of Akron in Ohio. His professional interest is in the development of materials, including foams, coatings, primers, and adhesives. Matt is the co-author of several papers and patents and is currently involved in zero ODP blowing agent development and PU/PIR foam catalyst system investigation for cryogenic applications.

Doug MacArthur graduated from Eastern Michigan University in 1965 with a B.S. in Biology. Since 1967 he has held various technical positions in the polyurethane industry in the United States, Australia, and Canada. In 1983 he joined Martin Marietta. He is currently responsible for developing zero ODP blowing agent foam systems for use on the External Tank of the Space Shuttle at the Marshall Space Flight Center in Huntsville, Alabama.

Jon Sharpe received his B.S. degree in Chemical Engineering from the University of Alabama and M.S. degree in Engineering Management from Florida Institute of Technology. He is Manager of Development and Test Engineering at Martin Marietta's Marshall Space Flight Center Operations in Huntsville, Alabama. His current responsibilities include development and testing of materials for cryogenic and high heat applications for use on the External Tank of the Space Shuttle.

Figure 9. HFC-236ea Foam Aging Trend.



The HFC-236ea thick panel had an initial k-value of 0.1778 Btu-in/hr-ft^2°F, increasing to 0.2278 Btu-in/hr-ft^2°F, after 43 days of aging. The thin sliced panels appeared to be completely aged at day 1. They exhibited an initial k-value of 0.2333 Btu-in/hr-ft^2°F, increasing to 0.2348 Btu-in/hr-ft^2°F, after 43 days of aging. This would indicate that the HFC-236ea foam had a relatively open cell structure (supported by attempts to determine closed cell content) and/or that the HFC-236ea diffuses quickly from the foam. More studies will help understand and compensate for this characteristic.

CONCLUSIONS

Both HFC-245ca and HFC-236ea have been compared to CFC-11 as blowing agents in a simple, non-optimized urethane formulation. Both materials have been shown to have potential as foam blowing agents should they become commercially viable.

The HFC-245ca foam exhibited similar handling characteristics and reactivity to the CFC-11 control. The boiling point and solubility of this material make it easy to blend and hand pour using conventional techniques. Mechanical and physical properties of the HFC-245ca foam were also comparable to CFC-11 except that the HFC-245ca foam exhibited a coarse, high density layer adjacent to the substrate. Also, the HFC-245ca foam exhibited an initial thermal conductivity approximately 16 to 22% higher than the CFC-11 control. These results indicate that HFC-245ca should be relatively easy to process using conventional equipment, but that changes in formulations may be required to approach equivalent insulation or adhesion characteristics (or other properties) compared to CFC-11 foam.

The HFC-236ea blown foam was somewhat more difficult to prepare due to the lower boiling point of the material and resulting tendency to froth when mixed at ambient conditions. This characteristic resulted in poor wetting and adhesion to the aluminum substrate evaluated in this study. Additionally, the initial thermal conductivity of the foam prepared with HFC-236ea was between 23 and 44% higher than that of CFC-11 and it aged very quickly to a thermal conductivity approximately 50% higher than the CFC-11 foam. These characteristics indicate that considerable more effort will be required to optimize a foam formulation and/or process to achieve satisfactory results with HFC-236ea as the sole blowing agent.

ACKNOWLEDGEMENTS

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REFERENCES

1. Phase-Out of Ozone Depleting Substances, Federal Register 58 FR 65018, 40 CFR Part 82, December 10, 1993.

2. Beyerlein, A. L., D. D. Des Marteau, S. H. Hwang, N. D. Smith, and P. A. Joyner, "Physical Properties of Fluorinated Propane and Butane Derivatives as Alternative Refrigerants," ASHRAE Transactions 1993, v.99, Pt.1.

ALTERNATIVES TO OZONE DEPLETING REFRIGERANTS IN TEST EQUIPMENT

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ABSTRACT

This paper describes the initial results of a refrigerant retrofit project at the Aerospace Guidance and Metrology Center (AGMC) at Newark Air Force Base, Ohio. The objective is to convert selected types of test equipment to properly operate on hydrofluorocarbon (HFC) alternative refrigerants, having no ozone depleting potential, without compromising system reliability or durability. This paper discusses the primary technical issues and summarizes the test results for 17 different types of test equipment: ten environmental chambers, two ultralow temperature freezers, two coolant recirculators, one temperature control unit, one vapor degreaser, and one refrigerant recovery system. The post-conversion performance test results have been very encouraging: system capacity and input power remained virtually unchanged. In some cases, the minimum operating temperature increased by a few degrees as a result of the conversion, but never beyond AGMC's functional requirements.

INTRODUCTION

The repair of aircraft inertial navigation and guidance equipment requires the use of environmental chambers, coolant recirculators, and other types of test equipment which contain refrigeration systems. There are more than 70 different types of test equipment used for processing or evaluating the inertial and navigational devices that are repaired at AGMC. Each type uses at least one of the following refrigerants: R-12, R-13, R-500, R-502, and R-503. All of these refrigerants are classified as stratospheric ozone depleting substances under the Montreal Protocol.[1,2]

This paper describes the interim results of the refrigerant retrofit project at AGMC. The goal is to modify various types of existing test equipment to properly operate on alternative refrigerants that have *no ozone depleting potential* without compromising system reliability or durability. Selecting a replacement refrigerant and lubricant for a given application involves the consideration of several factors including thermodynamic performance (cooling capacity and power consumption), environmental properties, materials compatibility, system reliability and durability, refrigerant and lubricant availability, chemical stability, flammability, and toxicity. Moreover, the equipment conversions must be technically feasible, cost effective, and the converted units must be safe to operate.

At a time when many equipment suppliers are marketing new products using hydrofluorocarbon (HCFC) refrigerants which have low ozone depleting potentials (primarily R-22 and mixtures based on R-22), this project focuses solely on hydrofluorocarbon (HFC) refrigerants that have no ozone depleting potential. This paper describes the technical approach and the primary lessons learned from the conversions completed prior to April 1, 1994.

REFRIGERANTS

CFC Refrigerants

The Montreal Protocol and the subsequent upgrades of this historic international agreement require the near-term phase out of chlorofluorocarbon (CFC) refrigerants including: R-11, R-12, R-113, R-114, and R-115. These same regulations also affect some commercially important azeotropic refrigerant mixtures[3]:

CFC-500	CFC-12 (74 percent) and HFC-152a (26 percent)
CFC-502	HCFC-22 (49 percent) and CFC-115 (51 percent)
CFC-503	HFC-23 (40 percent) and CFC-13 (60 percent).

HFC Refrigerants

The HFC refrigerant that appears to be the best alternative for both R-12 and R-500 in medium-temperature and high-temperature applications is R-134a. The operating pressures and thermodynamic performance of R-134a are very comparable to R-12 in those temperature regimes. Several compressor manufacturers now market hermetic and semi-hermetic compressors made specifically for R-134a.

Some HFC replacements for R-502 are now available commercially. This project has focused on R-404a (more specifically DuPont SUVA® HP62), a near-azeotropic mixture of R-125/143a/134a. DuPont provided sample quantities of SUVA® HP62 for use in this project beginning in July 1993. The properties of R-404a and R-502 are so similar that no significant performance change is expected. However, the higher operating pressures for R-404a has made it necessary to increase the pressure relief valve setting from 325 psig (2.34 kPa absolute) to 350 psig (2.52 kPa absolute).

Refrigerant R-23 has been produced commercially for several years but it has normally been combined with R-13 to create R-503, an azeotropic mixture used in low temperature refrigeration applications. Based upon its thermodynamic properties, R-23 appears to be the best HFC alternative for both R-13 and R-503. The properties of R-23 and R-13 are so similar that no performance change is expected in these cases. However, an increase in the minimum operating temperature is expected when R-23 is substituted for R-503 because there is a 12 F difference in their normal boiling points (-127.6 F [-88.7 C] for R-503 compared to -115.7 F [-82 C] for R-23)[4].

HCFC Refrigerants

The present regulations concerning HCFC refrigerants allow their use in new equipment until the year 2015 and in existing equipment until 2020. However, it is likely that the phase-out schedule for the HCFCs will be accelerated closer to the year 2000.

MATERIALS COMPATIBILITY

The most significant research work on materials compatibility regarding alternative refrigerants and lubricants is being done by a consortium called the Air Conditioning and Refrigeration Technology Institute (ARTI). Richard Ernst presented a summary of ARTI's work at the 1993 ASHRAE/NIST Refrigerants Conference that focused on R-22/R-502[6]. ARTI's scope includes three of the HFC alternative refrigerants listed in Table 1: R-134a, R-125, and R-143a (note that R-404a is a blend of R-125/143a/134a). The remaining alternative refrigerant, R-23, is not included. Refrigerant R-23 has been widely used in refrigerant systems for many years and is known to be comparatively benign from a materials compatibility standpoint.

A summary of the results of ARTI's work regarding compatibility of refrigerants and lubricants with motor materials appeared in a recent journal article[7]. The compatibility of elastomers with refrigerant/lubricant mixtures has also been reported[8]. Like their CFC predecessors, the selected HFC refrigerants and lubricants have little effect on the metals found in refrigerant systems (e.g., iron, steel, aluminum, and brass). The results of ARTI's work provides the primary basis for the position that the alternative refrigerants being retrofitted into AGMC's equipment are as compatible with the materials in the refrigeration systems as the original CFC refrigerants.

CONVERSION STEPS

Procurement of the new refrigerant, lubricant, and all replacement components should be completed prior to starting any conversion. One of the more important decisions is whether or not to replace an existing compressor (or condensing unit). The factors to consider are the age of the compressor relative to its expected life, the condition of the equipment prior to the conversion, the system reliability requirements, and the potential labor cost savings associated with changing out the compressor instead of flushing out the mineral oil using the procedures which follow. In general, nearly all of the hermetic and semi-hermetic compressors encountered thus far at AGMC have been replaced with new units, ones specifically designed for the new refrigerant wherever possible.

The conversion steps applied in this project are based on inputs from several sources[9,10,11]. The major steps for converting each refrigerant circuit are as follows:

1. Recover the CFC refrigerants using EPA-approved equipment.

2. Change out the compressor (if appropriate) and other circuit components (such as relief valves or liquid receivers). Thoroughly drain the lubricant from the compressor, suction accumulator, and other potential collection points.

3. Install a fresh charge of polyol ester oil into the compressor. Replace the filter-drier. Evacuate the circuit to 250 microns maximum, and re-charge the system with the original CFC refrigerant (unless the CFC refrigerant quality had been compromised by a motor burn-out or other event).

4. Run the compressor for at least 4 hours (24 hours is preferable) to allow residual mineral oil to collect in the compressor's sump.

5. Recover the CFC refrigerants, thoroughly drain the oil, and test for residual mineral oil (using a test kit or a refractometer).

6. Repeat Steps 3 through 5 two more times to flush out the residual mineral oil so that there is no more than about 1 percent mineral oil in the circuits.

7. Pressurize the system to 150 psig (1.14 kPa absolute) with dry nitrogen and monitor pressure decay for at least one hour to test for leaks.

8. Evacuate the circuit to 400 microns static vacuum as a preliminary step. Release the vacuum and quickly change the filter-drier and install a fresh charge of polyol ester oil.

9. Evacuate the circuit to 150 microns static vacuum maximum and then charge the circuit with the HFC replacement refrigerant.

10. Operate the unit at steady-state conditions and adjust the refrigerant charges and the thermostatic expansion valves as required.

11. Change the placards to clearly indicate the new refrigerant and oil charges.

The above basic steps are modified as appropriate to suit each different type of test equipment.

STATUS SUMMARY

Prior to April 1, 1994, one sample of 17 different types of test equipment have been converted and functionally tested to validate the changes (Table 2). Included on this list are ten environmental chambers, two ultralow temperature freezer, two coolant recirculators, one specially-built temperature control unit, one vapor degreaser, and one refrigerant recovery system.

The post-conversion performance test results have been very encouraging. In most cases, the minimum set point temperature increased by a few degrees as a result of the conversion, but never beyond the functional requirements. For example, the minimum set point on one environmental chamber increased from -73 C (-99 F) to -71 C (-96 F) which still satisfies the -65 C (-85 F) requirement for this particular equipment type.

CONCLUSIONS

The primary conclusions drawn from the work consist of the following:

- Suitable HFC alternatives for CFC refrigerants are commercially available.
- The HFC alternative refrigerants are not "drop-in" replacements but the measured performance changes have been small. Replacing R-23 for R-503 creates the largest difference—the minimum operating temperature increases by about 12 F (7 C).
- Lubricant producers have developed polyol ester lubricants which appear to meet the system requirements in terms of miscibility, lubricity, and materials compatibility.
- Compressor manufacturers are developing a data base on many alternative refrigerant/lubricant combinations.
- Suitable filter-driers and other refrigerant system components are currently available.

Table 2. Refrigerant Conversion Experience at Newark Air Force Base

Equipment Manufacturer	Part Number	Equipment Description	CFC Refrigerants	HFC Refrigerants	Minimum Temperature
Thermotron	WP-666	Environmental Chamber	R-502	R-404a	-30 F (-22 C)
Thermotron	S-32	Environmental Chamber	R-502/R-13	R-404a/R-23	-90 F (-68 C)
Thermotron	S-4	Environmental Chamber	R-502/R-13	R-404a/R-23	-100 F (-73 C)
Russells Technical Products	RB4-1-1	Environmental Chamber	R-502/R-13	R-404a/R-23	-100 F (-73C)
Standard Environmental Systems	TK/5	Environmental Chamber	R-502/R-503	R-404a/R-23	-96 F (-71 C)
Tenney	TTC	Environmental Chamber	R-502/R-503	R-404a/R-23	-100 F (-73 C)
Tenney	T5-100350	Environmental Chamber	R-502/R-503	R-404a/R-23	-100 F (-73 C)
Tenney	TJR	Environmental Chamber	R-12/R-503	R-134a/R-23	-112 F (-80 C)
BMA	TM-5CC	Environmental Chamber	R-502/R-503	R-404a/R-23	-98 F (-72 C)
Bemco	F100/350-8	Environmental Chamber	R-502/R-13	R-404a/R-23	-100 F (-73 C)
Revco	ULT390	Ultralow Temperature Freezer	R-500/R-503	R-134a/R-23	-123 F (-86 C)
So-Low Environmental Equipment	A13-120	Ultralow Temperature Freezer	R-502/R-13	R-404a/R-23	-105 F (-76 C)
Northrop	113050	Coolant Recirculator	R-12	R-134a	Not Applicable
Electro Impulse	30324	Temperature Control Unit	R-12	R-134a	Not Applicable
Neslab	CFT75	Coolant Recirculator	R-12	R-134a	Not Applicable
Branson	B250R	Vapor Degreaser	R-12	R-134a	Not Applicable
Redi/Controls	RRS-503/13	Refrigerant Recovery Unit	R-502	R-404a	Not Applicable

REFERENCES

[1] United Nations Environment Programme (UNEP), "*Montreal Protocol on Substances That Deplete the Ozone Layer - Final Act*," 1987.

[2] "*Montreal Protocol Revised in Copenhagen*," ASHRAE Journal, February, 1993, p. 14.

[3] ANSI/ASHRAE 34-1993, *Number Designation and Safety Classification of Refrigerants*, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, Georgia, 1993.

[4] "*1993 ASHRAE Fundamentals Handbook*," Chapter 16—Refrigerants, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, Georgia, 1993, p. 16.4.

[5] Salas, C. E., and Salas, M., Guide to Refrigeration CFC's, The Fairmont Press, 1992, p. 58.

[6] M. Menzer and D. Godwin, "Results of Compressor Calorimeter Tests in (ARI's) R-22 Alternative Refrigerants Evaluation Program," presented at the *ASHRAE/NIST Refrigerants Conference focused on R-22/R-502* held in Gaithersburg, Maryland on August 19-20, 1993.

[7] R. G. Doerr and S. A. Kujak, *Compatibility of Refrigerants and Lubricants with Motor Materials*, ASHRAE Journal, August, 1993, p. 42-47.

[8] G. R. Hamed and R. H. Seiple, *Compatibility of Elastomers with Refrigerant/Lubricant Mixtures*, ASHRAE Journal, August, 1993, p. 173-176.

[9] *Castrol Retrofill Procedure*, as described in Castrol's sales literature for "Castrol Icematic SW Synthetic Ester Lubricants," Castrol, Inc., Irvine, California, 1993.

[10] *Refrigerant Changeover Guidelines, CFC-12 to HFC-134a*, Copeland Corporation, Sidney, Ohio, 1993.

[11] *Guidelines for Utilization of R-134a*, Tecumseh Products Company, Tecumseh, Michigan, 1993.

ENVIRONMENTALLY SAFE AVIATION FUELS

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ABSTRACT

In response to the Air Force directive to remove Ozone Depleting Chemicals (ODCs) from military specifications and Defense Logistics Agency's Hazardous Waste Minimization Program, we are faced with how to ensure a quality aviation fuel without using such chemicals. Many of these chemicals are found throughout the fuel and fuel related military specifications and are part of test methods that help qualify the properties and quality of the fuels before they are procured. Many years ago there was a directive for military specifications to use commercially standard test methods in order to provide standard testing in private industry and government. As a result the test methods used in military specifications are governed by the American Society of Testing and Materials (ASTM). The Air Force has been very proactive in the removal or replacement of the ODCs and hazardous materials in these test methods. For example, ASTM D3703 (Standard Test Method for Peroxide Number of Aviation Turbine Fuels), requires the use of Freon 113, a known ODC. A new rapid, portable hydroperoxide test for jet fuels similar to ASTM D3703 that does not require the use of ODCs has been developed. This test has proved, in limited testing, to be a viable substitute method for ASTM D3703. The Air Force is currently conducting a round robin to allow the method to be accepted by ASTM and therefor replace the current method. This paper will describe the Air Force's initiatives to remove ODCs and hazardous materials from the fuel and fuel related military specifications that the Air Force Wright Laboratory.

INTRODUCTION

The 1990 Clean Air Act Amendments requires phasing out the domestic use of Ozone Depleting Chemicals (ODCs) by 1995. Section 326 of the National Defense Authorization Act of Fiscal Year 1993 mandates the Department of Defense (DoD) to stop requiring the use of ODCs within specifications and standards in contracts awarded after 1 June 1993. Air Force personnel were also directed by the Secretary of the Air Force and Chief of Staff to review all standards, specifications, and engineering handbooks for required use of materials identified by the EPA as Hazardous/Toxic (HAZTOX) and ODCs. The HAZTOX materials are better known as the 17 chemicals of the EPA's 33/50 source reduction program as listed in Table 1 [1].

As the preparing activity and technical focal point of the Air Force fuel and fuel related material specifications (listed on Table 2), the Fuels Branch of Wright Laboratory's Aero Propulsion and Power Directorate has been looking at alternatives to the ODCs and HAZTOX materials. There have been several programs initiated in order to allow the procurement of quality and environmentally safe fuels.

Table 1: EPA's 17 Chemical Groups

Benzene	Cadmium and Compounds
Carbon Tetrachloride	Chloroform
Chromium and Compounds	Cyanides
Lead and Compounds	Mercury and Compounds
Methylene Chloride	Methyl Ethyl Ketone
Methyl Isobutyl Ketone	Nickel and Compounds
Trichloroethane	Toluene
Tetrachloroethane	Trichloroethylene
Xylenes	

Table 2: WL/POSF Specifications

Number	Title	Latest Revision
MIL-T-5624P	Aviation Turbine Fuel, Grades JP-4, JP-5, and JP-5/JP-8 ST	29 Sep 92
MIL-I-25017E	Fuel Soluble Corrosion Inhibitor/Lubricity Improver	15 Jun 89
QPL-25017-17 Amendment 1	Qualified Products List for Fuel Soluble Corrosion Inhibitor/Lubricity Improver	24 Mar 94
MIL-T-25524D	Thermally Stable Aviation Turbine Fuel	8 Apr 94
MIL-P-25576C Amendment 2	Kerosene Propellant, RP-1	1 Mar 82
MIL-I-27686F	Fuel System Icing Inhibitor	10 Jun 91
MIL-T-38219B	Low Volatility Turbine Fuel, JP-7	1 Mar 85
MIL-T-83133D	Kerosene Types Aviation Turbine Fuels NATO F-34 (JP-8) and NATO F-35	29 Jan 92
MIL-P-87107C	High Density Synthetic Hydrocarbon Type Propellant, Grade JP-10	21 Feb 89
MIL-P-87173A	ALCM Engine Priming Fluid Propellant, Grade PF-1	23 Jun 89

BODY

The aviation fuels required by the military services are procured by the Defense Fuel Supply Center (DFSC) of the Defense Logistic Agency (DLA) using military specifications that require the fuel to meet certain property standards. The Fuels Branch of Wright Laboratory (WL/POSF) is the preparing activity of these specifications. The fuel quality results from it's properties and through proper handling of the fuel. The properties are monitored through many standardized test methods listed on the military specification. In the past, Federal Test Methods were developed to evaluate fuels. In order to obtain cost reduction and create standardization between military and commercial jet fuels, there has been a transition away from Federal Test Methods to commercial test methods, in particular, test methods standardized by the American Society for Testing and Materials (ASTM). Additives required in military aviation fuels are also monitored by commercial test methods governed by ASTM.

Some of the test methods used in the military specifications require the use of ODCs. With the enactment of the 1990 Clean Air Act Amendments and Section 326 of the National Defense Authorization Act of Fiscal Year 1993 the Air Force was faced with the immediate removal of ODCs from the fuel specifications. Unfortunately the Air

Force has only one vote in ASTM and removal of the ODCs would not occur before June 1993. DLA received an ODC waiver until 1 December 1993. Private industry has until 1995 to phase out Class I ODCs. In order to comply with the regulations, DLA will not require the use of ODCs when buying military items from the manufacturer. If the manufacturer decides to use ODCs during production then it is their responsibility to phase the ODCs out of their manufacturing process by 1995 in order to comply with the law. DLA is using the same interpretation to the American Society of Testing and Materials (ASTM) test methods that are listed in the fuel specifications. They regard the commercial test methods as a commercially packaged test method. The government can not unilaterally change these commercial methods. If ASTM requires the use of an ODC, they must phase the ODC out by 1995 in order to comply with the law. This alleviates the immediate ODC problems for DLA using the ASTM test methods [2]. The Air Force has taken a different position concerning this matter. The Air Force will not allow the use of any Class I ODC as of 1 December 1993. So, even though DLA will buy items from industry that use ODCs during their manufacturing, the Air Force will not be allowed to test their quality using any Class I ODCs. In summary, the Air Force policy on ODCs, regardless that they were part of commercial test methods, is to remove them as soon as possible.

As preparing activity, WL/POSF reviewed all of their fuel and fuel related specifications, the test methods, and the fuel additives to determine which required the use of ODCs. Five test methods which were included in nine military specifications were found to contain ODCs. All of the test methods were governed by ASTM and are listed in Table 3. The Fuels Branch wrote a letter to ASTM detailing the Air Force position and suggesting the removal of ODCs from their test methods. In the subsequent meetings of the committees governing the test method WL/POSF personnel have been representing the Air Force and working with ASTM to remove the ODCs.

Table 3: Test Methods Containing ODCs

TEST METHOD	METHOD TITLE
ASTM D2276	Standard Test Method for Particulate Contamination in Aviation Fuel by Line Sampling
ASTM D3703	Standard Test Method for Peroxide Number of Aviation Turbine Fuels
ASTM D4306	Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
ASTM D4308	Standard Test Method for Electrical Conductivity of Liquid Hydrocarbons by Precision Meter
ASTM D5452	Standard Test Method for Particulate Contamination of Aviation Fuels by Laboratory Filtration

The Air Force and ASTM efforts have been very successful. Currently the ODC, freon, which was used as a flushing fluid has been removed from ASTM D2276 [3] and D5452 [4] and petroleum ether is the current approved replacement. A task force is currently looking for a replacement to freon, which is used as a cleaning solvent, in ASTM D4306 [5]. Freon, also used as a cleaning solvent, has been removed from ASTM D4308 [5] and substituted with either a toluene/isopropyl alcohol mixture or n-heptane.

The final ODC that needed to be removed from the military specifications was in the peroxide test. The determination of peroxide number is very important for aviation fuel, especially fuel that has been in storage for more than six months. Peroxides can lead

to gums and deposits that clog fuel nozzles and degrade engine components. A new, rapid, portable hydroperoxide test for jet fuels, similar to ASTM D3703 [5], that does not require the use of ODCs has been developed by the University of Dayton Research Institute (UDRI), sponsored by WL/POSF. The Peroxide in Fuel Estimation and Concentration Test, called PERFECT, is a rapid, portable method suitable for laboratory use or in remote areas. It was developed to determine the hydroperoxide content of stored and transported fuels. It uses a voltammetric based detection system with a solid probe. The PERFECT also reduces sample size by 90%, reduces laboratory waste by 95%, and can analyze samples twelve times faster than the old method [6]. As preparing activity of the aviation jet fuel specifications, WL/POSF has established a team of Air Force, Army, Navy, Defense Fuel Supply Center, and industry personnel to expedite development of the new environmentally safe peroxide test into an industry accepted test method to be used in both military and commercial aviation jet fuel specifications. To prove this technology, a preliminary round robin was completed in April 1994 and resulting data presented to the Coordinating Research Council Aviation Fuel Committee meeting in April. The test results were well received and has resulted in many inquiries about standardizing this test method for commercial diesel fuels as well as aviation turbine fuels. In June 1994, WL/POSF managed a larger round robin test program that included ten different military and commercial laboratories testing both diesel and aviation fuel samples. The purpose of this test was to prove the technology of the test method and provide ASTM with the data needed for ASTM approval. The test data was well received by the ASTM committees and the new method is currently being balloted to become an ASTM standard test method. WL/POSF is currently revising the military specification for aviation fuel, JP-5, to require the use of the PERFECT test method thus eliminating the use of ODCs.

Although the timely removal of ODCs from military specifications have been first priority, there are other environmental concerns, like the EPA 33/50 program. Currently this has been a voluntary program for industry to reduce national pollution releases and off site transfer of 33% in 1992 and 50% in 1995 of the chemical groups listed in Table 1 [1]. DLA has adopted the EPA's 33/50 source reduction program under the Defense Logistics Agency's Hazardous Waste Minimization Program. The objectives of the program are to reduce the generation of hazardous waste by reviewing and revising military specifications to prevent hazardous waste generation [7]. Air Force personnel were also directed by the Secretary of the Air Force and Chief of Staff to reduce the use of hazardous materials in the operation of our weapons systems and on our bases [8]. As a result of these directives, the Fuels Branch has been working with DFSC and ASTM to reduce and possibly remove these chemicals from military specifications and test methods. DFSC has created a data base of all the chemicals required by all of the specifications used to procure aviation turbine fuels. The data base has been a very valuable tool in determining which test methods and specifications need to be reviewed for possible hazardous materials. WL/POSF has been working with ASTM to develop possible replacements for some of the hazardous materials. In particular, toluene is used in many test methods. It has been proposed for some tests a 50/50 mixture of heptane and isopropanol may be used as a replacement. Additive manufacturers whose additives contain chemicals listed on the EPA's Chemical List have been contacted to look at potential alternate formulations for their additives. The Fuels Branch is also sponsoring a non toxic fuel system icing inhibitor (FSII) program, which is trying to replace the current FSII, diethylene glycol monomethyl ether, with a non toxic additive.

There still remains questions concerning the guidance the Fuels Branch has been given regarding the EPA 17 Chemicals. It is a Air Force Materiel Command (AFMC)

goal to reduce them by 50% before 31 December 1996 and to near zero by 31 December 1999, using 1992 baseline. The top five chemicals, Methylene Chloride, Perchloroethylene, Methyl Ethyl Ketone, Trichloroethane, and MIBK make up 90% of the EPA-17 purchased by AFMC in 1992 [9]. As mentioned, ASTM and the Fuels Branch are looking at alternatives but no mandates have been made. Once specific goals concerning specifications have been established the Fuels Branch, utilizing DFSC's data base will respond.

CONCLUSIONS

Removal of ODCs from military fuel and fuel related specifications has been first priority for the Fuels Branch of Wright Laboratory. Working with ASTM, many of the ODCs have been removed. The D4306 test method that still requires an ODC is being studied for replacements. The new peroxide test method has been successfully tested and is currently replacing the old test method that utilizes ODCs. It is envisioned that it will become an industry standard.

Although the Fuels Branch has not been mandated to remove the EPA-17 Chemicals from the specifications and test methods, potential substitutes are currently being considered. Environmentally friendly additives are being developed for fuels. ASTM and DFSC have shown great cooperation and commitment to help in the removal of these chemicals.

REFERENCES

[1] "The 33/50 Program: Forging an Alliance for Pollution Prevention", United States Environmental Protection Agency, August 1992.

[2] DoD Coordination Meeting on the Removal of Ozone Depleting Chemicals from Military Specifications/Standards, Alexandria, VA, November 1993.

[3] "1994 Annual Book of ASTM Standards," Vol. 05.01, 1994.

[4] "1994 Annual Book of ASTM Standards," Vol. 05.03, 1994.

[5] "1994 Annual Book of ASTM Standards," Vol. 05.02, 1994.

[6] Kauffman, Robert E., "Development of a Rapid, Portable Hydroperoxide Test for Jet Fuels," American Chemical Society, San Diego, CA, March 1994.

[7] DGSC letter "DLA Hazardous Waste Minimization Program - Review and Revision of Specifications and Standards", dated 17 November 1988.

[8] Secretary of the Air Force letter "Air Force Pollution Prevention Program," dated 13 November 1991.

[9] S&T Environmental Leadership course notes, WPAFB, OH, 2 February 1994.

Next Generation Fire Suppressants

by

Jerry A. Brown

presented to

Aerospace Environmental Technology Conference

Spectrex, Inc., located in Cedar Grove, NJ is a manufacturer of fire detection and suppression equipment. Spectrex is one of the original pioneers in high speed fire detection and suppression systems for combat vehicles. Spectrex has installed fire suppressions systems in thousands of combat vehicles and ships throughout the world. Additionally, they manufacture flame explosion detectors, ship damage control systems, and optical gas and vapor detectors.

The culmination of several years of research and development has recently produced an innovative electro-optical continuous monitoring systems called SharpEye 20/20I IR^3 and SAFEYE that provide fast and reliable gas, vapor, aerosol, flame, and explosion detection.

SharpEye 20/20I IR^3 is a self-contained triple spectrum flame detector which scans for oscillating IR radiation (1 to 10 Hz) in the spectral bands ranging from 4.0 to 5.0 microns and uses programmed algorithms to check the ratio and correlation of data received by the three sensors to make the system highly immune to false alarms. It is extremely sensitive as it can detect a 1x1 square foot gasoline pan fire at 200 feet in less than 3 seconds. The sensitivity is user-programmable, offering 4 ranges of detection.

SAFEYE is comprised of a selected number of multispectral ban microprocessors controlled detectors which are in communication with one or more radiation sources that is projected along a 600 feet optical path. The signals from the selected narrow bands are processed and analyzed by highly sophisticated algorithms. It is ideal for high risk, remote, large areas such as petroleum and chemical manufacturing sites, waste dumps, aircraft cargo bays, and ship compartments. The SAFEYE will perform direct readings of the presence or rate of rise of concentrations of gases, vapors, or aerosols at the range of parts per million and provide alarms at various set points at different levels of concentrations.

IN SEARCH OF A HALON ALTERNATIVE

However, without an efficient, environmental friendly extinguishing agent, detection technological advances such as the SAFEYE can solve only part of the fire extinguishing problem. When Halon 1301 was rapidly being taken from our arsenal of agents because of the Montreal Protocol, we began an aggressive search for a Halon Alternative. Spectrex took the philosophical approach *"Don't think you are necessarily on the right track just because it's a well-beaten path"*. Spectrex's research, development, and engineering team went back to the basics of fire extinguishment by looking at the technologies that most efficiently attacked the basic contributors of a fire: fuel, oxygen, heat, and chemical process. The Spectrex R&D team conducted a worldwide technology search for the most promising technologies.

SPECTREX R&D EFFORT

As a result of their R&D efforts, they have registered patents and continue the development of three promising technologies.

1. The first is an Electric Field Extinguishing Method
2. The second is extinguishing by using micron size dry powders.
3. The third method is not an extinguisher, but a method of converting halon/CFCs into non ozone-depleting materials.

1. NOVEL METHODS OF EXTINGUISHMENT (ELECTRIC)

The application of an electric field to a combustion system can produce potentially useful results either increasing the efficiency of the flame or reducing its efficiency to the point of extinguishment. When a strong electrical field is applied to the base of certain types of fires, it will result in extinguishment of the fire.

Electrical Field Extinguishment (Mechanism)

An electric field applies several mechanisms that extinguish fires. The electric field creates an Ion Wind that dissipates the heat, inhibits the oxygen and fuel to support the fire, and interferes with the chemical reaction involved in the combustion. We have extinguished fires from fixed locations for the electric field generator and from portable units which allow us to manually direct the generated electric field to the base of the fire thus causing extinguishment. An intense electric field and/or gaseous plasma is directed at the base of the fire; extinguishment can occur by means of a corona discharge. The most efficient corona device for the extinguishment of pool flames appears to be a thin wire moving parallel to the liquid surface at the rate of about 10cm/s. The remarkable extinguishing capability is explained by the unique sharp velocity profile associated with a maximum high velocity of up to 3m/s which occurs 1 to 2 millimeters above the liquid surface.

Electrical Field Extinguishment (Limitations)

At this point in our development, we know of the following limitations:

- We need to know in advance the configuration of the fire.
- Can only extinguish a limited fire surface area.
- Equipment must be tailored to specific applications.

Electrical Field Extinguishment (Advantages)

However, the following advantages exist:

- It is a non-ozone depleter, clean, fast, safe, and quiet.
- It can be applied in an unlimited number of operations.
- There are no consequences to unwanted activation.
- There is great potential savings in weight and volume.

I see this technology as having great potential for automotive and aircraft engine applications as well as tank farm fires.

2. SFE-NOVEL EXTINGUISHING MATERIAL

The second novel extinguishing material is called SFE or EMAA, Encapsulated Micron Aerosol Agent. EMAA is the product name assigned to SFE by the USAF under a Cooperative Research and Development Agreement between Spectrex and the USAF. SFE/EMAA is a family of agents that are originally in solid, powder, or gel form. When the SFE burns, it forms an aerosol cloud

which has powerful extinguishing capabilities. We have developed various chemical formulations, and it can be manufactured and tailored to meet any shape or size requirements.

SFE–Extinguishment (Mechanism)

SFE agent is at least 5–7 times more powerful than halon 1301 in terms of fire extinguishment, weight, and volume. The reason that SFE is so effective is that it attacks the fire's structure by interfering in the chemical chain, by absorbing heat extremely well, by hindering the flame propagation, and by disturbing the rate of burning. SFE is composed of small particles, less than 1 micron in size mixed with gases, primarily nitrogen and oxygen. The agent consists of about 60% gases and 40% particles. Once ignited the aerosol that is produced stays suspended for substantial amounts of time. It has a superior total flooding capability that allows it to quickly fill the entire volume of an area regardless of obstacles.

Extinguishing Comparison

A comparison of various performance parameters of Halon 1301, Gaseous Replacements, CO2, and SFE shows the many advantages that SFE has over the other agents. SFE is an extremely environmentally–friendly agent, a zero ozone depleter, and practically zero in Global Warming Potential. Although testing is not complete, recent toxicological analysis by the Naval Medical Research Institute has shown SFE to have a low toxicity rating. A post fire analysis shows that the air consists of 78–79% Nitrogen, 18–20% Oxygen, .4–2.3 % Carbon Dioxide, .19–.56% Carbon Monoxide, 1–300 PPM of hydrocarbons, and traces of other elements depending on the formulation. These results strongly indicate that the products produced fall in the range of low to no toxicity. In addition, we have recently received notice from the EPA as a part of its Significant New Alternatives Policy (SNAP) program that SFE is acceptable for use in normally occupied areas, pending medical assessment by a peer review panel.

SFE/EMAA Applications

Even if the environmental issues were not important, the fact that SFE provides substantial reductions in weight, volume, and cost is enough to make this technology very attractive to the marketplace. SFE can be developed and adapted into fire extinguishing systems that can satisfy fire protection requirements of many commercial and military applications. For example, our many experiments have shown that SFE is very kind to electronics, leaving very little residue on printed circuit boards. Another promising application of SFE appears to be with aircraft cargo bay fires where weight and volume are of great importance.

Additional advantages of SFE are listed below:

- SFE can be easily combined with various detection technologies or designed as a simple, stand–alone system.

- SFE helps prevent fire reignition. A common problem with halon and CO2 extinguishing systems is that fires reignite after the agent dissipates. We have not experienced reignition in our tests to this point.

- SFE can be activated while immersed in water or fuel and extinguish a fire on the surface. SFE percolates through the fuel or water to extinguish the flames.

Advantages of SFE/EMAA

DOD needs an efficient agent to meet critical survivability issues. SFE appears to address many of those issues. This is not a technology that represents just a marginal improvement over halon 1301; it appears to be at least five times more effective in terms of weight and volume and thus clearly represents a leap ahead in technology. SFE shows great promise of being adapted to many commercial and defense applications thereby reducing life cycle costs.

And we should not forget the engine that is driving this train, environmental issues such as ozone depletion and greenhouse warming. SFE clearly addresses these major environmental issues and appears to be a solution.

3. CONVERSION OF HALONS/CFCs INTO NON OZONE-DEPLETING MATERIALS

The third technology that I would like to briefly describe is a system aimed at protecting the stratosphere from accumulation of ozone destroying halogen atoms. Upon detection of the release, escape, or discharge of halogenated hydrocarbon into the atmosphere, we can apply concentrated energy sources at the halocarbons which separate the halogen atom from the halon carbon molecule. The separated halogen atom is converted to a halide salt as a result of being energized. The products of such a reaction can be controlled by the amount of energy applied to the material.

Our Halogenated Hydrocarbon Neutralization system can be designed to be portable or permanent, and activated manually or automatically. It can be added to any system that uses CFCs as refrigerants or halons for fire extinguishing agents. For example, the halogenated hydrocarbon neutralization system can be designed so as to continuously monitor the halon carbon concentrations within the air conditioning enclosure and block the flow of ozone-depleting species from leaving the enclosure. We have designed a system that is composed of a detection unit capable of detecting small amounts of halon/CFCs that have been accidently been released into the air and a pumping device which draws the air containing the halocarbons into a cyclone separator where heavy haloncarbons are separated from the air. The haloncarbons are pumped into a dissociation chamber where energy pulses delivered by means of radiation cause complete cleavage of the halogen atom from the molecule. The product of the dissociation are pumped into the reaction chamber where the halogen products of the selected dissociation are scrubbed, absorbed, or treated with alkali materials to produce harmless salts.

CONCLUSION

We believe that there are solutions to many of our environmental problems and some of the technologies presented by Spectrex show promise in making our environment safer and cleaner. The technologies explained above are at the technological forefront of today's fire extinguishing and environmental research and show great promise for improving techniques for extinguishing fires while preventing damage to the environment.

FM-200™, THE NEW SOLUTION FOR FIRE PROTECTION

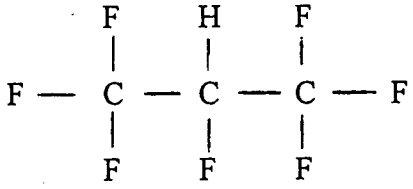
Alfred J. Thornton & Gerald J. Walter
Great Lakes Chemical Corporation
P. O. Box 2200
West Lafayette, IN 47906-0200
Phone: 317-497-6206

For more than two decades, halon 1301 has been protecting personnel and valuable aircraft and aerospace equipment from the hazards of fire. Only halon 1301 offered the advantages of being clean, odorless, colorless, electrically non-conductive and safe for occupied areas. However, concerns about the depletion of stratospheric ozone and the resulting Montreal Protocol mandated the production phase-out of halon 1301 on December 31, 1993.

Prior to this phase-out, Great Lakes Chemical Corporation, the world's leading manufacturer of halon, directed substantial research efforts toward the rapid development of a safe, clean, and effective halon replacement. Some of the criteria for the development of a clean agent included:

- that it be an effective fire extinguisher;
- that it be safe for personnel;
- that it be safe for the environment;
- that it be safe for valuable assets;
- that it be cost effective; and,
- that it be able to withstand the rigors of independent approvals.

Much effort was put into this endeavor. As a result of this research, Great Lakes developed FM-200™. Chemically FM-200™ is 1,1,1,2,3,3,3-hepta-fluoropropane. The molecular structure for FM-200™ is as follows:



Studies show that the decomposition of FM-200™ begins with loss of the single hydrogen atom. This provides a point of reaction giving FM-200™ a low atmospheric lifetime of 31 years. FM-200™, unlike its predecessor halon 1301 contains no bromine and has a zero ODP.

The physical properties of FM-200™ compared to halon 1301 are:

	FM-200™	Halon 1301
Chemical Formula	CF_3-CHF-CF	CF_3Br
Molecular Weight	170.03	148.91
Boiling Point oF	2.55	-71.95
Vapor Pressure @ 70oF	58.8 psia	214 psia

FM-200™ is an effective fire extinguisher and is U.L. listed at a concentration of 5.8% v/v for Class A fires. For Class B fires, 5.5 to 6.7% v/v of FM-200™ will extinguish fires from unleaded gasoline, aviation gasoline, number 2 diesel, n-heptane and hydraulic fluid. FM-200™ is also effective against Class C hazards and is approved for this use by U.L. and FM (Factory Mutual Research Corporation).

As a fire suppression agent, FM-200™ is more of a physical-acting agent compared to halon, which is primarily a chemical-acting agent. FM-200™ physically removes heat from the flame front. This lowers the flame temperature and reduces the combustion reaction rate to the point where the combustion reaction can no longer sustain itself. Furthermore, it is likely that extinguishment by FM-200™ also involves a chemical mechanism. Trace amounts of Fluorine are released from the FM-200™ molecule and reacts with transient combustion species in the chain propagation reactions. This ultimately halts these reactions. Because of this slightly different flame suppression mechanism, the design concentration of FM-200™, accounting for a higher molecular weight, is 1.66 v/v times higher than halon. Extinguishant times are less than 10 seconds or about the same as halon 1301.

In addition to its efficiency as an extinguishant, FM-200™ has been thoroughly tested and is proven safe for occupied enclosures. The acute toxicity of FM-200™ is above 800,000 ppm. At 80% concentration (800,000 ppm) in 20% oxygen, all the animals survived exposure. The cardiac sensitivity of FM-200™ was tested. Based on the results of these tests, the U.S. EPA SNAP assigned a NOAEL of 9% v/v and a LOAEL of greater than 10.5%. Other agencies interpret the cardiac sensitivity differently. Australia allows 14% v/v as a safe level for occupied exposure providing egress takes place within 30 seconds of discharge. In contrast, the NOAEL for halon 1301 was 7% and the LOAEL was 10%. In other toxicity tests, FM-200™ demonstrated the following:

- negative results in a 14-day screening in male and female rats at 10% active;
- negative in central nervous system suppression;
- negative in developmental and reproductive toxicity;

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- negative results in a 14-day screening in male and female rats at 10% active;
- negative in central nervous system suppression;
- negative in developmental and reproductive toxicity;

- non-mutagenic in all genotoxicity tests;
- negative as a respiratory sensitizer;
- not metabolized or retained by living systems;
- exhaled unchanged by living organisms.

FM-200™ is safe for valuable assets. FM-200™ is a highly purified reagent-grade gaseous chemical that leaves no residue. FM-200™ is non-conducting and non-corrosive; furthermore, it has a higher dieletric constant than halon 1301.

FM-200™ is safe for the environment because FM-200™ is not an emissive agent. In contrast, a fire is a very polluting event that emits copious amounts of gases, many of which are toxic and greenhouse gases. In addition, the remnants of fires leave significant residue for clean up. Furthermore, the repair or rebuilding process from fires also contributes considerably to global warming or climate change. The advantage of FM-200™ is that it quickly extinguishes a fire, which greatly reduces the emissions of toxic gases. FM-200™ also reduces collateral damage as an HFC. FM-200™ has a zero ozone depletion potential and a low atmospheric lifetime of 31 years according to the U.S. EPA SNAP document. The GWP over a 500-year integrated time horizon is 600.

FM-200™ has withstood the rigors of independent approvals. The U.S. EPA's SNAP program accepts FM-200™ as the most effective HFC replacement for halon 1301. Underwriters' Laboratories (U.L.) and Factory Mutual (FM) recognize equipment approvals and component listings. In addition to the above approvals, FM-200™ is included in the NFPA 2001 standard as a halon 1301 replacement. Furthermore, FM-200™ is approved by the Loss Prevention Council in the U.K. (LPC), NICNAS in Australia, the Japanese Fire Defense Agency, the Hong Kong Fire Authority, the U.S. Coast Guard, the U.S. F.A.A., and the International Maritime Organization in addition to several others.

Thank you for the opportunity to tell you about FM-200™, the most widely accepted halon replacement on the market.

CORROSION PROTECTION REPLACEMENTS

ASSESSMENT OF POLLUTION PREVENTION AND CONTROL TECHNOLOGY FOR PLATING OPERATIONS

Authors:

Paul D. Chalmer, Ph.D. (National Center for Manufacturing Sciences)
William A. Sonntag (National Association of Metal Finishers)
George C. Cushnie Jr. (CAI Engineering)

ABSTRACT

The National Center for Manufacturing Sciences (NCMS) is sponsoring an on-going project to assess pollution prevention and control technology available to the plating industry and to make this information available to those who can benefit from it. Completed project activities include extensive surveys of the plating industry and vendors of technologies and an in-depth literature review. The plating industry survey was performed in cooperation with the National Association of Metal Finishers. The contractor that conducted the surveys and prepared the project products was CAI Engineering. The initial products of the project were made available in April, 1994. These products include an extensive report (ref. 1) that presents the results of the surveys and literature review and an electronic database. The project results are useful for all those associated with pollution prevention and control in the plating industry. The results show which treatment, recovery and bath maintenance technologies have been most successful for different plating processes and the costs for purchasing and operating these technologies. The project results also cover trends in chemical substitution, the identification of compliance-problem pollutants, sludge generation rates, off-site sludge recovery and disposal options, and many other pertinent topics.

BACKGROUND

The theme of this session is the evaluation of new environmentally friendlier replacement technologies for corrosion protection. The focus of this presentation is somewhat more retrospective, but we feel it is just as crucial to the session's purposes. Every old replacement technology began life as a new replacement technology. The best survived to become the established technologies of today, while back rooms and landfills are littered with the others' bones. A sense for what has historically worked and what has not may be as useful in assessing a new replacement's chances as are the usual brochures, specifications and testimonials in which each candidate comes clad.

Many corrosion protection processes involve electroplating. Environmental considerations have loomed increasingly large in the development of plating technologies for the past several years. In thousands of individual facilities throughout the country, many examples of pollution prevention techniques and pollution control equipment have been tried, and many have been accepted or discarded based on factors intrinsic to the technology, as well as factors peculiar to each individual shop.

The National Center for Manufacturing Sciences (NCMS) and the National Association of Metal Finishers (NAMF) have sponsored a project designed to capture the lessons learned across the industry, and to make that information available to the general public. The project involved a detailed survey of individual plating facilities, a thorough literature review, and input from technology suppliers. The purpose of this brief summary is to convey some idea of how the project was put together, and to give an overview of some of the key findings to emerge from the study. For those interested in specific details, the full report is now available as a four hundred page book, and the survey results are available on disk.[1] Some of these results were presented at the AESF-EPA Conference in January, 1994. The results have been revised, updated, and extended below.

A diagram showing the various stages of the project is provided in Exhibit 1. The assessment was conducted using three major sources of information and data:

(1) A mailed questionnaire-survey sent to approximately 2,000 electroplating and metal finishing plants (Users Survey).

(2) A mailed questionnaire-survey of approximately 60 vendors of pollution prevention and control equipment and off-site metals recycling services (Vendors Survey).
(3) A literature search that gathered approximately 600 articles, reports, conference papers and other sources of relevant information.

[1]For information contact the NCMS contractor, CAI Engineering at 703-264-0039.

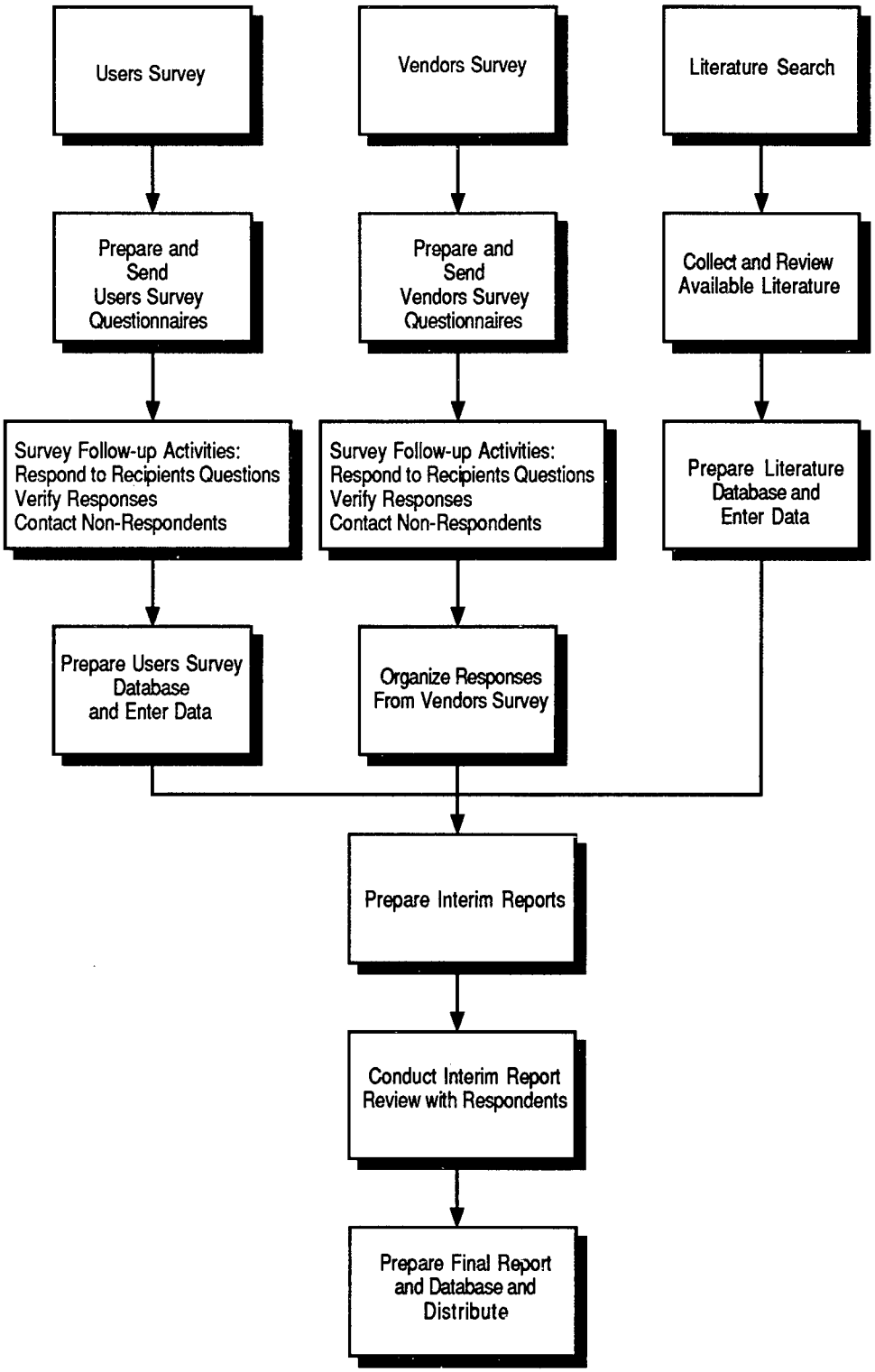


Exhibit 1.
Assesment of Pollution Prevention and Control Technology for Plating Operations
Overview of Project Activities

Using the collected materials, information and data, a set of seven Interim Reports was written covering the following topics:

- Interim Report No. 1: Overview of Project Results
- Interim Report No. 2: General Waste Reduction Practices
- Interim Report No. 3: Chemical Recovery
- Interim Report No. 4: Chemical Solution Maintenance
- Interim Report No. 5: Process Substitution
- Interim Report No. 6: Wastewater Treatment
- Interim Report No. 7: Off-Site Metals Recycling

The Interim reports were distributed to the respondents of the Users and Vendors Surveys and other interested parties. Based on comments received during the review process, the Interim Reports were revised and subsequently consolidated into a single final report. The report and Users Survey database are being distributed for NCMS by CAI Engineering. The reports and database will be updated once these results are disseminated and feedback is received. This will include additional data that will be accepted from new respondents to the Users Survey and Vendors Survey. Firms wanting to participate in updating these reports and database should contact the NCMS Project Manager.[2]

CHARACTERIZATION OF RESPONDENTS

The plating shops that responded to the Users Survey were diverse in terms of geographical location, size, the processes they employ and other factors. One general similarity of the respondents is that they mostly represent the job shop sector of the plating industry. Of the 300[3] initial respondents, 253 are electroplating job shops and 47 are captive shops. Distributions of other characteristics of the respondents are shown in Exhibit 2.

The geographical distribution of the respondents was relatively diverse, but concentrated in major electroplating regions. The majority of respondents (86%) are located in the Far West, Midwest and Northeast U.S. With respect to shop age, the average and median year that respondents commenced metal finishing operations was 1965. The range of commencement dates is 1867 to 1992. Approximately 18% of the respondents commenced metal finishing operations after August 31, 1982, the cut-off date where newer facilities are required to meet pretreatment standards for new sources (PSNS). The data show that the majority of the companies responding to the survey have 100 or fewer employees (86.8%). The average and median number of employees is 67 and 35, respectively. The range of employees is from 1 to 3,000.

METAL FINISHING PROCESS CHARACTERIZATION

Collectively, the respondents to the Users Survey operate 154 different types of metal finishing processes. The 25 most frequently found processes are identified In Exhibit 3 (excludes pre-plating, post-plating and stripping processes).

WASTEWATER AND DISCHARGE CHARACTERIZATION

The majority of the respondents to the Users Survey are indirect dischargers (i.e., discharge to a publicly owned treatment works, rather than directly to a stream, river or other water body). The percentage of shops that are either indirect, direct, both indirect and direct and zero discharge are shown in Exhibit 4. These data indicate that captive shops are more likely to be direct dischargers than are job shops. EPA estimates in 1984 indicated a similar trend (ref. 2).

The electroplating discharge rates (average daily flows) of the survey respondents vary from 0 gpd to 420,000 gpd (some higher discharge rates were reported for combined plating and non-plating industrial discharges). The average and median plating discharge rates for respondents were 34,600 gpd and 14,000 gpd, respectively (see Exhibit 2 for additional statistics regarding flow rates). Many shops indicated that they have made drastic progress in reducing wastewater flow rates, the most significant of which are the following:

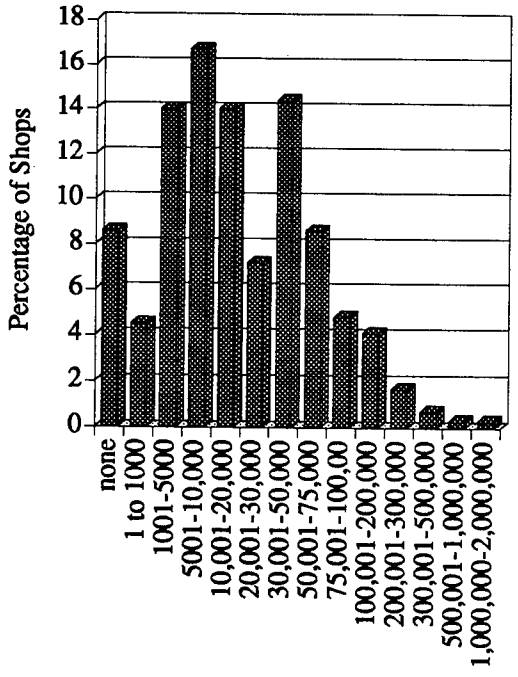
- PS 022[4]: from 140,000 gpd to 70,000 gpd (50% reduction since 1980)
- PS 036: from 52,700 gpd to 2,700 gpd (95% reduction since 1978)
- PS 059: from 90,000 gpd to 10,000 gpd (89% reduction since 1977)
- PS 118: from 232,630 gpd to 42,630 gpd (82% reduction since 1983)
- PS 139: from 127,000 gpd to 52,000 gpd (59% reduction since 1986)

[2]Paul Chalmer; NCMS; 3025 Boardwalk Drive; Ann Arbor, MI; 48108-3266; 313/995-4911.

[3]Data presented in this paper are based on the initial 300 responses. Additional responses are included in the final NCMS database and report.

[4]The names of respondents to the Users Survey are maintained in confidence by using a code sysem (PS stands for plating shop).

Average Plating Discharge Rate (gpd)



Company Size Distribution by Number of Employees

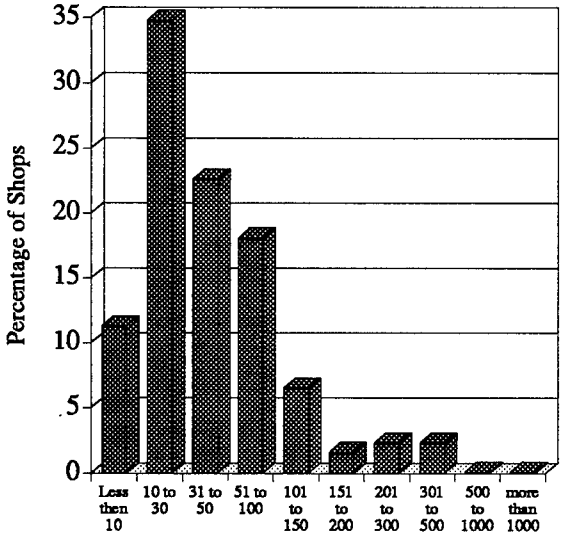
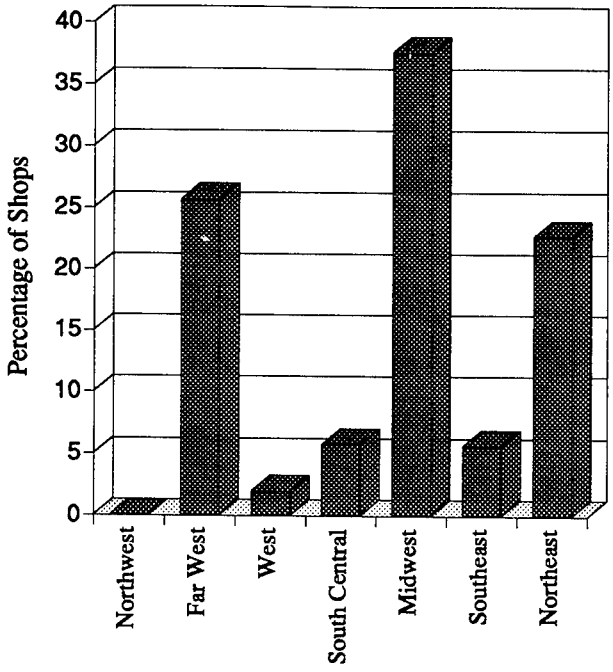


Exhibit 2.
Characterization of Respondents to the Users Survey

Geographical Distribution of Respondents



Shop Age Distribution
(year shop commenced metal finishing operations)

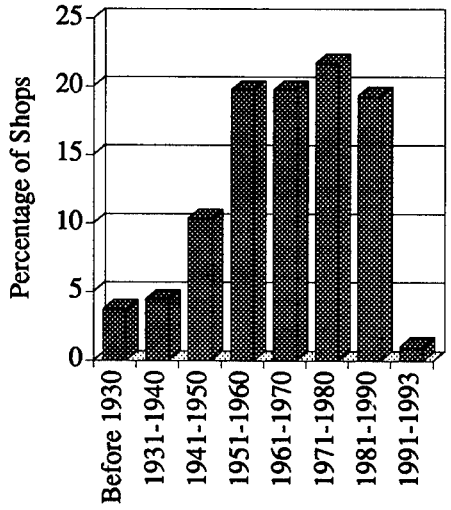


Exhibit 2.
Characterization of Respondents to the Users Survey (continued)

- PS 150: from 400,000 gpd to 100,000 gpd (75% reduction since 1986)
- PS 172: from 150,000 gpd to 70,000 gpd (53% reduction since 1975)
- PS 184: from 121,000 gpd to 11,000 gpd (91% reduction since 1982)
- PS 207: from 68,000 gpd to 18,000 gpd (74% reduction since 1986)
- PS 213: from 130,000 gpd to 50,000 gpd (62% reduction since 1985)
- PS 250: from 91,000 to 11,000 gpd (88% reduction, base year not given)
- PS 268: from 87,000 gpd to 17,000 gpd (80% reduction since 1987)
- PS 292: from 160,000 to 60,000 gpd (63% reduction since 1985)
- PS 296: from 1,900,000 gpd to 1,700,000 gpd (11% reduction, base year not given)
- PS 298: from 160,000 gpd to 90,000 gpd (70% reduction since 1990)

Exhibit 3.
The Twenty-Five Most Frequently Operated Metal Finishing Processes

Process Name	Percent of Shops Using Process	Average Volume of Solution per Shop*	Process Name	Percent of Shops Using Process	Average Volume of Solution per Shop*
1. Nickel (Watts) plating	42	4,102	14. Silver (CN) plating	25	465
2. Zinc (non-CN) plating	39	5,276	15. Chromate on cadmium	24	388
3. Chromate on zinc plate	39	1,594	16. Zinc phosphate	23	1,065
4. Chromate on aluminum	38	607	17. Tin-lead plating	21	256
5. Passivation (all types)	38	244	18. Gold (CN) plating	20	166
6. Copper (CN) plating	38	852	19. Bright dip of Cu/Cu	19	80
7. Cadmium (CN) plating	30	1,360	20. Copper (sulfate) plating	19	1,761
8. Electroless nickel plating	30	809	21. Black oxide	17	319
9. Decorative Cr (+6) plate	29	1,637	22. Brass plating	17	713
10. Tin (acid) plating	27	581	23. Hard coat anodizing	15	1,661
11. Nickel (sulfamate) plate	26	681	24. Zinc (CN) plating	15	4,221
12. Sulfuric acid anodizing	26	1,590	25. Chromic acid anodizing	14	814
13. Hard chromium plating	25	3,978			

*Often involves a multiple number of tanks per shop containing the same solution.

The respondents to the Users Survey are required to meet either CFR 413 (Electroplating Categorical Standards), CFR 433 (Metal Finishing Categorical Standards), or non-standard effluent limitations. Non-standard limitations are more stringent than the categorical standards for one or more pollutant parameters. Some of the non-standard limitations are written in terms of pollutant mass and flow rates (e.g., 0.37 lbs/day of chromium with a maximum flow of 40,000 gpd) rather than concentration limitations. The percentage of respondents that are required to meet each type of effluent limitation are as follows:

40 CFR 413: 28%
40 CFR 433: 8%
Non-Standard: 64%

In addition to concentration or pollutant mass discharge standards, 16% of the respondents indicated that they are also subject to aquatic-based effluent standards. These limits require that an industrial wastewater be sufficiently treated such that certain percentages of organisms (typically fish and water fleas) are able to survive in the effluent for a given time period.

The Users Survey asked platers to indicate the pollutant parameters for which they have compliance difficulty. A summary of their responses is shown in Exhibit 5.

DRAG-OUT AND RINSE WATER REDUCTION

For the typical electroplating job shop, the drag-out of process solutions and the subsequent contamination of rinse waters are the major pollution control problems. The NCMS report explains the basic principles of drag-out theory and explores the function and applicability of the various drag-out minimization techniques in use today. Because of the importance of drag-out and drag-out loss prevention, numerous questions in the Users Survey were related to this topic. The responses to these questions are statistically evaluated in the report and summarized in this paper.

The Users Survey asked respondents to indicate the methods they employ to reduce the formation or loss of drag-out and the usage rate of rinse water. A summary of their responses is presented in Exhibits 6 and 7. The most frequently used drag-out reduction methods are: allowing parts/racks to drip over process tanks; the use of drag-out rinses; reducing the speed of rack/part withdrawal; use of drip shields; and positioning the workpiece to minimize solution holdup. On the average, all of the drag-out reduction methods that are used by the respondents have been successfully applied. Some shops had specific problems with one or more methods (e.g., buildup of bath contaminants). These problems are discussed in the report along with potential solutions.

Exhibit 4.
Distribution of Respondents by Type of Discharge

Type of Discharge	Percentage of All Respondents with the Type of Discharge Indicated	Percentage of Job Shop Respondents with the Type of Discharge Indicated	Percentage of Captive Shop Respondents with the Type of Discharge Indicated
Direct Discharge	12.6%	10.8%	22.0%
Indirect Discharge	78.9%	80.6%	70.0%
Both Direct and Indirect	0.9%	0.7%	2.0%
Zero Discharge	7.5%	7.8%	6.0%

Exhibit 5.
Pollutant Parameters for which Compliance Difficulty was Reported by Respondents

Parameter	Percentage of Respondents Reporting Compliance Difficulty	Parameter	Percentage of Respondents Reporting Compliance Difficulty
Nickel	19	Lead	7
Zinc	19	Cyanide (amenable)	2
Chromium (total)	17	Chromium (+6)	2
Copper	12	Silver	2
Cyanide (total)	12	Total Toxic Organics	1
Cadmium	10		

Note: some shops listed two or more parameters.

The most frequently used methods of reducing water use involve the application of: flow restrictors; counterflow rinses; manually turning off water; and air agitation. As with drag-out methods, the rinse water reduction methods have been generally successfully, with the highest success ratings given to the use of flow restrictors and counterflow rinsing.

CHEMICAL RECOVERY TECHNOLOGIES

According the respondents of the Users Survey, chemical recovery technologies are most frequently purchased to (in order of frequency): help meet effluent regulations; reduce wastewater treatment costs; reduce plating chemical purchases; and to reduce the quantity of waste shipped off-site.

The Users Survey requested platers to provide detailed technical, performance and operating cost data for chemical recovery technologies. Also, during their survey, vendors were requested to provide technology descriptions, operating data and capital cost data. As a result of obtaining data from these two sources, plus the information from the extensive literature review, the NCMS report contains a substantial quantity of

Exhibit 6.
Summary of Users Survey Data Relating to Drag-Out Loss Prevention

Drag-Out Reduction Methods	% of Respondents Using Method	Success Rating (1 to 5)
Drag-out rinse tanks w/ rtn. of chem. to proc bath (manual)	61	3.8
Drag-out rinse tanks w/ rtn. of chem. to proc bath (auto.)	19	3.7
Drip tanks; w/ rtn. of chem. to proc bath (manual)	27	3.4
Drip tanks; w/ rtn. of chem. to proc bath (auto.)	7	3.2
Reducing speed of rack/part withdrawal (manual)	39	3.2
Reducing speed of rack/part withdrawal (auto.)	22	3.6
Allow rack/part to drip over plating tank (manual)	61	3.5
Allow rack/part to drip over plating tank (auto.)	25	3.8
Using a drag-in/drag-out arrangement (manual)	21	3.4
Using a drag-in/drag-out arrangement (auto.)	11	3.9
Fog/spray rinses installed over proc.bath (manual)	18	3.7
Fog/spray rinses installed over proc.bath (auto)	10	3.3
Air knives that blow off drag-out (manual)	2	3.1
Air knives that blow off drag-out (auto)	6	3.8
Drip shields between tanks	57	3.7
Lower bath concentrations	34	3.3
Increasing solution temperature	17	3.1
Using a wetting aqent	32	3.0
Positioning workpiece to minimize solution holdup	52	3.8
Average		3.3

Manual and automatic refer to the level of automation of the plating line.
The success rating is based on a scale of 1 to 5, with 5 being most successful.

Exhibit 7.
Summary of Users Survey Data Relating to Rinse Water Use Reduction

Rinse Water Reduction Methods	% of Respondents Using Method	Success Rating (1 to 5)
Manually turning off rinse water when not in use	66	3.6
Conductivity or pH rinse controls	16	3.2
Timer rinse controls	11	3.8
Flow restrictors	71	4.2
Counterflow rinses	68	4.2
Spray rinses	38	3.8
Air agitation in rinse tanks	58	3.7
Flow meters/accumulators to track rinse water	12	3.7
Reactive rinsing or cascade rising	25	3.8
Average		3.8

Exhibit 8.
Distribution and Ratings of Chemical Recovery Technologies

Process Name	ED[a]	EW	ATM EV	VAC EV	IX	MP	RO
Anodize, Chromic Acid	-	-	-	-	ND (1)	4.0 (2)	-
Anodize, Hardcoat	-	2.0 (1)	-	-	-	-	-
Brass	-	3.5 (2)	4.0 (2)	-	-	-	-
Cadmium, Cyanide	-	2.7 (29)	3.0 (4)	3.0 (3)	2.0 (4)	-	5.0 (1)
Cadmium, Non-cyanide	-	ND (1)	4.0 (1)	-	-	-	-
Chromate (Aluminum)	-	-	-	-	5.0 (1)	-	-
Chromium Etch	-	-	-	4.5 (2)	-	-	-
Chromium, Hard	-	-	4.3 (4)	-	2.0 (2)	4.1 (15)	-
Chromium, Decorative (Cr^{+6})	-	-	3.5 (11)	4.0 (5)	5.0 (3)	-	-
Chromium, Decorative (Cr^{+3})	-	-	5.0 (2)	-	-	4.0 (1)	-
Copper, Electroplating[b]	-	3.0 (15)	3.7 (4)	4.0 (1)	ND (3)	-	2.0 (1)
Gold, Electroplating[c]	-	4.0 (4)	-	-	4.0 (13)	-	-
Lead-Tin	-	-	-	4.0 (1)	-	-	-
Nickel, Electroplating[d]	1.0 (3)	4.0 (6)	4.1 (20)	4.0 (3)	3.8 (12)	-	1.0 (4)
Nickel, Electroless Plate	-	ND (1)	3.0 (2)	-	1.7 (3)	-	-
Seal, Nickel	-	-	-	-	-	-	4.0 (1)
Silver, Electroplate	-	4.4 (12)	2.0 (1)	-	-	-	-
Zinc, Cyanide	-	1.7 (7)	3.0 (2)	1.7 (3)	ND (1)	-	1.0 (1)
Zinc, Non-cyanide[e]	-	2.0 (7)	3.7 (9)	-	2.6 (7)	-	5.0 (1)
Zincate	-	-	4.0 (1)	-	-	-	-

[a]Technology key: ED=electrodialysis, EW=electrowinning, ATM EV=atmospheric evaporation, VAC EV=vacuum evaporation, IX=ion exchange, MP=meshpad mist eliminator, RO=reverse osmosis. Ratings are based on a scale of 1 to 5, with 5 being the most successful. Number of applications from the Users Survey is shown in parenthesis. "-" = no applications, ND = no data.
[b]Includes cyanide plate, cyanide strike and sulfate baths.
[c]Includes cyanide and non-cyanide baths.
[d]Includes bright, sulfamate, sulfate, Watts and Woods baths.
[e]Includes acid and alkaline baths.

information for the following chemical recovery technologies: electrodialysis, electrowinning, atmospheric evaporators, vacuum evaporators, ion exchange, reverse osmosis and mesh pad mist eliminators. A separate subsection of the report is devoted to each of these technologies. Within each subsection, the following are provided: technology overview; development and commercialization; applications and restrictions (with diagrams showing different potential configurations); technology/equipment description; capital costs; operating costs; performance experience; and residuals generation.

Exhibit 8 presents a summary of the chemical recovery applications covered by the Users Survey data. Exhibit 9 presents an example (vacuum evaporators) of the Users Survey data summaries contained in the report.

SOLUTION MAINTENANCE METHODS AND TECHNOLOGIES

Metal finishing solutions are subjected to a variety of forces that cause them to become unusable. The key contributing factors are: (1) depletion of bath chemicals; (2) chemical break-down of process chemicals or chemical side reactions; (3) contamination from impurities in make-up water, chemicals or anodes; (4) anodic/cathodic etching of parts and inert electrodes; (5) corrosion of parts, racks, bussing, tanks, heating coils, etc.; (6) drag-in of non-compatible chemicals; (7) buildup of by-products (e.g., carbonates); (8) breakdown of maskant, fume suppressant and wetting agents; (9) errors in bath additions; and (10) airborne particles entering the tank.

Solution maintenance replaces the practices of: (1) using a fresh chemical solution until it is degraded and replacing it with fresh solution or (2) decanting a

Exhibit 9. Partial Summary of Users Survey Data for Vacuum Evaporation (chemical recovery applications)

Plating Shop Code	Plating Solution Application	Manufacturer	Year Purchased	Capital Costs			Operating Costs ($/Yr.)			Savings					Use Code (3)	Satisfaction Level with Technology (4)	Future Decision (5)
				Equip.	Other	Total	Non-labor	Labor	Total	Bath Chem.	Treat. Chem.	Sludge Disp.	Other	Total			
034	Zinc (CN)	McDermid	1980	$35,000	$8,000	$43,000		$5,000	$5,000	$500	$200	$1,000	$2,500	$4,200	3	2	2
039	Zinc (CN)	Wastesaver	1975	$50,000	$4,000	$54,000	$9,000	$2,400	$11,400	$5,000				$5,000	2	1	2
082	Dec. Cr +6	Pfaudler (1)		$150,000	$25,000	$175,000	$50,000	$15,000	$65,000	$130,000	$115,000	$30,000		$275,000	1	4	1
088	Cd (CN)	Pfaudler (2)	1982	$23,000	$2,050	$25,050	$10,000	$6,000	$16,000	$9,900	$15,000	$5,000		$29,900	1	4	1
102	Cu(CN)	McDermid	1972												2	4	3
123	Sn/Pb	Calfran	1991	$60,000	$2,000	$62,000	$6,912	$14,560	$21,472	$214,700		$34,260		$248,960	1	4	1
124	Dec. Cr +6	Corning	1980	$108,210	$0	$108,210									1	4	1
125	Dec. Cr +6	Homemade	1985	$35,000	$10,000	$45,000	$15,000	$2,600	$17,600	$18,500				$18,500	1	4	1
125	Ni (Watts)	Homemade	1985	$70,000	$210,000	$280,000		$2,600	$2,600	$38,000				$38,000	1	4	1
132	Cd (CN)	Corning	1981												2	1	3
143	Cd (CN)	Water Vap	1992	$10,000	$500	$10,500	$3,000		$3,000			$500	$1,000	$1,500	1	4	1
196	Dec. Cr +6	Corning		$240,000	$25,000	$265,000	$10,000	$2,000	$12,000	$450,000	$15,000	$12,000	$18,000	$495,000	1	4	1
197	Dec. Cr +6	McDermid	1979	$44,646	$56,890	$101,536	$28,565		$28,565						1	4	1
197	Ni (Watts)	McDermid	1978	$41,521	$56,950	$98,471	$40,016		$40,016						1	4	1
197	Ni (Watts)	McDermid	1979	$54,172	$56,960	$111,132	$40,016		$40,016						1	4	1
213	Cr Etch	Corning	1988	$80,557	$0	$80,557									2	5	1
275	Dec. Cr +6	Corning	1984	$70,000	$6,500	$76,500	$10,000	$4,250	$14,250	$200,000	$200,000	$38,000		$438,000	1	4	2
280	Cr Etch	Corning	1990	$90,000	$8,000	$98,000				$16,400	$80,700	$10,000		$107,100	1	4	3
298	Zinc (CN)	Wastesaver	1991	$43,000	$29,000	$72,000	$15,600	$7,800	$23,400	$31,000	$13,000		$3,000	$47,000	1	2	2
	Average		*1983*	*$70,889*	*$29,462*	*$100,350*	*$19,842*	*$6,221*	*$21,451*	*$101,273*	*$62,700*	*$16,345*	*$6,125*	*$142,347*		*3.5*	

Exhibit 10. Partial Summary of Users Survey Data for Ion Exchange (bath maintenance applications)

Plating Shop Code	Plating Solution Application	Manufacturer	Year Purchased	Capital Costs			Operating Costs ($/Yr.)			Savings					Use Code (3)	Satisfaction Level with Technology (4)	Future Decision (5)
				Equip.	Other	Total	Non-labor	Labor	Total	Bath Chem.	Treat. Chem.	Sludge Disp.	Other	Total			
049	Cr Anodize	Kinetico	1990	$18,000	$1,000	$19,000		$1,200	$1,200	$2,000	$1,000	$10,800	$2,500	$16,300	1	5	2
067	Hard Cr	Eco-Tec	1993	$49,000	$3,000	$52,000	$9,000		$9,000						1	5	1
077	Hard Cr	Eco-Tec	1991	$60,000	$40,000	$100,000	$50,000		$50,000	√	√	√			1	4	1
131	Hard Cr	Eco-Tec	1975	$26,000	$3,500	$29,500	$10,000		$10,000						1	4	1
150	Hard Cr	Eco-Tec	1992	$65,000	$16,000	$81,000		$2,900	$2,900						1	4	1
165	Hard Cr	Eco-Tec	1987	$31,000	$12,000	$43,000	$6,912	$2,640	$9,552						1	5	1
191	Dec. Cr +3	Kinetico	1991	$34,121	$1,500	$35,621		$3,000	$3,000	$16,000	$1,000	$2,500		$19,500	1	5	1
198	Hard Cr	Aqua Line	1990	$10,000	$800	$10,800	$15,000	$1,000	$16,000	$2,000		√		$2,000	1	4	1
234	Hard Cr	Eco-Tec	1983	$17,000	$0	$17,000									2		3
244	Cr Anodize	Eco-Tec	1982	$14,647	$1,500	$16,147		$15,600	$15,600						2	1	3
273	CrO3 Cu Strip	ILL Water Treat	1987	$58,000	$0	$58,000	$3,000		$3,000			$500	$1,000	$1,500	2	2	3
	Average		*1987*	*$34,797*	*$7,209*	*$42,006*	*$15,652*	*$4,390*	*$12,025*	*$6,667*	*$1,000*	*$4,600*	*$1,750*	*$9,825*		*3.9*	

Notes:

(1) Purchased used..

(2) Purchased second hand, but unused.

(3) Use Codes: 1-currently operating; 2-not currently operating and no intension for future use; 3-not currently in use, but intend to use in future.

(4) Satisfaction levels 1 to 5, with 1=lowest and 5=highest (database also contains satisfaction levels for manufacturer's support).

(5) Future decision codes: 1-purchase the same technology from the same vendor; 2-purchase the same technology from a different vendor; 3-purchase a different technology; 4-do nothing.

(6) "√" indicates that a savings was realized, but not quantified.

(7) Average capital costs do not account for differences in purchase dates.

portion of a degraded solution and replacing it with fresh solution. In both cases, the spent solution is usually either treated on-site or transported to a treatment/disposal site. On-site treatment is not always possible because concentrated wastes may upset treatment facilities designed primarily for treating dilute rinse waters.

Two major categories of solution maintenance were identified during the project: preventative and corrective. Within the NCMS report, preventative solution maintenance refers to the practices that avoid bath contamination or involve monitoring and adjusting of solution chemistry. Corrective solution maintenance refers to the practice of removing contaminants from the bath, whether they are dissolved or particulate, organic or inorganic. Both preventative and corrective solution maintenance involve the use of methods, techniques and technologies. Methods and techniques are typically procedural in nature or low capital items that can be implemented quickly and have an almost immediate payback. Technologies are generally equipment packages that have a moderate to high capital cost and payback periods of one year or greater. Most preventative measures are either methods or techniques. However, some technologies such as an electroless nickel bath automatic replenishment system would also fall into this category. Corrective measures include both methods/techniques such as dummy plating and technologies such as microfiltration (ref. 1).

Within the NCMS report, the corrective technologies, which are generally less familiar to platers, are covered in detail. The methods of preventative and corrective solution maintenance that are commonly applied by plating shops (e.g., filtration) are more familiar to platers and therefore are covered less extensively. Exhibit 10 presents an example (ion exchange) of the Users Survey data summaries contained in the report. Other technologies covered by the report include: microfiltration, acid sorption, ion transfer, membrane electrolysis and diffusion dialysis.

SUBSTITUTE TECHNOLOGIES

The results of the Users Survey show that respondents have made significant strides in reducing or eliminating the use of chlorinated solvents, cadmium, cyanide and chromium. Sometimes referred to as the four Cs, these materials have been identified by EPA as key targets for control within the metal finishing industry. Approximately 60 percent of the respondents attempted material input changes that potentially reduce or eliminate the use of one or more of the four Cs or another pollutant problem. Based on the comments received from respondents, these changes were made in an effort to reduce the impacts of their processes on the environment and worker health, to help meet environmental regulations and to reduce operating costs.

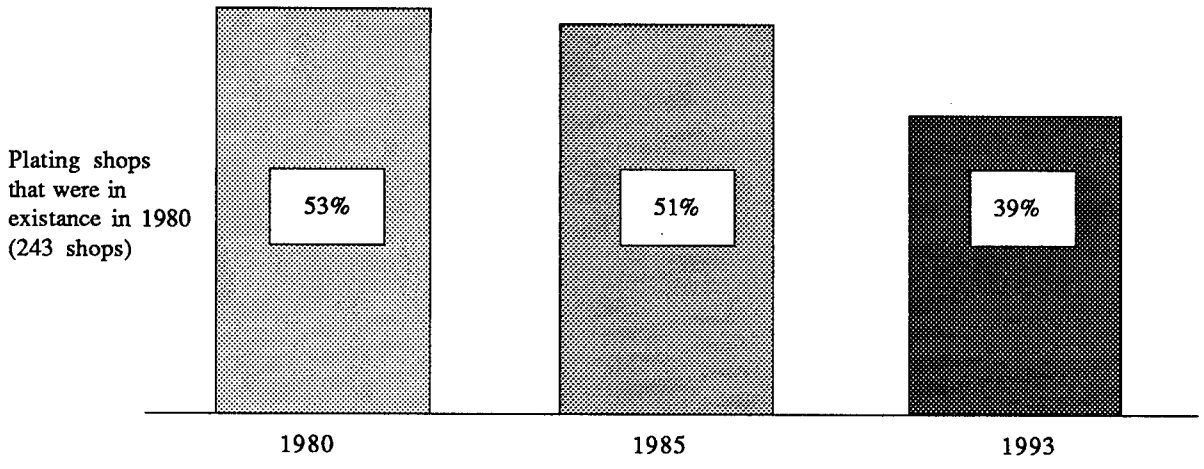
Although most of the material input changes attempted by survey respondents have been successful, there have been some failures and in many cases, even with successful changes, there have been adverse production impacts. The NCMS report summarizes the status of change in these areas and conveys the attitudes and concerns of the respondents.

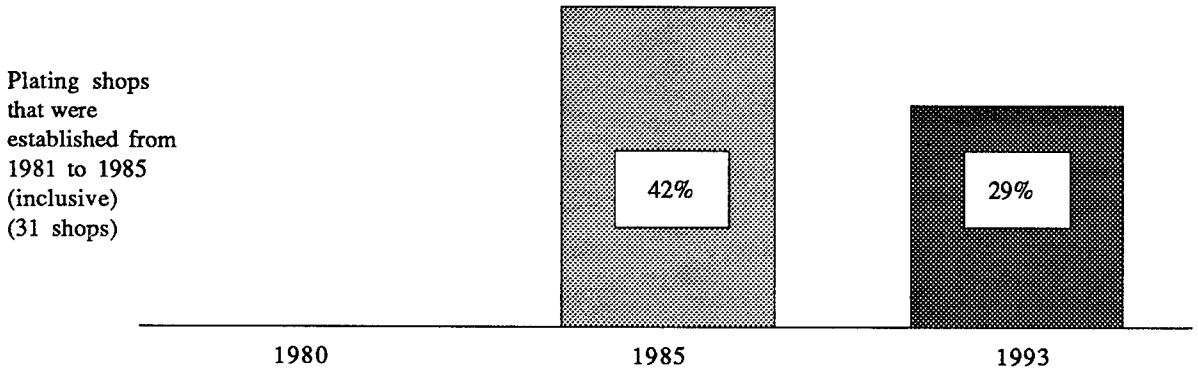
An example of a data summary regarding substitute technologies is presented in Exhibit 11. This exhibit shows that among respondents to the Users Survey, the number of solvent users has changed since 1980. In Exhibit 11, the shops are divided into three groups: (1) those in existence in 1980; (2) those established from 1981 to 1985 (inclusive); and (3) those established from 1986 to 1993 (inclusive). For the older shops, the number of solvent users remained approximately the same from 1980 to 1985 and then declined substantially from 1986 to 1993. In 1980, 53% of the shops used solvent and by 1993 only 39% used solvent. Therefore, 26% of the solvent users in 1980 have eliminated its use. For shops established from 1981 to 1985, the frequency of solvent use was below that of the older shops in 1985 and then from 1986 to 1993, the percentage declined similarly to the declining use rate of the older shops. Thirty-one percent of the shops established from 1981 to 1985 that originally used solvent have eliminated its use. The most recently established shops (1986 to 1993) presently have approximately the same percentage of solvent use as the shops established in 1981 to 1985.

END-OF-PIPE TREATMENT/SLUDGE DISPOSAL/RECOVERY

Various technologies are used by platers for end-of-pipe treatment. These technologies have been grouped during the NCMS project into conventional and alternative methods. Conventional treatment is a series of unit processes used extensively by industry that have provided reliable treatment for many electroplating operations (e.g., metals precipitation using sodium hydroxide and polymer). Alternative treatment methods are sometimes used by platers to reduce capital and/or operating costs or to improve pollutant removal efficiency.

The Federal electroplating and metal finishing pretreatment wastewater standards were developed by EPA by identifying commonly used treatment practices and determining their effectiveness by





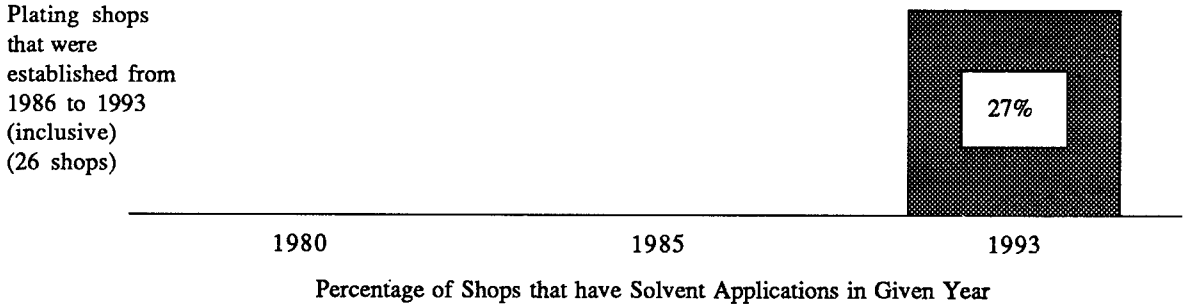


Exhibit 11.
Assessment of Pollution Prevention and Control Technology for Plating Operations
Distribution of Solvent Usage from 1980 to 1993 by Shop Age

collecting effluent data from well operated systems. Conventional treatment was selected by EPA as the standard system. Therefore, for most plating shops, use of conventional treatment will provide sufficient pollutant removal to meet discharge standards. There are two major exceptions to this rule. First, many plating shops are regulated by local discharge standards that are more stringent than the Federal standards and conventional treatment may be insufficient to meet these limitations. Second, the treatment systems selected by EPA for establishing the Federal standards were those systems that EPA determined to be "properly operating facilities." For example, EPA omitted facilities that: (1) did not have well operated treatment processes; (2) had complexing agents (e.g., non-segregated wastes from electroless plating); and (3) had dilution from non-plating wastewaters. As a result, some plating facilities may not meet the properly operated facility criteria used by EPA and may have difficulty meeting Federal standards using conventional treatment.

In cases where conventional treatment is insufficient to meet discharge limitations for a given facility, there are three basic choices for attaining compliance: (1) correct or upgrade the existing processes; (2) make internal changes (e.g., improve rinsing, add recovery, segregation of waste streams) to "normalize" the wastewater, (3) use conventional treatment plus additional treatment (i.e., polishing), and (4) use alternative treatment processes. Information on each of these methods is covered in the NCMS report.

One of the most frequent concerns of platers is the availability and cost of disposal for treatment process residuals (mainly F006 sludge). Respondents to the Users Survey generate an average of 160,000 lbs of sludge per year (median value is 50,000 lbs/yr) and spend an average of $27,300 per year for sludge disposal. The NCMS report provides data from each respondent covering sludge generation rates, the location of their disposal site, the distance that sludges are hauled, the solids concentration of the sludge, and the disposal charges. Many platers (33% of the respondents) are using off-site metals recyclers as an alternative to land disposal of their treatment residuals and spent process solutions. The NCMS report identifies the recycling companies used by the respondents, presents an overview of their recovery processes (provided by the recycling companies themselves), presents criteria for determining the applicability of off-site recycling, and compares the costs of recycling to land disposal.

SELECTED CONCLUSIONS DRAW FROM SURVEY RESULTS

The NCMS report contains such a wealth of information and data that a complete analysis of the results would take years to perform. One of the reasons for including a disk copy of the database with the report is to allow platers, vendors, researchers and other interested individuals the opportunity to perform their own analyses and develop their own conclusions. The following are conclusions drawn from several key areas of the survey results by the authors of this paper.

Pollution Control Technology Changes from 1975 to 1993

Pretreatment standards for the electroplating industry were first established in 1974, but it was not until promulgation of 40 CFR 413 on September 7, 1979 that Electroplating Categorical Pretreatment Standards became a reality. Several years later, EPA promulgated the Metal Finishing Categorical Standards (40 CFR 433). Prior to the existence of Federal standards, plating shops were regulated locally (if at all), presumably, with wide variation in effluent limitations and levels of enforcement. Most plating shops did not have treatment systems for cyanide destruction and metals removal. Approximately 12 percent of the surveyed plating shops that were in business in 1975 (excludes zero discharge shops) indicated that their initial treatment system was installed by that year. Exhibit 12 presents a breakdown of the data in five year increments. These data indicate that by 1985, after the compliance dates for Federal regulations, 70 percent of the surveyed plating shops had installed their initial treatment system (excludes zero discharge shops).

Exhibit 12. Distribution of End-of-Pipe System Installation Dates

Initial Treatment System Installed By:	Percent of Shops*
1975	16%
1980	32%
1985	70%
1990	95%
1993	98%

*Percent of shops in business by the date indicated. Excludes zero discharge shops.

Most initial treatment systems were installed between 1980 and 1985, although by 1985 there were

still a substantial number of shops that had not installed their initial system.

Most plating shops installed conventional treatment to meet Federal regulations. Although it is difficult to assess exactly the respondents' data concerning end-of-pipe technology, it appears that an early trend occurred during the late 1970's and early 1980's when a significant percentage of shops attempted to utilize advanced technology in place of conventional treatment. These early efforts generally resulted in failure and the shops later resorted to conventional systems. One prominent example of this trend is the implementation of high surface area electrowinning as an end-of-pipe technology. Between 1979 and 1983, approximately 4 percent of the shops (excludes zero discharge shops) in existence installed this technology at an average cost of $66,360. Only one of these systems is currently operating and that unit was extensively modified by its user. Early failures such as these appear to have had a negative impact on advanced technology. No single technology has since emerged as a significant replacement for conventional treatment. In fact, changes in end-of-pipe methods have tended toward simpler technologies. Proof of this statement is that the most significant technology change with respect to end-of-pipe treatment since 1975 is the use of sludge dehydration equipment (i.e., sludge dryers) to reduce the volume of sludge shipped off-site (29 percent of the respondents have installed this relatively simple technology with approximately 80% purchased between 1988 and 1993). Approximately 10% of all the shops surveyed presently rely on non-conventional treatment methods (includes zero discharge shops). The most popular non-conventional end-of-pipe treatment methods (ion exchange, evaporation, and membrane technology) are covered in the NCMS report.

It should be noted that the majority of respondents to the Users Survey were job shops. More frequent use of advanced end-of-pipe technology may exist in other industry segments such as captive aerospace facilities.

Approximately 8% of the shops surveyed have attained zero discharge. These shops are generally smaller and less diverse than the shops with discharges. The average and median number of employees at the zero discharge shops is 16 and 15, respectively (for all shops the employee figures are: average = 67 and median = 35). Of the zero discharge shops, 58% are primarily hard chrome platers. The hard chrome process is one of the easiest to operate as a close-loop because of the high ratio of evaporation to drag-out (i.e., permits use of spray rinsing over the bath, drag-out recovery rinsing, etc.). The remaining zero discharge shops operate various metal finishing processes, including: cadmium, nickel and zinc plating; conversion coating; and aluminum finishing. Details of their metal finishing processes and pollution prevention and control technologies are contained in the NCMS database and summarized in the NCMS report.

Status of Pollution Prevention

Pollution prevention has emerged as an important method of attaining compliance and reducing operating costs. Widespread success has been achieved using simple methods and techniques that reduce drag-out losses and rinse water use. More than 90 percent of the shops indicated that they utilize these tools and have benefited from them. Although some shops have had great success with chemical recovery technologies, these have generally been much less frequently applied than drag-out and rinse water reduction efforts. The most successful of the chemical recovery technologies is atmospheric evaporation, which is generally regarded as the most simple to use. Bath maintenance technologies are less frequently used than are chemical recovery and have generally been less successful. Exhibit 13 shows ratings given by the respondents for some common pollution prevention methods.

Causes of Failure for Some Advanced Technology Applications

Many installations of chemical recovery technologies and advanced bath maintenance have not been successful (approximately 30 to 40 percent). The survey respondents indicate that failure is most frequently caused by: maintenance problems, misapplication of the technology (often due to ignorance on the part of manufacturer's representatives and/or the plating shop personnel), poor design, inability to purchase replacement parts (usually manufacturer went out of business), poor technical support by manufacturers, improper operation of technology by shop personnel, technically too complex for employees, chemical recovery caused a build-up of contaminants in plating bath, recovery process destroyed plating chemicals, recycled water was of insufficient quality, chemical product was insufficiently concentrated for return to plating bath, inadequate capacity, and high residuals generation.

Maintenance problems were the most frequent cause of system failure. The maintenance problems most often reported with advanced technologies are: low quality system components, mechanical problems with pumps and valves, damage to or fouling of components by plating chemicals, and excessive labor requirements for system cleaning. Exhibit 14 indicates the operational status of the chemical recovery and bath maintenance technologies purchased by survey respondents.

Exhibit 13. Ratings for Pollution Prevention Methods and Technologies

Method	Average Rating*
Good Operating Practices (all methods)	3.9
Drag-Out Reduction (all methods)	3.5
Rinse Water Reduction (all methods)	3.8
Chemical Recovery:	
Atmospheric Evaporators	3.8
Vacuum Evaporators	3.5
Ion Exchange	3.2
Electrowinning (all)	3.1
Electrowinning (excluding high surface area)	3.4
Electrodialysis (one data point)	1.0
Reverse Osmosis	3.0
Weighted Avg. for Chemical Recovery	*3.4*
Bath Maintenance:	
Microfiltration	–
Ion Exchange	3.9
Acid Sorption	4.3
Ion Transfer	3.5
Membrane Electrolysis	3.0
Diffusion Dialysis	–
Weighted Avg. for Bath Maintenance	*3.7*

Number of data points shown in parenthesis)
*(1 to 5 with 5 being the most successful)

Most Pressing Environmental Problems and Environmental Technology Needs

The respondents to the Users Survey indicated that their most pressing environmental problems were (percent identifying problem shown in parenthesis): increasing costs of compliance (73%); frequently changing regulations (55%); meeting effluent discharge standards (38%); eliminating the use of solvents (25%); meeting air emissions standards (24%); and lack of disposal sites (19%).

The environmental technology needs identified by the respondents were (percent identifying need shown in parenthesis):

- Alternatives to solvent cleaning/degreasing (12%)
- Better cyanide plating alternatives or controls (11%)
- Improved methods for water reduction, closed-loop processing, source reduction, recycling or zero discharge (9%)
- Better cadmium plating alternatives or controls (8%)
- Improved methods or more affordable end-of-pipe treatment (7%)
- Alternative to chromium metal finishing (includes all uses such as anodizing, plating and conversion coating) (6%).

Exhibit 14. Operational Status Of The Chemical Recovery And Bath Maintenance Technologies Purchased By Survey Respondents

Technology	% of Technologies That are Still Operating	Average Age of Operating Units (years)	Average Age of Non-Operating Units (years)	Age of Oldest Operating Unit (years)
Recovery:				
Atm Evap.	90%	5.4	6.1	18
Vacuum Evap.	74%	8.3	13.8	15
Ion Exchange	61%	6.5	5.4	18
Electrowinning	59%	5.5*	6.9	13*
Electrodialysis	0%	--	9.0	--
Reverse Osmosis	50%	4.0	9.3	6
Bath maintenance:				
Microfiltration	0%	4.4	1.0	--
Ion Exchange	73%	9.0	1.0	18
Acid Sorption	100%	4.9	--	15
Ion Transfer	70%	5.0	7.7	7
Membrane Electrolysis	60%	--	4.0	9
Diffusion Dialysis	--	--	--	--

*Excludes 43 year old homemade silver recovery unit that is still operating.

Future NCMS Survey Efforts

The initial NCMS project activities have established a benchmark assessment of pollution prevention and control technology for plating operations. The project products will assist platers in various ways, including: sharing ideas for drag-out and water use reduction; providing useful technology descriptions; providing an explanation of EPA's pollution prevention concept; summarizing cost and performance data from actual technology installations involving chemical recovery, bath maintenance and waste treatment; summarizing plater's experiences with alternative process chemicals that may reduce the hazardousness of the plating processes and the resultant wastes; and providing detailed data for off-site metals recycling options. This assessment has been made possible by the efforts of numerous platers, technology vendors and other interested parties. Hopefully, this industry will continue these efforts by participating in updates of the assessment. Each iteration of the assessment process will refine our technical knowledge and lead to more cost effective means of complying with environmental regulations.

References:

1. Cushnie, George, *Assessment of Pollution Prevention and Control Technology for Plating Operations*, National Center for Manufacturing Sciences, Ann Arbor, MI, 1994.

2. USEPA, *Guidance Manual for Electroplating and Metal Finishing Pretreatment Standards*, Effluent Guidelines Division, Washington, DC, 1984.

Thin-Film Sulfuric Acid Anodizing as a Replacement for Chromic Acid Anodizing

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Chromic acid has long been used to produce a thin, corrosion resistant (Type I) coating on aluminum. Following anodizing, the hardware was sealed using a sodium dichromate solution. Sealing closes up pores inherent in the anodized coating, thus improving corrosion resistance. The thinness of the brittle coating is desirable from a fatigue standpoint, and chromium was absorbed by the coating during the sealing process, further improving corrosion resistance. Unfortunately, both chromic acid and sodium dichromate contain carcinogenic hexavalent chromium. Sulfuric acid is being considered as a replacement for chromic acid. Sulfuric acid of 10-20% concentration has traditionally been used to produce relatively thick (Types II and III) or abrasion resistant (Type III) coatings. A more dilute, that is five weight percent, sulfuric acid anodizing process, which produces a thinner coating than Type II or III, with nickel acetate as the sealant has been developed. The process was evaluated in regard to corrosion resistance, throwing power, fatigue life, and processing variable sensitivity, and shows promise as a replacement for the chromic acid process.

Introduction

Aluminum hardware at Rocketdyne is chromic acid anodized primarily for corrosion resistance, which sealing further improves. Therefore, corrosion testing is a necessary step in evaluating replacements for chromic acid for anodizing and sodium dichromate for sealing. Chromic acid anodized coupons must pass a 336-hour salt fog test per ASTM B117, so thin-film sulfuric acid anodized coupons were subjected to the same test. Galvanic corrosion has been a problem in the past, so the relative performance of the anodized coatings under galvanic conditions was examined. Also, the atmospheric corrosion resistance of the two anodized coatings was evaluated using actual hardware.

Published literature has shown that fatigue life is dependent upon anodized coating thickness - the thicker the coating, the shorter the fatigue life and the lower the endurance limit (Reference 1). This is due to the brittleness of the aluminum oxide layer. The fatigue specimens anodized in this study at various thin-film sulfuric anodizing parameters showed a wide range of endurance limits, so the relationship between endurance limit and anodized coating thickness was investigated to determine a maximum allowable coating thickness.

The chromic acid anodizing process is very tolerant of variations in processing variables. The anodizing bath temperature can range from 90 to 105°F. Manufacturing practice is to keep the hardware in the chromic acid anodizing bath until the current drops down to zero indicating that the reaction has stopped. This practice suggests that the chromic acid anodized coating goes to completion, that is, the coating reaches a thickness where the reaction stops and the coating does not get too thick. Also, all alloys are anodized under the same parameters and it would be desirable if the same could be done with thin-film sulfuric anodizing. It was necessary to determine the sensitivity of thin-film sulfuric coating thickness to processing variables such as bath temperature, anodizing voltage, and anodizing time, and whether the process goes to completion to develop parameters and tolerances for thin-film sulfuric acid anodizing. Throwing power - the ability to anodize in blind holes and passageways - of thin-film sulfuric anodizing was also evaluated and compared to the throwing power of chromic acid.

Procedure

Sulfuric Acid Anodizing

Coupon specimens were tightly positioned in an aluminum anodizing rack and processed as follows in a laboratory-scale line:

1) Degrease - 20 vol. percent Turco 3878 LF-NC at 145-160°F for 10 minutes;
2) Rinse in deionized (D.I.) water spray;
3) Alkaline clean - 6-8 oz./gal. Turco 4090 at 150-190°F for 7 minutes;
4) Rinse in D.I. water spray;
5) Deoxidize - 16 oz./gal. Turco Smut-Go NC plus 4 oz./gal. HNO_3 at room temperature for 15 minutes with air agitation;
6) Rinse in D.I. water spray;
7) Anodize - 3-7 weight percent sulfuric acid at 66-72°F at 15-25 volts for 5-120 minutes with air agitation and lead cathodes on all four sides of the tank, voltage slowly ramped from 0 to voltage of interest;
8) Rinse in D.I. water spray;
9) Seal - 2% Novamax Anoseal 1000 nickel acetate solution at 160-190°F for 10 minutes (with mechanical stirring prior to adding specimens);
10) Rinse - D.I. water at 175-185°F for 10 minutes.

The panels for galvanic corrosion testing and the hardware for atmospheric corrosion were processed on a manufacturing line at Rockwell Space Systems Division at Downey, CA to parameters similar to those above.

Chromic Acid Anodizing

Control specimens were chromic acid anodized on the Rocketdyne production line per Rocketdyne specification RA0109-021, Type I Chromic Acid Anodizing. The procedure consists of degreasing, alkaline cleaning, deoxidizing, anodizing, and sealing. The anodizing is done in 4-8% chromic acid at 90-105°F at 40±1 volts. The hardware is left to anodize until the voltage drops to zero. Sealing is done in 1.3-2.2 oz./gal. sodium dichromate at 195-205°F for 20 minutes.

Corrosion Testing

Salt fog corrosion testing was done at Rockwell Space Systems Division. Five panels 10 in. x 3 in. x 0.050 in. were tested for each anodizing and sealing condition. The alloy 2024 was used, as it is inherently the least corrosion-resistant and produces the thinnest anodized coating of the alloys of interest. The panels were racked at an angle of 5% from vertical and exposed to a 5% salt fog for 336 hours (14 days). The panels were examined visually at up to 100 times magnification for corrosion and evaluated with respect to ASTM B117 which states, "...test specimens shall show no more than a total of 15 isolated spots or pits, none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces; nor more than 5 isolated spots or pits none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces: except those areas within 0.062 inch from identification marks, edges, and electrode contact marks remaining after processing." The sulfuric acid specimens were anodized using 5% sulfuric acid, 25 volts, at 70°F for 20 minutes. The sealing was done using sodium dichromate or Anoseal 1000. The chromic acid specimens were anodized per RA0109-021.

The galvanic corrosion specimens consisted of 4 in. x 4 in. x 0.030 in. anodized panels of 2024, 6061, 7075, and Tens-50 alloys. One panel of each alloy was anodized in sulfuric acid and one of each in chromic acid for a total of eight panels. Each panel had a hole 0.25 in. in diameter punched in the center. Through this hole was fitted a screw, a nut, and two washers, all of brass, to form a galvanic couple (Figure 1). The panels were exposed to a 5% salt fog environment like the salt fog corrosion specimens above except that the specimens were exposed for 168 hours.

The atmospheric exposure test specimens consisted of scrapped valve housings, which are Tens-50 castings. The housings are approximately 12 inches in diameter by 4 inches thick. One specimen was anodized in sulfuric acid and one in chromic acid. The hardware was initially exposed to a suburban environment for five months, and then to a coastal environment for nine months.

Fatigue Testing

High cycle fatigue testing was performed at Metcut Research Associates, Inc., Cincinnati, Ohio under the following conditions:

Mode - cantilever load control;
Stress ratio - R = 0.1
Frequency - 30 Hz
Waveform - sinusoidal
Atmosphere - air
Temperature - room
Machine - calibrated Sonntag SF-1-U rotating mass type universal fatigue

Stress levels for the different alloys were chosen such that failures would be evenly distributed between 10^4 and 10^7 cycles. Flexural fatigue specimens were machined from 0.08 inch thick sheet of each alloy, 2024-T3, 6061-T4, and 7075-T6.

Throwing Power

A test specimen for evaluating throwing power consisted of a flat 3 in. x 3 in. x 0.030 in. 2024 aluminum panel with a nylon block screwed tightly to it, Figure 2. The nylon block has a groove machined into it so that when it is attached to the aluminum panel, it simulates a blind hole in a piece of hardware. The specimens were specifically designed to be easy to fabricate and analyze. The block can be removed following anodizing and reused with other panels. The 2024 alloy was chosen for this study because, of the three wrought alloys evaluated, it is the hardest to anodize since it consistently produces the thinnest coating. Panels were anodized in 5% sulfuric acid at 70°F and 20 volts for times of 5 to 60 minutes. A panel was also anodized in chromic acid per RA0109-021.

Results and Discussion

Corrosion Testing

Table 1 shows the results of salt fog corrosion testing. Alloy 2024 was used for this test because it has the least corrosion resistance and produces the thinnest coating at any given anodizing condition of the alloys being evaluated. This test compared the effectiveness of thin-film sulfuric acid anodizing and the effectiveness of nickel acetate sealing. The chromic acid specimens showed no pitting and were oxide-free over the entire surface of the panels. The thin-film sulfuric specimens sealed with sodium dichromate showed one pit for the set with the remainder of the panels being oxide-free. The thin-film sulfuric specimens sealed with nickel acetate showed one pit for the set with some edge corrosion, but edge corrosion is exempted by ASTM B117. Although the sulfuric acid specimens showed a pit and the nickel acetate specimens showed some edge corrosion, these specimens passed ASTM B117 making them acceptable processes.

All galvanic corrosion specimens showed severe corrosion after 168 hours in salt fog. It was not expected that anodizing would provide much protection against galvanic corrosion. Based on visual examination of the panels, and cross-sections of the corroded area, it was concluded that the chromic acid anodized panels and the sulfuric acid anodized specimens performed similarly.

After five months in a suburban environment, the sulfuric acid anodized hardware and the chromic acid anodized hardware showed no degradation. The hardware had experienced a little rain and fog. After

nine months in a coastal environment, the anodized portions of the hardware showed no degradation while the areas of the hardware that were not anodized showed the beginnings of corrosion.

Table 1. Results of salt fog testing per ASTM B117 on anodized 2024 aluminum

Anodizing Process	Sealant	# Pits/ Set	Pass/ Fail	Coating Thickness, mils	Comments
Chromic	Sodium Dichromate	0	Pass	0.09	Oxide-Free Panels
Thin-Film Sulfuric	Sodium Dichromate	1	Pass	0.14	Oxide-Free Panels
Thin-Film Sulfuric	Anoseal 1000	1	Pass	0.12	Some Edge Corrosion

Fatigue Testing

Figures 3 through 5 show the plots of anodized coating thickness versus endurance limit for the alloys 2024, 6061, and 7075. Clearly, there is a relationship between coating thickness and fatigue life for thin-film sulfuric acid anodized specimens and it is possible to achieve an endurance limit equal to or greater than that of chromic acid anodized aluminum given a thin enough coating. By comparing the endurance limit of the chromic acid anodized specimens with the sulfuric acid anodized specimens, it can be seen that for all three alloys, the endurance limit begins to fall below that of the chromic acid anodized specimens at a coating thickness greater than 0.2 mils. This agrees with published observations (Reference 1) where it was found that anodized coating thicknesses between 0.2 and 0.3 mils began to affect fatigue life.

Throwing Power

Figure 6 shows the results of the throwing power tests. The sulfuric acid specimens showed a decrease in coating thickness with increasing depth into the blind hole. The coating thickness at the base of the hole varied from 24 to 44% of the coating thickness at the outside surface of the hole. In general, the ratio of coating thickness at the base of the hole to the coating thickness on the outside surface decreases with increasing anodizing time. This shows that even by increasing the anodizing time, the thickness inside the hole never catches up to the outside thickness, suggesting that the process is not going to completion. As a comparison, a specimen was anodized in chromic acid and it too showed a decrease in coating thickness with increasing depth into the blind hole. These results show that the throwing power of 5% sulfuric acid is no worse than the throwing power of chromic acid.

Process Tolerance

The effect of various processing variables on coating thickness is shown in Figures 7 through 9. Figure 7 shows the effect of changes in temperature with voltage and time held constant. The thin-film sulfuric acid process is fairly temperature sensitive, and to the same degree for all three alloys. If all alloys are to be anodized under the same conditions, the temperature of the bath should be kept at 72°F or less when using 20 volts for 20 minutes to keep the coating thickness at 0.2 mil or less for fatigue life. The process is also sensitive to voltage, especially the 6061 and 7075 alloys, Figure 8. If all alloys are to be anodized under the same conditions, at 70°F for 20 minutes, the voltage should be kept at 20 volts or less to keep the thickness at 0.2 mil or less. The results of the time versus thickness tests, Figure 9, show a strong dependence of thickness on time. Optimum anodizing conditions for a 5% sulfuric solution would be 70°F and 20 volts for 20 minutes. The tolerance on these variables is tight: ± 1 volt; ± 2°F; and ± 2 minutes.

Coating thicknesses of the 6061 alloy increased linearly to 0.96 mil in 120 minutes (Figure 9), strongly suggesting that the process does not go to completion with this alloy. Coating thicknesses of the 2024 alloy increased parabolically to 0.41 mil in 120 minutes. If the process does go to completion with this alloy, it would be at a point where the coating thickness is much greater than the recommended 0.2 mil. During anodizing of the coupons, the current slowly increased with time, also indicating that the process is not going to completion. In chromic acid anodizing, the current drops to zero, indicating that the process is complete. If the thin-film sulfuric acid anodizing process is to be successfully implemented, close control of the anodizing time, temperature, and voltage must be maintained, especially if all alloys are anodized with the same parameters.

Conclusions

1. Thin-film sulfuric acid anodizing with nickel acetate sealing provides adequate corrosion resistance per ASTM B117.

2. Thin-film sulfuric acid anodized 2024, 6061, and 7075 alloys can have the same or greater fatigue life as chromic acid anodized specimens provided the coating thickness is 0.2 mil or less.

3. The throwing power of 5% sulfuric acid is comparable to the throwing power of chromic acid.

4. The 5% sulfuric acid anodizing process does not go to completion.

5. Close control of anodizing time, voltage, and temperature is very important to prevent overly thick coatings, especially if all alloys are to be anodized with the same parameters.

Reference

1. Stickley, G.W., "Additional Studies of Effects of Anodic Coatings on the Fatigue Strength of Aluminum Alloys", *Proceedings*, American Society for Testing Materials, Vol. 60, 1960, pp. 577-588.

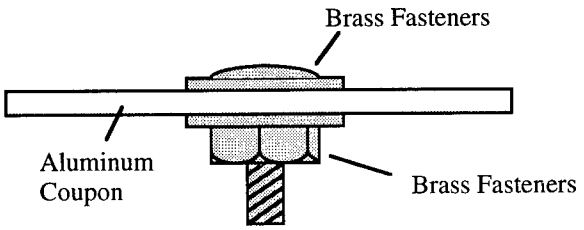

Figure 1. Cross-section of galvanic corrosion test specimen.

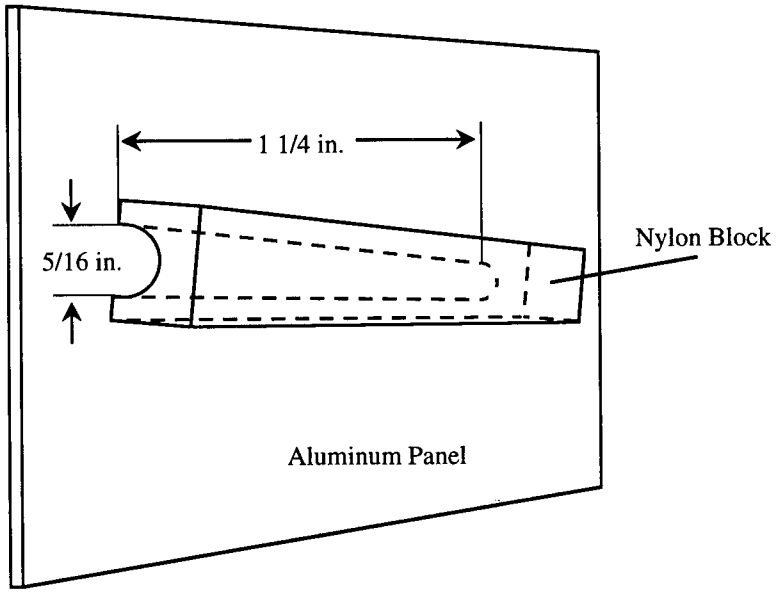

Figure 2. Throwing power test specimen.

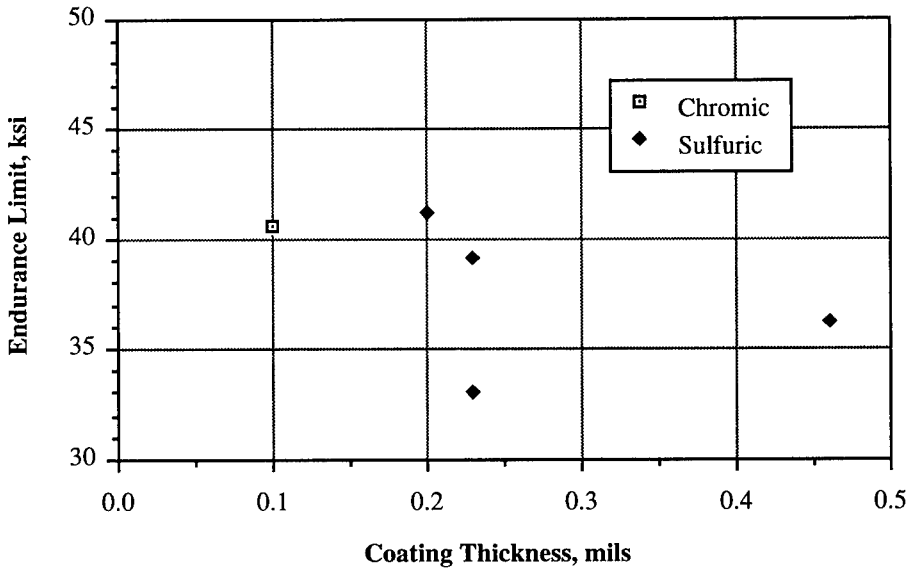

Figure 3. Endurance limit versus coating thickness of 2024 aluminum anodized in chromic and sulfuric acids.

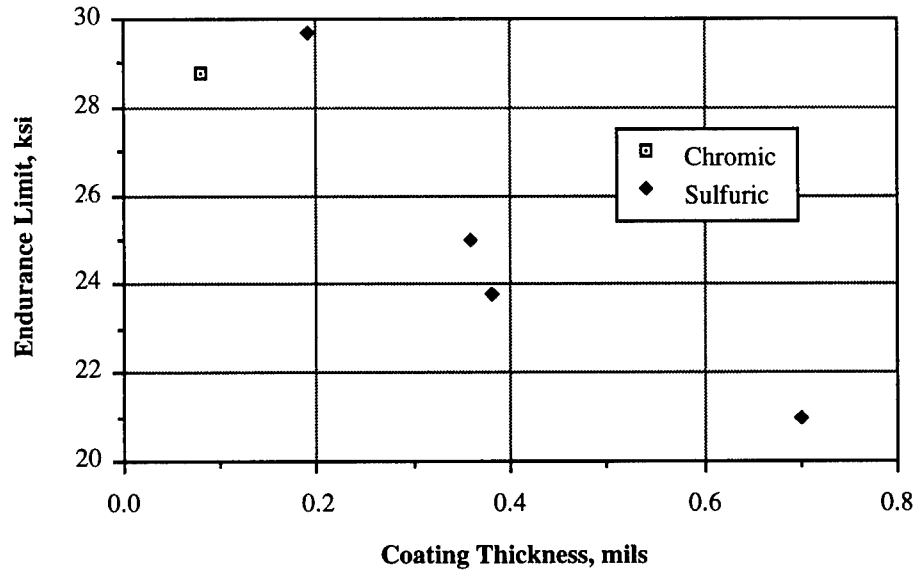

Figure 4. Endurance limit versus coating thickness of 6061 aluminum anodized in chromic and sulfuric acids.

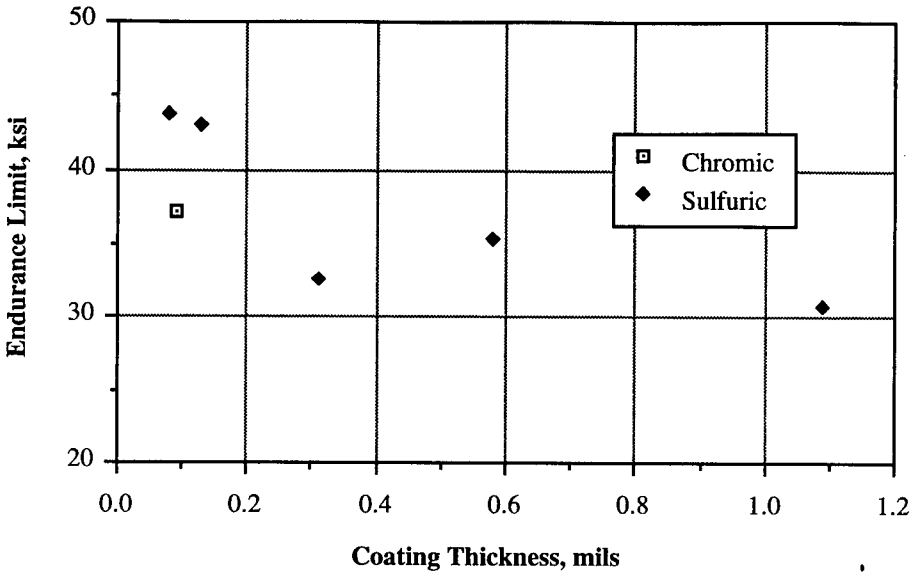

Figure 5. Endurance limit versus coating thickness of 7071 aluminum anodized in chromic and sulfuric acids.

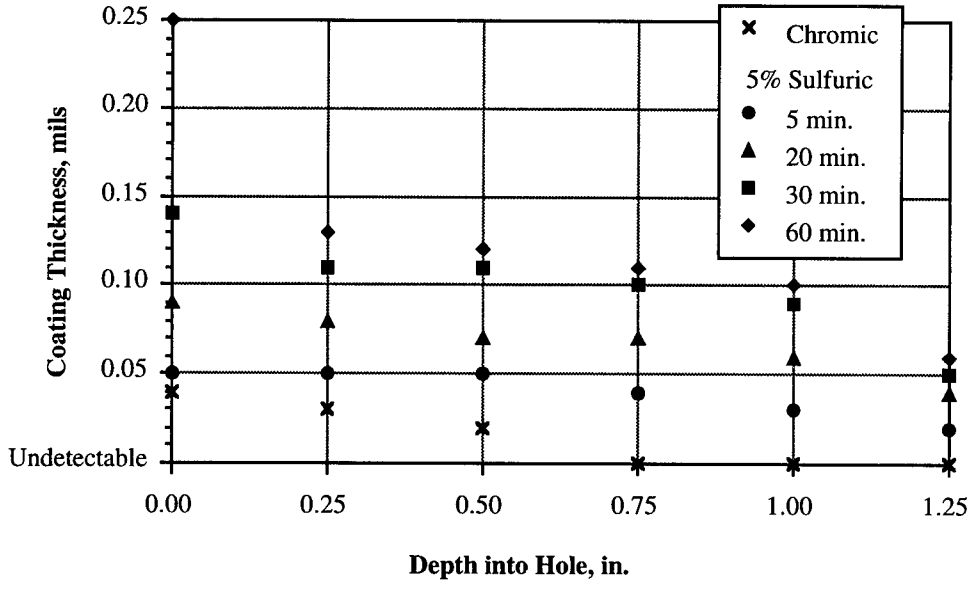

Figure 6. Anodized coating thicknesses versus depth into blind hole of throwing power test specimens of 2024 alloy. Sulfuric acid specimens were anodized at 70°F with 20 volts.

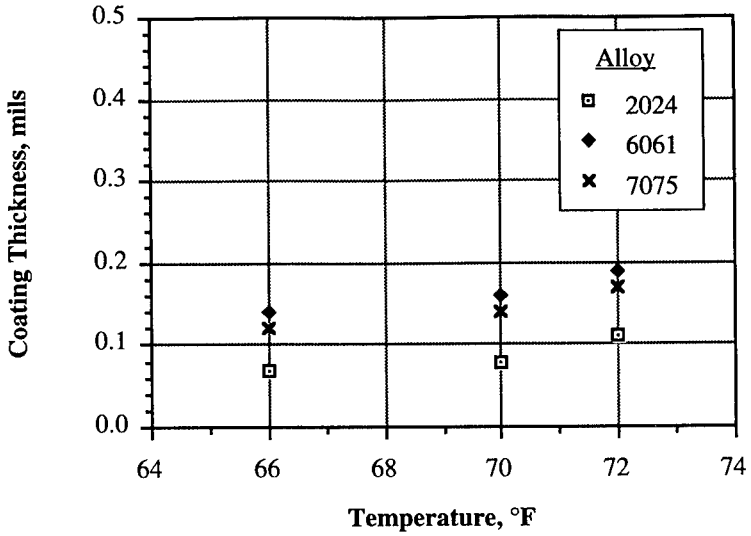

Figure 7. Effect of temperature on coating thicinesses of various alloys anodized in 5% sulfuric acid for 20 minutes at 20 volts.

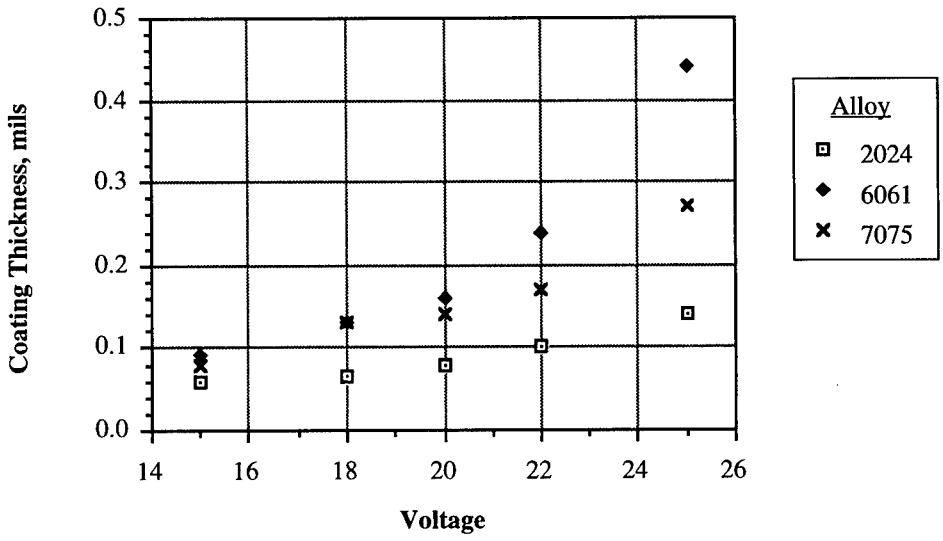

Figure 8. Effect of voltage on coating thicinesses of various alloys anodized in 5% sulfuric acid for 20 minutes at 70°F.

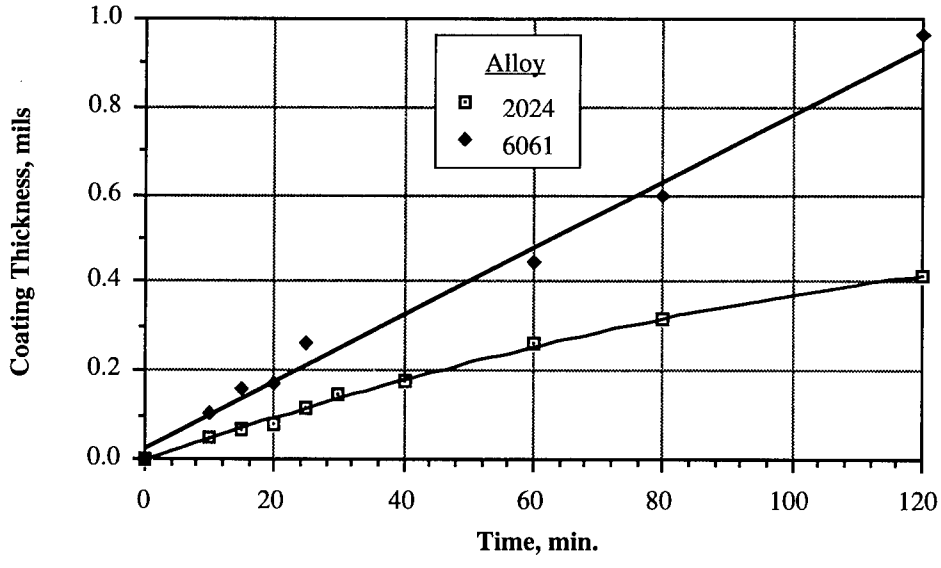

Figure 9. Effect of time on coating thicinesses of various alloys anodized in 5% sulfuric acid at 70°F and 20 volts.

On a worldwide basis, the most widely used HCFC refrigerant is R-22 which has a low ozone depletion potential[5]. Candidate alternatives for R-22 are being evaluated by a consortium of manufacturers in a project called *ARI's R-22 Alternative Refrigerants Evaluation Program*[6]. DuPont, Allied Signal, and other refrigerant producers have made sample quantities of various HFC refrigerants candidates for this work. However, it is not yet clear which candidates will eventually become the replacements for R-22 and production quantities of the replacement refrigerants are not expected to be available until 1996. Consequently, there are no plans (within the scope of the present project) to retrofit any test equipment that utilizes R-22.

Proprietary Refrigerants

A few of the equipment types at AGMC operate using a proprietary refrigerant which is a combination of CFC-13, CFC-14, CFC-114 and R-740 (argon). The manufacturer of this equipment has developed a drop-in replacement which is a different proprietary mixture of HCFC, HFC, and hydrocarbon gases that substantially reduces the ozone depletion potential. However, there are no plans to retrofit any of AGMC's test equipment that use this proprietary refrigerant as part of the present project.

LUBRICANTS

The minerals oils normally used with CFC refrigerants are not miscible in the HFC refrigerants. After considering several alternatives of various lubricant types including alkylbenzenes and poly-alkylene glycols (PAGs), the leading independent compressor manufacturers selected polyol ester oils (POEs) for use with HFC refrigerants. However, at this point in time, Copeland, Bristol, and Tecumseh each recommend a different polyol ester for use in their respective products. Copeland endorses Mobil's EAL™ Arctic 22 CC, Tecumseh approves Castrol's SW-32, and Bristol favors ICI's RL32S. These compressor manufacturers are now working to qualify additional candidates. For the present work at AGMC, the selection of the polyol ester lubricant is keyed to the compressor manufacturer except for the R-23 applications as described in the paragraph which follows.

The polyol ester that appears to be the best choice for use with refrigerant R-23, regardless of the compressor manufacturer, is CPI's Solest® LT-32. Preliminary tests indicate that Solest® LT-32 can be used with R-23 in low temperature applications *without* the addition of a hydrocarbon (such as propane) that has traditionally been used with mineral oils. Another factor in the decision to select Solest® LT-32 for this project is that procurement regulations make it difficult for the Air Force maintenance staff to obtain propane for these uses. Table 1 summarizes the alternative refrigerants and lubricants applied to the retrofit of AGMC's test equipment.

SYSTEM COMPONENTS

As previously mentioned, compressor manufacturers are beginning to market compressors and condensing units designed specifically for use with R-134a and R-404a. Compressors previously used for applications with R-13 and R-503 can be used with R-23 after the mineral oil is thoroughly removed and replaced with polyol ester oil.

Beyond the compressor and the heat exchangers, the other system components that must be considered include thermostatic expansion valves, capillary tubes, oil separators, suction accumulators, liquid receivers, solenoid valves, hot gas bypass valves, pressure relief valves, and filter-driers (Figure 1). Suppliers of these various components already have products on the market that are intended for use with the HFC alternative refrigerants listed in Table 1.

Table 1. Alternative Refrigerants and Lubricants

CFC Refrigerant	HFC Refrigerant	Polyol Ester Lubricant
R-12	R-134a	Mobil EAL™ Arctic 22 CC (Copeland) ICI Emkarate® RL-32S (Bristol) Castrol Icematic® SW-32 (Tecumseh)
R-500		
R-502	R-404a (SUVA® HP62)	
R-503	R-23	CPI Solest® LT-32
R-13		

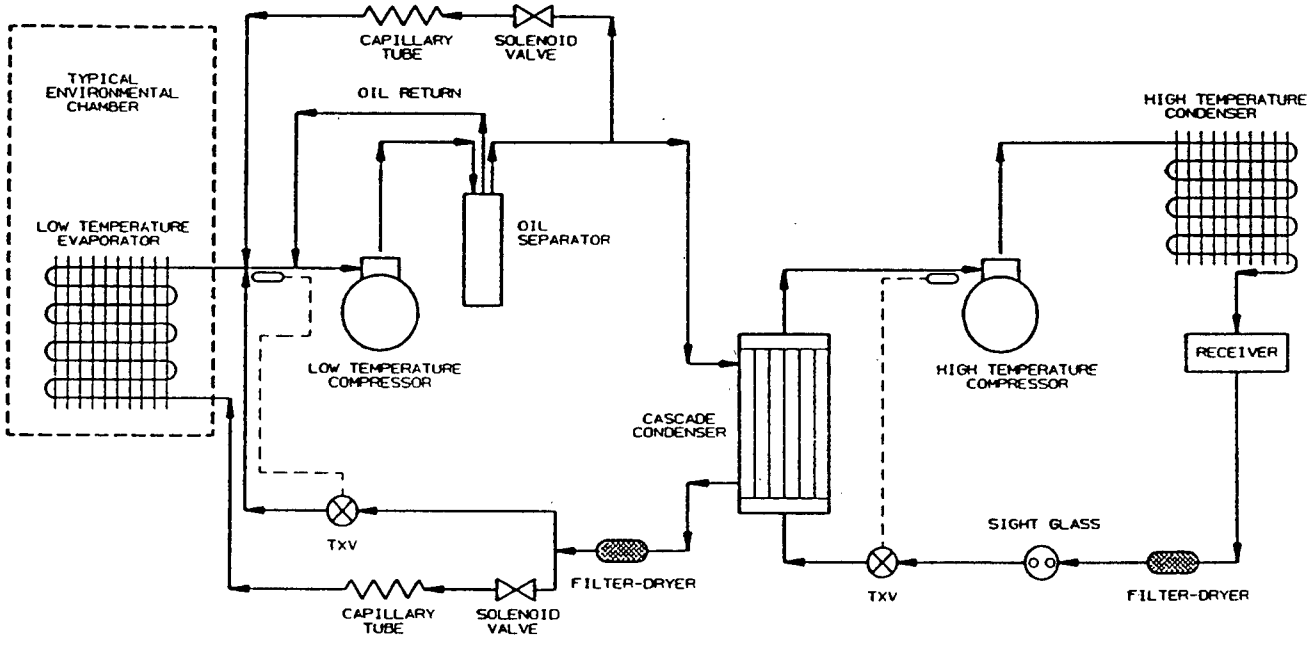

Figure 1. Typical Cascade Refrigeration Circuits

Cadmium Plating Replacements

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Abstract

The Boeing Company has been searching for replacements to cadmium plate. Two alloy plating systems seem close to meeting the needs of a cadmium replacement. The two alloys, zinc-nickel and tin-zinc are from alloy plating baths; both baths are neutral pH. The alloys meet the requirements for salt fog corrosion resistance, and both alloys excel as a paint base. Currently, tests are being performed on standard fasteners to compare zinc-nickel and tin-zinc on threaded hardware where cadmium is heavily used. The Hydrogen embrittlement propensity of the zinc-nickel bath has been tested, and just beginning for the tin-zinc bath. Another area of interest is the electrical properties on aluminum for tin-zinc and will be discussed. The zinc-nickel alloy plating bath is in production in Boeing Commercial Airplane Group for non-critical low strength steels. The outlook is promising that these two coatings will help The Boeing Company significantly reduce its dependence on cadmium plating.

Introduction

Boeing has been studying cadmium replacements for over 10 years. The original impetus came when Japan strictly limited and then outlawed the use of cadmium after elevated levels of cadmium were found in marine life. Cadmium accumulates in the liver and kidneys; therefore, long term exposure is harmful to humans. Cadmium is most frequently plated from a cyanide bath, and the acute toxic affects of cyanide are well-known[1]. In 1990 Environmental Protection Agency's (EPA) "33/50" Plan for reduction of 17 chemicals including cadmium and cyanide became a goal for Boeing to reduce its hazardous chemical usage. Heretofore, Boeing has been looking for a replacement to cadmium.

Cadmium has some unique properties. One of its most useful properties is its lubricity. Cadmium plate smears and lubricates as it is pushed or torqued against itself or other metals, hence its usefulness on fasteners and gears. The sacrificial corrosion tendency is also a valuable asset of cadmium; cadmium is used on steel fasteners, gears, and various steel parts which need protection from corrosion. The ease of application and sacrificial corrosion properties of cadmium have made it the material of choice for dissimilar metal stackups.

Two alloy plating systems are the promising candidates for replacing cadmium at Boeing. Zinc-nickel alloy (90-10%) plated from a neutral chloride bath has been in production for a year in the Boeing Commercial Airplane Group. The typical parts plated in the zinc-nickel bath are clips and brackets, mostly flat, low alloy steel parts. The second alloy plating being pursued is tin-zinc alloy (80-20%) from a neutral, tin^{+2}, bath. This system is still being tested on a laboratory scale. This paper will discuss the properties

such as: corrosion resistance, adhesion, paint adhesion, torque tension, hydrogen embrittlement, and electrical resistance of these alloy plates.

Technical Accomplishments:

Corrosion Resistance.

One of the most important aspects of cadmium plate is its corrosion resistance. Any replacement must meet or exceed its performance. Boeing uses the requirement of no corrosion products after 96 hours of salt fog testing per ASTM B117[2] as the determination of corrosion protection, the same criteria as cadmium, QQ-P-416, type II. Unofficially, 500 hours and no red rust is also a criteria to beat. Zinc-nickel and tin-zinc alloys (with a chromate conversion coating) have been shown to pass the 96 hours of salt spray, and also to pass 500 hours typically with no red rust. Zinc-nickel routinely lasts 1100 to 2000 hours before red rust occurs[3]. Tin-zinc has lasted up to 1000 hours before red rust occurred.

One concern with the tin-zinc alloy is the variability of the alloy composition and its effect on salt spray. Figure 1 shows salt spray data for various alloy compositions; the best salt spray results for tin-zinc are seen at a composition of 8 to 18% zinc with red rust appearance averaging 850 hours of salt spray. Panels with very low zinc concentrations (1% or less) exhibit the properties of a pure tin coating, i.e., the coating is no longer a sacrificial coating, but a barrier type coating, and the thin (8 to 13 μm) coating does not protect against corrosion.

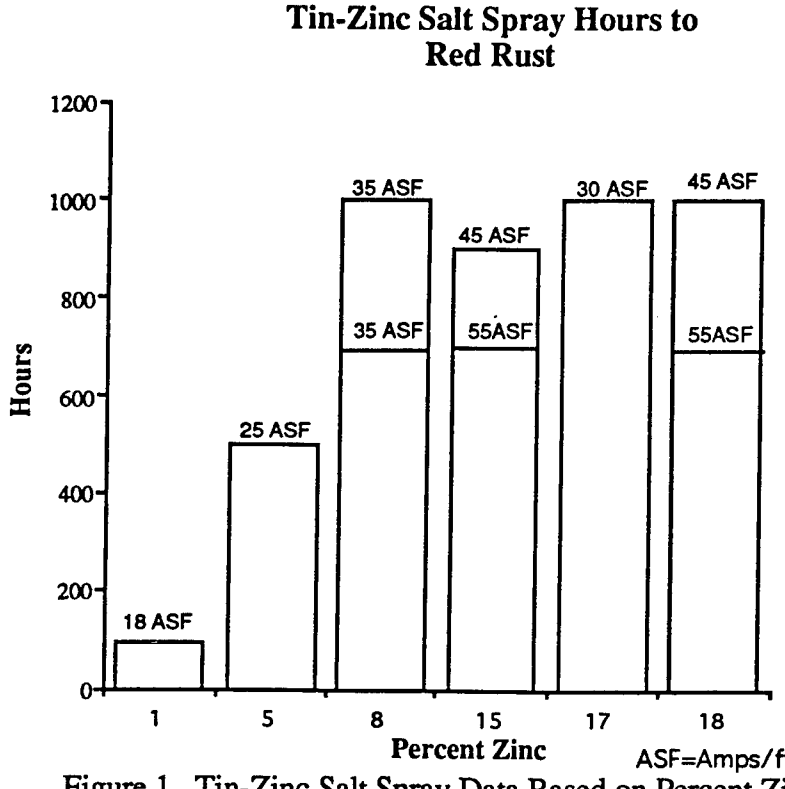

Figure 1. Tin-Zinc Salt Spray Data Based on Percent Zinc

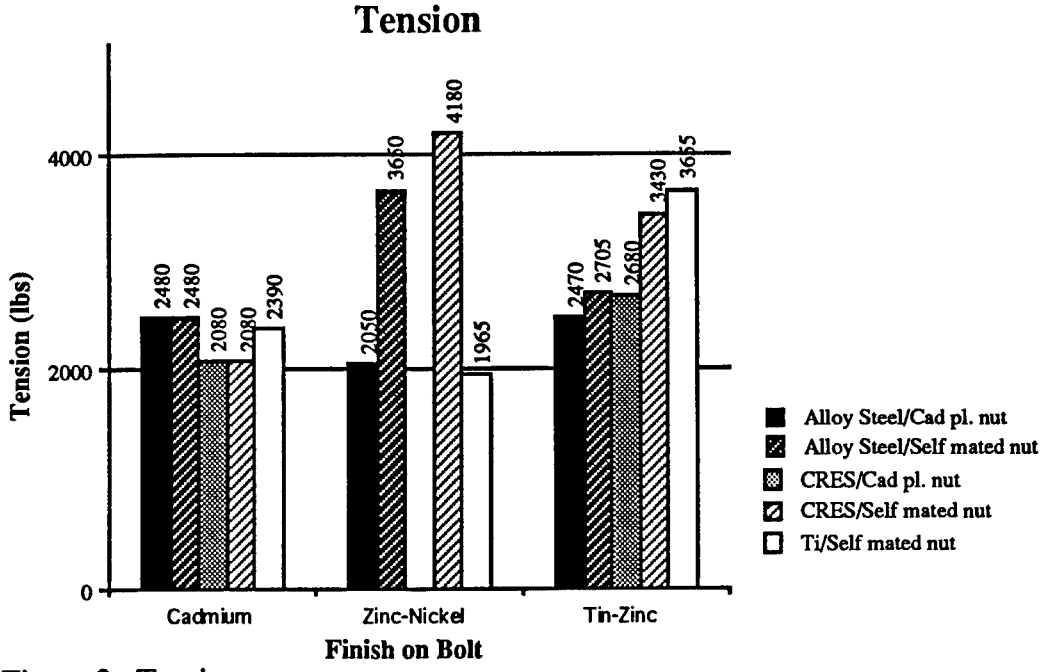

Figure 3. Tension

The nut and bolt combinations were then placed into the salt spray chamber for 500 and 1000 hours. There was not a standard test procedure for salt spray testing of fasteners, so the cadmium breakaway torque specimen was considered the control, and any large deviations from its value would be considered unacceptable. The data from 500 hours indicated tin-zinc and zinc-nickel breakaway torques were much higher than cadmium, and would probably be unacceptable for removal and reinstallation. Breakaway torque values at 1000 hours of salt spray were improved for tin-zinc, the values were similar to cadmium in every combination except alloy steel nuts and bolts (Figures 4 through 7). The alloy steel combination is the most important in terms of usage; however, since this is a small sample size further testing is necessary to confirm. Zinc-nickel nuts and bolts had high breakaway torques after 1000 hours on all combinations.

Concurrently nuts and bolts were installed on a block of bare 7075 Aluminum, then primed and painted with an epoxy primer and enamel, to see the corrosion potential in such a coupling. The cadmium and titanium controls performed the best after 1000 hours of salt spray with very little corrosion. Next, tin-zinc looked better than the zinc-nickel except for one set of CRES with tin-zinc. Zinc-nickel is not being pursued as a coating for fasteners, but more testing is being planned to determine the viability of tin-zinc on fasteners.

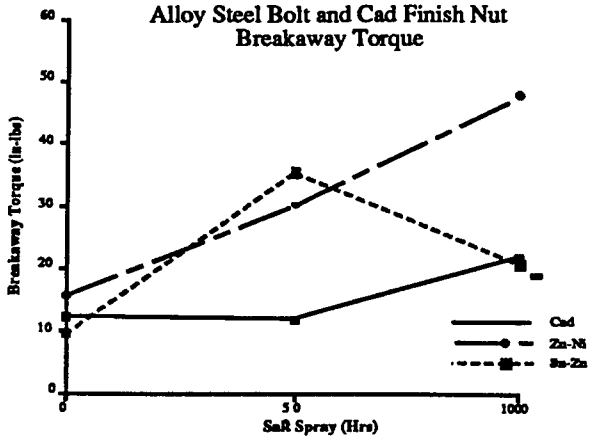

Figure 4. Breakaway Torque for Alloy Steel Bolts with Cad Plated Nuts

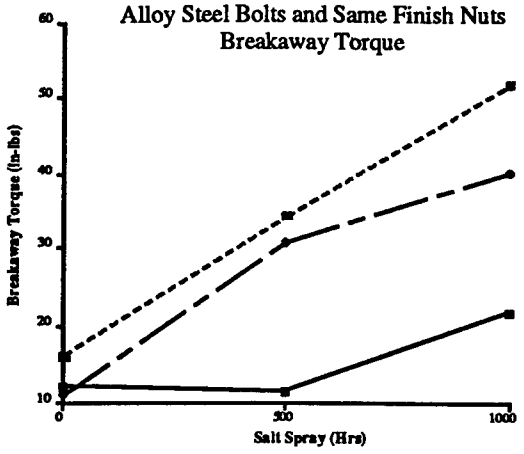

Figure 5. Breakaway Torque for Alloy Steel Bolts with Same Finish Nuts

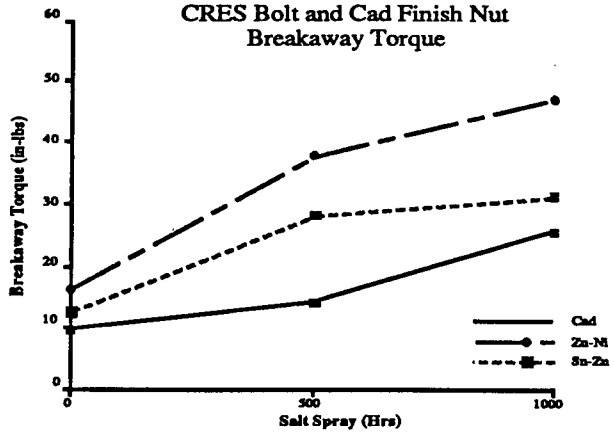

Figure 6. Breakaway Torque for Corrosion Resistant Steel Bolts with Cadmium Finish Nuts

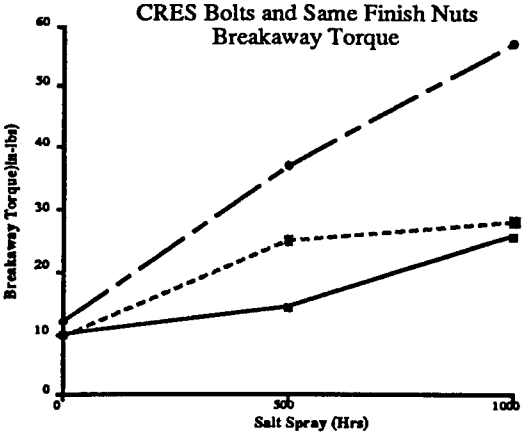

Figure 7. Breakaway Torque for Corrosion Resistant Steel Bolts with Same Finish Nuts

Hydrogen Embrittlement

Hydrogen embrittlement is a critical concern on high strength steel parts due to the possibility of catastrophic failures. Boeing currently uses a cadmium-titanium alloy plating[7] for high strength steel parts needing corrosion protection. During the development of the zinc-nickel plating process, the propensity to low hydrogen embrittlement was considered a critical criteria. Over 150 notched tensile specimens were tested per ASTM F519[8,9]. Specimens passed when they were baked for hydrogen removal[9]. A Boeing-developed system for measuring hydrogen pick-up[10] in cadmium-titanium alloy is used to reduce the time to qualify the bath from 200 hours for ASTM F519[8] testing to less than one day. This system does not work for the zinc-nickel system. The lack of a quick method for measuring hydrogen in zinc-nickel plating has hindered the implementation of zinc-nickel for high strengths steels.

Boeing has spent a great deal of time researching the properties and control of the alloy compositions from the alloy baths, since alloy composition can impact performance.

Boeing's zinc-nickel alloy does not have this problem of alloy dependant corrosion protection. The alloy composition remains stable when the bath is controlled within the ranges given in the process specification[4]. An experiment (full factorial with 3 replicates) varying the current density, pH, and temperature resulted in a stable alloy of 80 to 94% zinc, 20 to 6% nickel with a 3% variation per panel[3,4]. Although composition was in the given range, high pH values at ambient temperatures did result in salt spray failures. Another experiment (half-fractional factorial) with four factors was run on zinc-nickel specifically to identify alloy composition variations. The four factors were zinc and nickel concentrations, pH, and current density. Results showed a steady alloy composition of 81 to 89% zinc. An incompatibility of high zinc concentration and higher than pH 7.0 caused a precipitate to form during two runs, and the baths were not used in the experiment. If an all zinc panel were to be plated, it would still protect sacrificially, and thereby ensuring corrosion protection. A pure zinc coating is not optimum since excessive white corrosion products can form.

Tin-zinc is much more difficult to control for alloy composition. An experiment was run using a half-fractional factorial with five factors (resolution III). The five factors were: tin+2, zinc, pH, agitation, and temperature. This experiment was run in a Multi-cell (similar to a Hull cell), so that the current density was also a variable measured. Current density has been shown to influence the alloy composition, low current density plates out lower zinc concentrations (Figure 1). This experiment was completed in June, and thorough analysis of all the data has not been completed. However, the initial trend is that the most significant factor is the current density; temperature also appears to be significant. The zinc concentration and pH do not appear to effect alloy composition. Confirmation runs need to be completed to double check these results. The next step is to determine the practical ways to control the factors to yield optimum alloy composition for corrosion resistance with every run.

Adhesion/Paint Adhesion

There have been few problems with either alloy plate acheiving adhesion on various substrates. The most common use is on low alloy steels. Substrate preparation involves: degreasing, descale/derust, alkaline clean and activation, dilute acid dip and plate. A strike in the zinc-nickel bath (60 to 90 ASF for 60 seconds initially) increases adhesion. Plating on stainless steel has also been accomplished using a nickel strike prior to plating. Both alloys have been plated onto aluminum, for experimental purposes only, following a Boeing Process Specification[5] for activation of the aluminum, and with adequate adhesion following plating.

Adhesion testing on steel[6] involves bending substrates around a mandrel equal to the thickness of the panel (essentially 180°) until fracture, then identifying any peeling or flaking as adhesion failure of the coating. Adhesion testing for aluminum is not as severe, with a 225°F bake for one hour and then noting any blistering as failures.

Both zinc-nickel and tin-zinc were also tested for adhesion of primers and topcoats to the plated surface. Electroplated panels were primed with an epoxy primer, and then tested. There was no loss of adhesion, for both chromated and non-chromated panels.

Fasteners

An important use of cadmium is on threaded hardware where its lubricating qualities allow easy installation and removal of fasteners. Although Boeing is not involved in fastener manufacturing or finishing, a great number are used in the manufacturing of airplanes, and other hardware. A replacement for cadmium on fasteners would be beneficial to the fastener manufacturers also in reducing their use of an EPA targeted material.

Zinc-nickel and tin-zinc alloys were plated onto standard nuts and bolts which had been stripped of their original cadmium finish. Next the nuts were dry lubed, this is the standard finish for cadmium plated nuts. The nut and bolt combinations were tested for: run-on torque, breakaway torque, and tension. A cadmium-cadmium combination was the control. Tests were run with the alloy-plated bolts mated with cadmium nuts, and alloy-plated bolts and nuts. All conditions except one produced desirable results as compared to cadmium in the as-plated condition. The only condition which failed was zinc-nickel on corrosion resistant steel with cadmium plated nuts (Figure 3). The run on torques and tensions were similar to cadmium for tin-zinc and zinc-nickel plated fasteners (Figures 2 and 3). Breakaway torque was also similar in the initial condition (Figures 4 through 7). Run-on torque, measured during the time the nut was screwed onto the bolt, was not to exceed 30 in-lbs, or excessive galling would occur. Breakaway torque is the torque needed to initially loosen a nut from a bolt, this should also be below 30 in-lbs. The tension is measured when the nut and bolt are mated. Ideal tension (lbs) is 60% of the ultimate tensile strength (UTS) for a particular bolt; in this case it is a 160ksi bolt = 6470 lb UTS yields 3882 lb ideal tension. If the tension is too low, the nut will not stay screwed in place, too high and it cannot be removed.

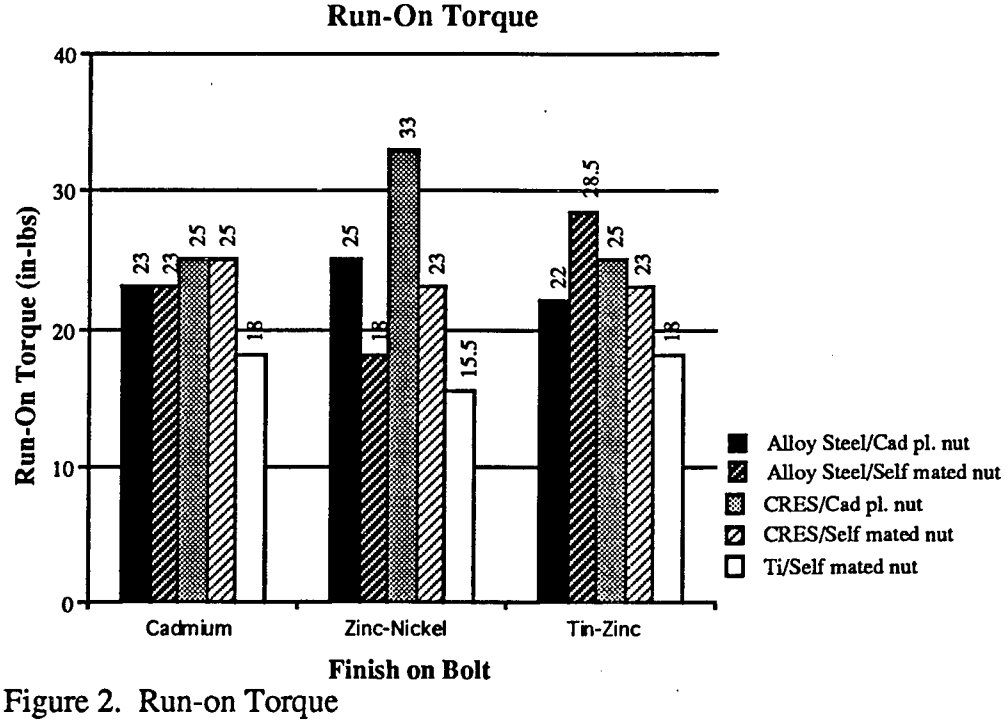

Figure 2. Run-on Torque

Preliminary testing on tin-zinc (six notched tensile specimens) has yielded one failure. The use of this bath as a low hydrogen embrittlement alloy is possible, but many more tests are needed.

Electrical Properties

Electrical conductivity across the overlapping joints is required of "black boxes" to prevent electromagnetic interference (EMI) problems. The conducting joints are not allowed to pass high frequency currents either into or out of the electrical boxes. These boxes are often made of aluminum which is nickel plated because of nickel's good radio frequency (RF) response. Nickel is; however, not compatible with aluminum so it is typically overplated with cadmium. Tin-zinc was tested as a replacement for cadmium in this situation.

Aluminum panels (2024-T3) were tested for electrical contact resistance. The following surface preparations were used prior to tin-zinc plating: 1) anodize with electroless nickel, 2) zincate no nickel plate, 3) zincate with nickel strike and plate, 4) zincate with iron strike and nickel plate. Low electrical resistance for tin-zinc plating, in the range of 0.5 to 2.5 milliohms was measured (Figure 9). The panels were then placed in salt spray for 96 hours. There was no change in the resistivity measurements. Corrosion resistance was worst using a nickel plate and nickel strike in method 3. The best corrosion results were using the zincate/copper strike and tin-zinc plate as in method 2. Although some corrosion products formed during the salt spray, it was not considered a result of galvanic incompatibility.

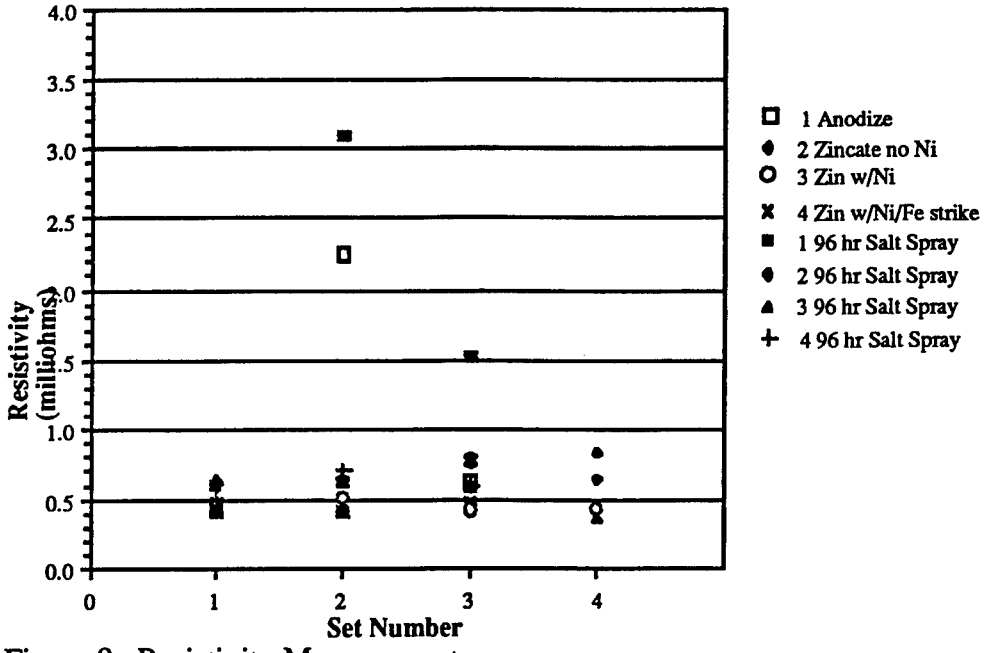

Figure 9. Resistivity Measurements

Conclusions

Zinc-nickel alloy is already in use at Boeing reducing our reliance on cadmium plate. As more production time is garnered, evidence of its superior corrosion resistance will be noted, and the question of its usefulness for high strength steels will be resolved. Tin-zinc is still in the developmental stages, but appears to be a superior coating for more lubricity type uses such as gears and possibly fasteners. Process control of the alloy composition still needs to be optimized, but the properties such as corrosion resistance, adhesion, resistivity and galvanic couplings are positive benefits of tin-zinc plating as a replacement for cadmium plating.

References

[1]National Bureau of Standards Conference, September, 1977, Washington D.C.

[2] ASTM B117 Salt Spray (Fog) Testing

[3] Tran, L.M., Phosphate Conversion Coating for Zinc-Nickel Alloy Plating, Boeing Defense & Space Group, OTDR 9-04001, March 1993, p. 7.

[4]BAC 5637, Zinc-Nickel Alloy Plating, Boeing Commercial Airplane Group.

[5] BAC 5714, Electroplating of Aluminum Alloys, Boeing Defense & Space Group.

[6] BSS7235, Adhesion Test Method, Plating,

[7] BAC 5804, Low Hydrogen Embrittlement Cadmium-Titanium Alloy Plating, Boeing Commercial Airplane Group.

[8] ASTM F519, Standard Method for Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals.

[9] Hsu, G.F., A New Zinc-Nickel Electroplating Process: Alternative to Cadmium Plating, SAE Technical Paper Series, Proceedings of the 19th Annual Airline Plating and Metal Finishing Forum, 830686, March 1983, PP. 3-14.

[10] BSS 7321, Hydrogen Detection Instrument Test Method, Boeing Commercial Airplane Group.

REPLACEMENT OF CORROSION PROTECTION CHROMATE PRIMERS AND PAINTS USED IN CRYOGENIC APPLICATIONS ON THE SPACE SHUTTLE WITH WIRE ARC SPRAYED ALUMINUM COATINGS.

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Abstract

With the advent of new environmental laws restricting volatile organic compounds and hexavalent chrome emissions, "environmentally safe" thermal spray coatings are being developed to replace the traditional corrosion protection chromate primers. A wire arc sprayed aluminum coating is being developed for corrosion protection of low pressure liquid hydrogen carrying ducts on the Space Shuttle Main Engine. Currently, this hardware utilizes a chromate primer to provide protection against corrosion pitting and stress corrosion cracking induced by the cryogenic operating environment. The wire arc sprayed aluminum coating has been found to have good potential to provide corrosion protection for flight hardware in cryogenic applications. The coating development, adhesion test, corrosion test and cryogenic flexibility test results will be presented.

Introduction

Chromate primers are used to provide corrosion protection for aerospace hardware in cryogenic applications. One such application is the Low Pressure Fuel Turbopump (LPFTP) Discharge Duct used on the Space Shuttle Main Engine. The LPFTP Discharge Duct carries liquid hydrogen (-423 °F) fuel from the Low-Pressure Fuel Turbopump discharge to the inlet of the High-Pressure Fuel Turbopump (see Figure 1). The LPFTP Discharge Duct is fabricated from 21-6-9 CRES (Mn 8.0 to 10.0, Cr 19.0 to 21.5, Ni 5.5 to 7.5) which is insulated with polyurethane foam and then nickel plated.

Pitting corrosion and stress corrosion cracking has been found on these ducts after various periods of service. Chloride contamination was identified as the initiator of the corrosion, although the exact source of the chlorides is not known. Even though 21-6-9 CRES is generally considered corrosion resistant, the corrosion problem is accentuated by the crevice corrosion situation created under the foam insulation (1). To prevent this corrosion, a chromated primer system was qualified and has proven to provide adequate corrosion protection for many years.

However, with increasing health risk and environmental harm due to hazardous materials, many materials are scheduled to be eliminated in the near future. Among the materials to be eliminated, due to excess emissions of hexavalent chromium and volatile organic compounds (VOCs), is the chromate primer system used on the LPFTP Discharge Duct. Other organic coatings have been evaluated for this application with little success, primarily because of difficulty meeting the cryogenic adhesion/flexibility

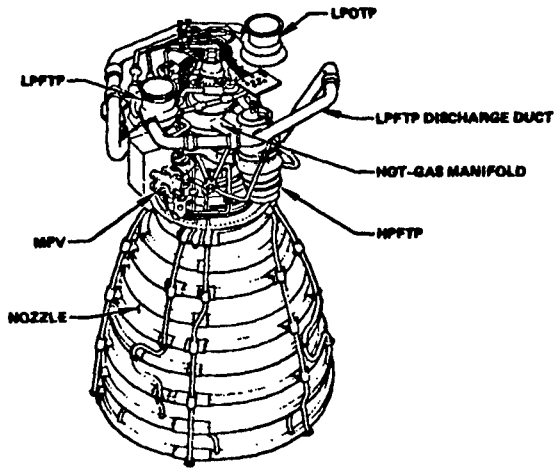

Figure 1 The Space Shuttle Main Engine showing the Low Pressure Fuel Turbopump Discharge Duct.

requirements. Due to the excellent adhesive strength and cryogenic material properties, a wire arc sprayed (WASed) aluminum coating is being developed to replace the chromate primers subjected to cryogenic conditions on rocket engine components.

Although thermal sprayed corrosion protection coatings have been used extensively to date, none have been developed for cryogenic applications. The WAS aluminum coating developed meets the stringent adhesion and cryogenic flexibility requirements of the LPFTP Discharge Duct and the coating offers very good corrosion protection for steels and other corrosion prone alloys.

This report presents the details of the coating development program completed including thermal spray parameter development, surface preparation and optimum coating thickness. Corrosion resistance, cryogenic flexibility and adhesion test results are also presented.

II. Coating Development

The coating development includes material and process selection, thermal spray parameter development and hardware processing development.

Process and Material Selection

The wire arc sprayed aluminum coating was selected based on environmental, cost, availability and performance concerns. Metalized coatings were chosen for their proven corrosion protection capabilities (2) and their typically high adhesive strength. These coatings not only act as an effective barrier coat but because they are more anodic than steel (see Table I), they act as a sacrificial anode and give galvanic protection to the substrate. Thus, corrosion of the substrate will be prevented even where coating coverage may be incomplete or where the coating may be damaged (3). With the addition of a sealant or topcoat, a thermal sprayed coating has long life and is easy to clean and maintain. The sealant does not affect the cathodic protection.

The wire arc spray process applies metal coatings using metal feedstock in wire form. Two wires serving as the positive and negative electrodes advance to meet in a location in the atomizing gas. A potential is applied to the wires so that an arc is formed at the wire intersection causing the wire tips to melt. Atomizing gas flows across the arc zone propelling molten metal droplets to the substrate (see Figure 2). Because of the high temperatures in the arc zone and the superheating of the molten particles, wire arc spray coatings tend to have excellent adhesion and cohesive strength. Substrate heating however, is significantly lower than most thermal spray processes because there is no flame. In addition, wire arc spray systems are light and portable allowing for on-site application or repair of coatings.

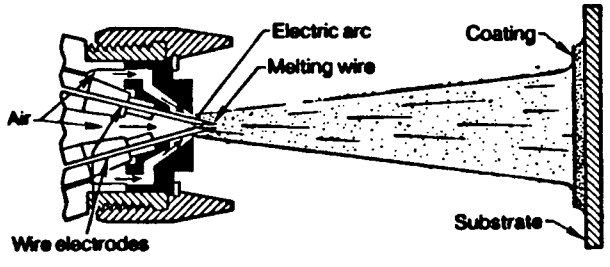

Figure 2 Schematic of the Hobart TAFA wire arc spray gun.

Aluminum and zinc and their alloys are the most commonly used metals for corrosion protection coatings. Zinc, however, was not considered due to it's excessive rate of corrosion (4). Aluminum and aluminum alloys were initially selected based on their electro-chemical potential, good material properties at cryogenic temperatures, low weight and availability.

Preliminary screening of aluminum and two alloys, Al 4043 and Al 5356, coatings was performed in an effort to select one coating for further study. The screening tests consisted of flexibility, adhesion and 30 day salt fog exposure. The best performing coating was selected for further evaluation in cryogenic flexibility, thermal cycle testing and extended salt fog exposure.

Parameter Development

The parameter development process concentrated on the setup of five fundamental parameters that are common with most thermal spray processes. These were:

1) Surface Preparation
2) Atomizing Gas
3) Standoff Distance
4) Power Settings
5) Gun and Part Motion

As with most development programs, it soon became evident that the controllable parameters were not independent of each other. In order to evaluate the affects of parameter changes a "goodness" criteria was developed and used to test each change. This criteria was the coatings performance in a bend test. This test is described in detail in the "Experimental Testing" section later in this paper. The coating passes the test if loss of adhesion or coating cracks do not occur. The test is made more severe by decreasing the bend radius.

Several surface preparation techniques were investigated ranging from grit blasting to a light hand sand. An important factor in the decision was the inspection requirements on the LPFTP Discharge Duct. Periodically the duct is taken out of service and the foam and chromate paint is stripped off so the exterior can be inspected for corrosion pitting and cracking using IVc dye penetrant. If the exterior of the duct had been severely roughened, as with grit blasting, the IVc dye penetrant would show many false indications because of its extreme sensitivity. Our testing proved this to be true so grit blasting was ruled out from the start. A variety of hand sanding techniques were tried with different grit sand paper. From these test, a light hand sand with 320 grit Al_2O_3 sand paper and acetone final clean gave a good surface for coating adhesion and was smooth enough for IVc dye penetrant inspection.

At the beginning of the study, it was assumed that an inert atomizing gas would perform better because of the less likelihood of oxide formation. This turned out to be a false assumption. A variety of atomizing gasses were tried including; argon, 95% Ar - 5% H_2, nitrogen, and air. The different gasses were tested using bend tests to evaluate adhesion and microstructure to determine oxide content and density. Surprisingly using argon, argon-hydrogen and nitrogen as the atomizing gas showed no decrease in oxide content within the microstructure as compared with using air. Also, using air as the atomizing gas showed a marked increase in bond strength over the other three. This higher bond strength is most noticeable on ferrous substrates, although air seems to generally give higher bond strengths

further study. Coatings were screened based on their adhesion, flexibility and corrosion resistance capabilities. The coating's adhesion strength was evaluated quantitatively from the pass or fail bend test starting with 0.5 in diameter mandrel and going to a 180 degree bend and tape test. In all cases the pure aluminum coatings performed the best, followed by the Al 5356 coating and lastly the Al 4043 coating.

Each coating was also evaluated after 30 days of salt fog exposure. Coated 21-6-9 CRES panels were scribed through the coating to the base metal to evaluate the cathodic protection provided by each material. After the 30 days of salt fog exposure, the coating and the scribe were visually examined for corrosion. The coating was then removed and the substrate was examined for signs of corrosion. The pure aluminum and the 5356 alloy showed little coating corrosion product and no substrate corrosion was apparent. There was significantly more corrosion product produced from the 4043 alloy and some rust stains were observed on the substrate.

Based on the results of the screening tests, the pure aluminum was chosen for further evaluation. Additional tests included cryogenic bend, extended salt fog exposure up to 120 days, and a thermal cycle cold flow test.

Parameter Development

Micrographs of the aluminum coating (see Figure 5) show the typical splat structure of a wire arc coating. The bond line shows an excellent interface even without a grit blasted surface. The coating also exhibits above average density (greater than 95%) for wire arc and no through

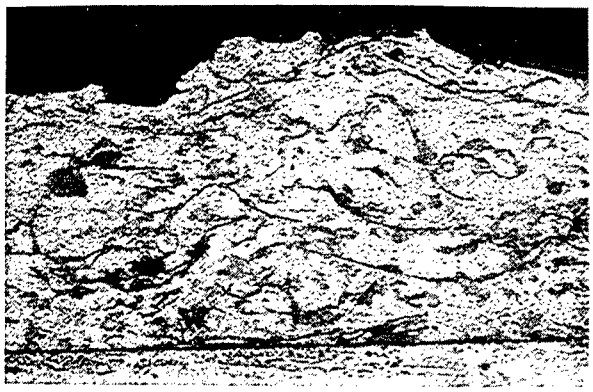

Figure 5 Wire arc sprayed aluminum microstructure deposited on non-grit blast substrate, etched, magnification 400x.

porosity, although for galvanic corrosion protection, some through porosity is acceptable. Surprisingly, there are few oxide strings between the splat particles even though air is used as the atomizing gas. Overall, a well adhered and dense wire arc spray coating.

The list of the final processing parameters is shown in Table II. Using these parameters, in conjunction with the Hobart TAFA 8835 Wire Arc Spray System, typical coatings as shown in Figure 5, were repeatably produced.

Table II WAS Aluminum Coat Processing Parameters

Wire Material	01T Al (Hobart TAFA)
Wire Size	1/16 in Diameter
Substrate Material	21-6-9 CRES (Nitronic 40)
Surface Preparation	Hand Sand 320 Grit Al_2O_3
Gun Hardware	Green End Cap Long Cross Nozzle
Spray Parameters	
Ionization Gas	Air
Gas Spray Pressure	80 psi
Wire Feed Rate	3.6 in/sec
Voltage	28 Volts
Amperage	150 Amps
Spray Distance	7 in
Motion	
Traverse Speed	15 in/sec
Up/Down Step	0.35 in

Hardware Processing Development

To prepare for wire arc spraying parts by-hand, a Taguchi design of experiments was performed to determine the primary parameters to control and their corresponding tolerances. The process parameters investigated were gun to part stand-off distance, angle of incidence, gun speed and coating thickness. Coating adhesion and flexibility were used to evaluate the coating quality. Evaluation of the data revealed that the coating thickness and gun to part stand-off distance were the primary parameters contributing significantly to the quality of the coating. Using this information, representative duct elbows were wire arc sprayed by-hand. Parts were processed with two passes while maintaining a stand-off distance of 5 inches to 7 inches. Visually, the coating appeared to be high quality. A tape test on the surface of the part verified good coating adhesion.

Caustic soda, alkaline cleaner and high pressure water was evaluated as coating removal methods. Samples were IVc dye penetrant inspected prior to coating the samples with aluminum. The coating was removed and the samples again IVc dye penetrant inspected. Methods resulting in no background contamination during the inspection were found acceptable. Both the caustic soda and the alkaline cleaner completely removed the coating efficiently, cleanly and no background contamination was found during penetrant inspection. Since the TURCO 4181 is currently used to clean flight hardware, the high pressure water was not pursued. However preliminary investigations showed that high pressure water (25,000 - 40,000 psi) satisfactorily removed the coating without damaging the part.

Experimental Testing

The experimental results reported are for samples prepared with the developed parameters shown above. The surface was prepared with a 320 grit hand sand and acetone hand wipe.

Adhesion and Flexibility. The pure aluminum coating passed all bend and tape test (see Figure 6). The Al 5356 alloy passed only the tape and bend test around the 0.5 inchmandrel. In general, the thinner coatings proved to have better adhesion and cohesive strength. But the pure aluminum coatings up to 0.010 inch thick were

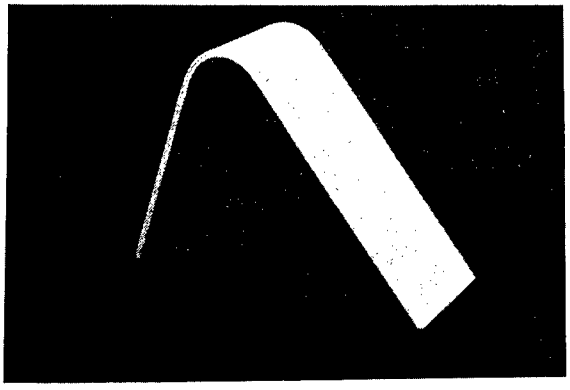

Figure 6 Typical bend test sample coated with wire arc sprayed aluminum (bent around 0.5 inch mandrel).

found to pass the all of the bend and tape test, including the 180 degree bend.

Cryogenic Flexibility. Pure aluminum coatings of varied thicknesses, ranging from 0.004 inch to 0.010 inch were prepared for the cryogenic bend test. All coatings passed the cryogenic bend test.

Corrosion Resistance. During the initial 30 day test phase, coatings of varied thickness were evaluated. Coating thicknesses of 0.003 inch, 0.007 inch and 0.010 inch were tested. Observations of the test panels after 30 days of exposure were:

1. no corrosion of the substrate
2. aluminum oxide formed covering the WASed aluminum coating
3. the thicker coatings tended to blister and loose adhesion
4. the 0.003 inch and 0.007 inch coatings remained in satisfactory condition

Since the life of the coating is directly related to the coating thickness, the 0.007 inch coating, which did not blister or debond, (and was expected to last longer) was chosen for further salt fog testing. Additional panels were prepared and tested for 60, 90 and 120 days. Panels before and after 90 and 120 day salt fog exposure are shown in figures 7-9. As shown, the coating remains intact and there is no corrosion of the substrate. Some exposed base metal can be seen along the edges of the panels and there are some blotchy areas where the coating appears to have thinned. The exposed metal area of the panel increased when exposed for 120 days. After removal of the coating, examination of the substrate revealed no corrosion.

IV. Conclusion

Although wire arc spray coatings have been used in the past for numerous corrosion prevention applications, its use in a cryogenic environment has been nonexistent. Rocketdyne's commitment to elimination of hazardous materials on the SSME and other rocket engine systems presented an excellent application for wire arc sprayed aluminum's use in a liquid hydrogen environment. In developing this alternative process for providing corrosion protection for the SSME, a number of innovations were refined.

Parameters were developed that enabled a dense well adhered wire arc sprayed aluminum coating to be applied to both flat and cylindrical 21-6-9 substrates. It was found that using air as the atomizing gas at a high pressure (80 psi) gave the best microstructure and bond strength. Using air as the atomizing gas was shown to give higher bonds strength on ferrous substrates than using an inert gas.

The wire arc sprayed aluminum coating was shown to survive cryogenic bend tests on a 2.8 in OD mandrel. This achievement is significant in the fact that no other corrosion protection paints, other than the currently used hazardous chromate primer, were able to survive this test.

It was shown that wire arc sprayed pure aluminum provided better corrosion protection on 21-6-9 than the Al 4043 and Al 4043. The wire arc sprayed aluminum proved that it could provide protection for 21-6-9 in 30, 60, 90, and 120 day salt fog test, a significant achievement for any cathodic protection coating.

It was shown that the coating could be sprayed onto representative SSME duct hardware and there are no apparent significant flight hardware processing issues. A cold flow test specimen was cycled from liquid hydrogen temperatures

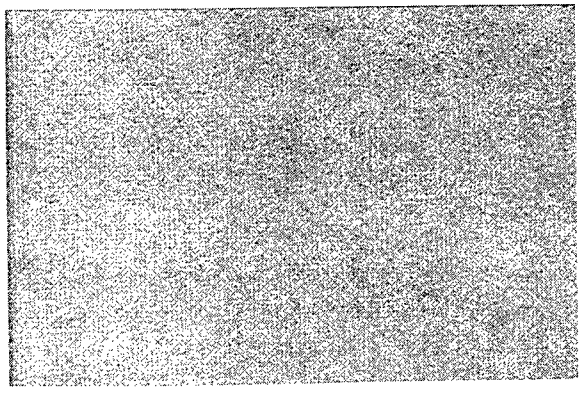

Figure 7 Corrosion test panel wire arc sprayed with aluminum (as-sprayed).

Figure 8 Wire arc sprayed aluminum coating after 90 days salt fog exposure.

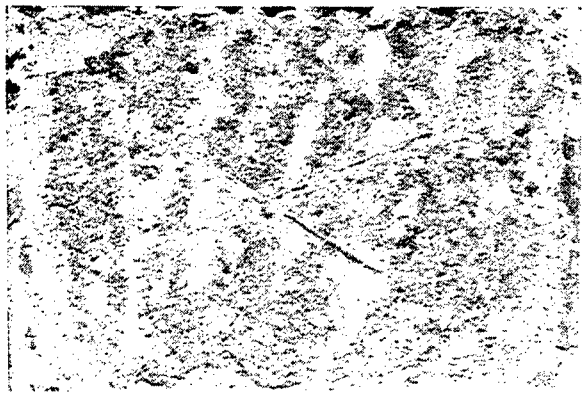

Figure 9 Wire arc sprayed aluminum coating after 120 days salt fog exposure.

to ambient repeatably without any degradation in the coating.

In summary, it was shown that wire arc sprayed aluminum can be used to replace environmentally undesirable chromate paints and primers used for corrosion protection of cryogenic hydrogen carrying ducts on the Space Shuttle Main Engine.

Acknowledgments

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References

1. West, John M., "Basic Corrosion and Oxidation", John Wiley & Sons Press, New York, NY, 1980.

2. Hollingsworth, E. H., and Hunsicker, H. Y., "Corrosion Resistance of Aluminum and Aluminum Alloys", ASM Metals Handbook, Ninth Edition, Vol 2, Properties and Selection: Nonferrous Alloys and Pure Metals, 1979, Pages 204-236.

3. Davision, Ralph M., Debold, Terry, and Johnson, Mark, "Corrosion of Stainless Steels", ASM Metals Handbook, Ninth Edition, Vol 13, Corrosion, 1987, Pages 547-565.

4. Ishikawa, K., Seki, M. and Tobe, S., "Application of Thermal Spray Coatings to Prevent Corrosion of Construction in Japan", Proceedings of the 1993 national Thermal Spray Conference, Anaheim, CA, 7-11 June 1993.

5. American Welding Society, Corrosion Test of Flame-Sprayed Coated Steel, 19 Year Report. AWS C2.14-74

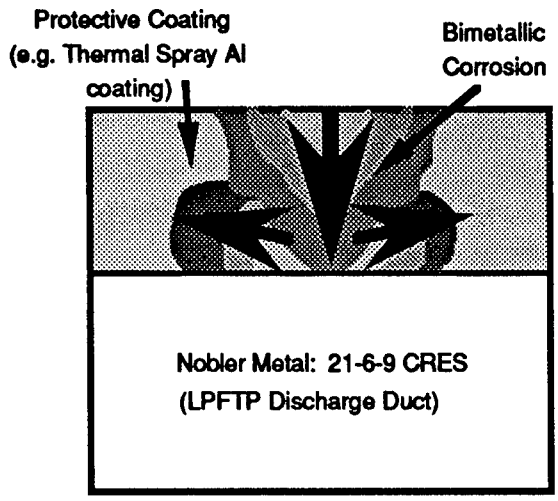
ENVIRONMENTALLY COMPLIANT COATING APPLICATIONS AND REMOVAL TECHNIQUES

Table I Relative EMF Potentials for Galvanic Corrosion (5)

EMF Potentials for Galvanic Corrosion

	METAL	EMF (V)
Noble End (cathode)	Inconel 625	0.24
	21-6-9 CRES	0.14
	Silver	0.00
	Inconel 718	-0.13
	Nickel 200	-0.14
	Copper	-0.16
	Al Alloy 2024	-0.65
	Al Alloy Tens-50	-0.79
(anode) Base End	Aluminum	-0.80
	Al Alloy 5052	-0.96

Cathodic Protection



- Nobler metal protected from corrosion due to sacrificial anodic coating.

on most metals when spraying aluminum.

Three different standoff distances were evaluated, these being 5 in, 7 in and 10 in. The 5 in and 10 in distances tended to degrade the microstructure by increasing porosity as compared to 7 in. 5 in and 7 in gave similar good results in the bend test, but the 10 in distance showed a marked reduction in coating adhesion. A standoff distance of 7 in gave the best overall results.

The settings for the power input to the wire arc gun are controlled by the power supply and the wire feed rate. The desired voltage is dialed in and the power supply will vary the amperage output needed to maintain that voltage. As the wire feed rate is increased, the amperage output at the power supply will increase to maintain the set voltage. These parameters were not varied much since there is only a narrow operating range for each particular wire material. The voltage is adjusted by running the equipment and varying the voltage until a smooth uniform arc achieved as the wired meet. If the voltage is slightly above or below the optimum point, the wire will pop and spit. The current is set by increasing the wire feed rate to a point just below the speed when wire popping occurs. The final parameters are shown in Table II.

Development of gun motion was done to achieve approximately 0.001 in of deposited material per pass. The gun motion was provided by an X-Y manipulator. The substrate was held stationary and the gun passed back and forth in front of it. After each crossing pass the Y axis moved up or down a specified amount to provide full coverage as the manipulator moved up and down the length of the substrate. It was found that a Y-step of 0.35 in after each X-pass gave a uniform coating with consistent thickness. An X-axis traverse velocity of 15 in/sec was found to deposit approximately 0.001 in of material.

Hardware Processing Development

Several issues were considered during the hardware process development phase. These include wire arc spraying large parts of complicated geometry's (elbows, bends, etc.), coating inspection and qualification, coating removal, coating repair and inspection after coating removal.

The insulated liquid hydrogen carrying ducts were the primary rocket engine components investigated requiring corrosion protection. Typically these parts have complicated geometry's and are difficult to handle and manipulate. With this in mind, part processing became a major consideration. Two methods for part processing were considered; robotics/ automation and wire arc spray "by-hand". Due to the high upfront expense for the required robotics to handle the ducts, spraying by-hand was pursued and will be discussed. To prepare for spraying by-hand, a Taguchi design of experiments was performed to determine the primary processing control factors and tolerances. Additional work includes spray by hand on practice ducts and elbows.

Inspection and qualification of the wire arc sprayed aluminum coating will be required after processing flight hardware. Methods condsidered, although the work has not been initiated, is visual, thickness measurement (eddy current, dimensional), tape test, and bend test witness coupons.

After a period of time, typically part refurbishment is required where by IVc dye penetrant inspection is used to determine the existence of corrosion. The primary issue investigated in this study, involves complete removal of the aluminum coating without surface contamination interfering with the penetrant inspection results. The methods of coating removal investigated were low concentration caustic soda (NaOH, KOH), TURCO-4181 alkaline cleaner (currently used to clean flight hardware) and high pressure water (25,000 to 40,000 psi). In addition to part refurbishment, coating removal is required during hardware change out, such as a fuel flow meter replacement. In this situation a small portion of the coating will be removed and later recoated.

Experimental Testing

Adhesion, corrosion resistance, cryogenic flexibility, and thermal cycle tests were performed to further evaluate the aluminum coating for use as a corrosion protection coating in cryogenic applications on flight hardware.

Adhesion and Flexibility. The bend and tape tests were used to evaluate the coating flexibility and bond strength. The bend test was done using a 1 in by 6 in by 0.050 in metal strip coated with the material to be tested. The coupon and coating were bent over a known radius while at room temperature. After bending, the coatings were inspected for signs of cracking or loss of coating adhesion. If the coating passed the bend test then a certified adhesive tape was applied over the coating at the bend area and quickly removed. The coating passed the test if none of the coating material spalled from the substrate. The bend and tape test was made increasingly more severe by decreasing the bend radius.

Initially samples were bent around a 0.5 in mandrel as this was the requirement for coatings on the LPFTP discharge duct. As the testing and development proceeded, the procedure included additional bends around a 0.3 in mandrel and a 180 degree bend applied by severely bending the sample back on itself and pressing it flat.

Cryogenic Flexibility. The cryogenic flexibility of the coating was evaluated by subjecting samples to a bend test in liquid nitrogen. The coated samples were loaded in a "V" block test fixture submerged in liquid nitrogen. The samples were allowed to stabilize at liquid nitrogen temperatures (-320 °F) and then bent to the radius of the fixture using a mandrel of 2.8 inch in diameter. The mandrel size was determined by examining the bend radii of dents in the LPFTP discharge ducts which were damaged by cryo-pumping and selecting the most severe case (the smallest radii) for testing. After warming the samples to ambient temperature, the coatings were examined for evidence of cracking or loss of adhesion.

Salt Fog Exposure. 4 in x 6 in panels were hand sanded and wire arc sprayed with aluminum. Scribes were placed on each sample penetrating the coating and marring the substrate, allowing for evaluation of the cathodic protection capabilities for each material tested. The samples were mounted 6 degrees from the vertical and were placed in a salt fog cabinet with a 5% salt solution conforming to ASTM B-117. The coatings and the substrate of the panels were visually examined after 30, 60, 90 and 120 days of exposure. Coatings were removed from the panels for substrate inspection with a weak caustic soda solution.

Thermal Cycle. A cold flow thermal cycle test was performed using liquid hydrogen (-423 °F). A 21-6-9 CRES

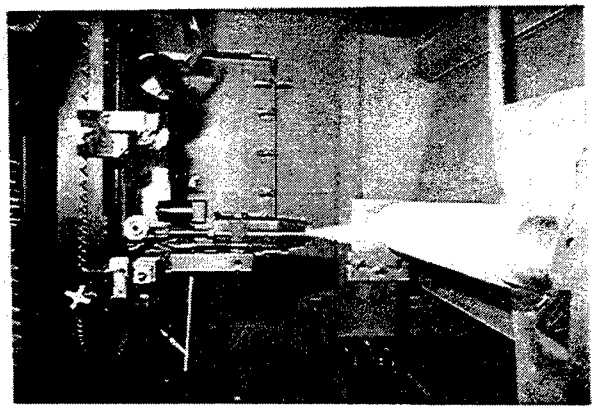


Figure 3 Cold flow test article during wire arc spray process.

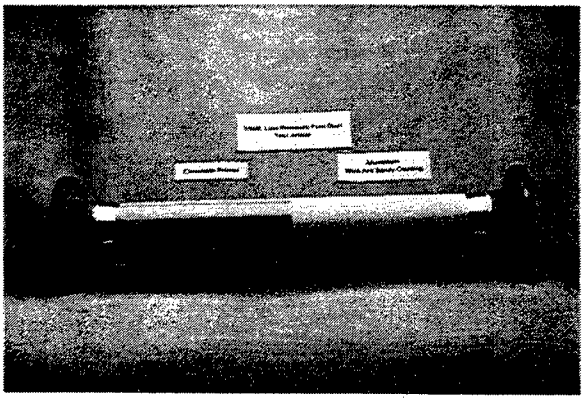


Figure 4. Cold flow test article prior to foam insulation.

test duct was coated with a WAS aluminum coating (Figures 3 - 4) and then insulated with polyurethane foam. Liquid hydrogen was passed through the duct until the duct wall temperature stabilized at approximately (-423 °F). That temperature was held for the desired length of time and then allowed to warm up to ambient temperature. Ten 30 minute steady state cycles were performed and one eight hour steady state cycle was performed. After the testing the insulation was removed and the WAS aluminum coating was examined for cracking or loss of adhesion.

III. Results and Discussion

Material Selection

Pure aluminum, Al 4043 and Al 5356 aluminum alloys were initially screened in an effort to choose one coating for

ENVIRONMENTALLY REGULATED AEROSPACE COATINGS

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ABSTRACT

Aerospace coatings represent a complex technology which must meet stringent performance requirements in the protection of aerospace vehicles. Topcoats and primers are used, primarily, to protect the structural elements of the air vehicle from exposure to and subsequent degradation by environmental elements. There are also many coatings which perform special functions, i.e., chafing resistance, rain erosion resistance, radiation and electric effects, fuel tank coatings, maskants, wire and fastener coatings.

The scheduled promulgation of federal environmental regulations for aerospace manufacture and rework materials and processes will regulate the emissions of photochemically reactive precursors to smog and air toxics. Aerospace organizations will be required to identify, qualify and implement less polluting materials. The elimination of ozone depleting chemicals [ODCs] and implementation of pollution prevention requirements are added constraints which must be addressed concurrently. The broad categories of operations affected are the manufacture, operation, maintenance, and repair of military, commercial, general aviation, and space vehicles.

The federal aerospace regulations were developed around the precept that technology had to be available to support the reduction of organic and air toxic emissions, i.e., the regulations cannot be technology forcing. In many cases, the regulations which are currently in effect in the South Coast Air Quality Management District [SCAQMD], located in Southern California, were used as the baseline for the federal regulations. This paper addresses strategies used by Southern California aerospace organizations to cope with these regulatory impacts on aerospace productions programs. ***All of these regulatory changes are scheduled for implementation in 1993 and 1994, with varying compliance dates established.***

INTRODUCTION

1.0 Regulatory Requirements and Policies

Clean Air Act Amendments. The 1990 Clean Air Act Amendments [CAAA] require the Environmental Protection Agency [EPA] to develop regulations designed to reduce the emissions of volatile organic compounds [VOCs] and hazardous air pollutants [HAPs] generated by the US aerospace industry. The EPA solicited data from major aerospace organizations, including both civilian and government sources,

to determine the processes which were the most polluting, emitting both reactive organic gases [precursors to urban smog] and hazardous air pollutants, which cause harm to the general public health.

Section 183[b][3] of the CAAA dictates the development of a control techniques guideline [CTG] which provides guidance to state and local agencies for the development of regulations to reduce VOCs. Only areas designated as in "non-attainment" with federal standards are mandated to follow the baseline emissions standards for VOC. Section 112 of the CAAA requires the promulgation of National Emission Standards for Hazardous Air Pollutants [NESHAP] to control the emissions of HAPs from major sources. A major source is defined as any source with the potential to emit 10 tons per year of a single HAP or 25 tons per year of the aggregate HAP emissions from a facility. Both regulations are scheduled for promulgation by the end of 1994, with compliance dates of 18 to 36 months following promulgation.

An aerospace facility, as defined by the EPA, is a facility that produces in any amount an aerospace vehicle or component, or a facility that reworks [or repairs] these vehicles or components. Aerospace operations at any major source that conduct both aerospace and non-aerospace work would be subject to the proposed standards, regardless of the relative proportion of aerospace and non-aerospace work at the facility. The EPA estimates there are 2,879 aerospace facilities that will be subject to the proposed standards. Of this number 1,395 manufacture or rework commercial products, and 1,474 manufacture or rework military products. The combined HAP emissions from these facilities [excluding subcontractors] are estimated to be over 208,000 tons per year.

The aerospace coatings regulated under the NESHAP are shown in **Figure 1**. Materials and processes regulated under the NESHAP are subject to maximum achievable control technology [MACT], as emissions from these materials are believed to be carcinogens, reproductive toxicants, or can create other serious health effects for exposed personnel. Additional materials and processes which are regulated under the NESHAP, but not discussed in this paper, are: cleaning operations; hand-wipe solvents; coating spray gun cleaning; flush cleaning; aircraft depaint operations; chemical milling maskants; and procedures for handling non-RCRA waste.

Figure 2 shows the aerospace coatings and materials proposed for regulation under the CTG. These materials are subject to reasonably available control technology [RACT], which has less stringent regulatory requirements and has a lower cost of compliance. The materials regulated under the CTG are 3% [6500 tons] of the total of the aerospace emissions.

SOURCE	REQUIREMENTS	DESCRIPTION
Primer & Topcoat	Standards	Uncontrolled Primers 1. Organic HAP content limit: 350 grams/liter [less water] as applied. 2. VOC Content limit: 350 grams/liter [less water and exempt solvents] as applied Uncontrolled topcoats 3. Organic HAP content limit: 420 grams/liter [less water] as applied. 4. VOC content limit: 420 grams/liter [less water and exempt solvents] as applied Uncontrolled Primers and Topcoats 5. Primers and topcoats can achieve compliance through: [1] being below limit in themselves or [2] average with compliant primers 6. Primers and topcoats cannot be averaged together. Controlled Primers and Topcoats 7. If control device is used, must be designed to capture and control all emissions from the application operations and must achieve an overall control efficiency of at least 81%. All Primers and Topcoats 8. Specific application techniques must be used. If alternative is sought, can only be used if emissions are less than or equal to HVLP or electrostatic spray application techniques as demonstrated under actual production conditions. 9. All application equipment must be operated according to manufacturer's specifications 10. Exemptions from 8 above provided for certain situations 11. Operating requirements for the application of primers that contain inorganic HAP, including control with either particulate filters or waterwash and shutdown if pressure falls outside manufacture's specified operating limits. 12. Exemptions from 11 provided for certain application operations.

Figure 1. NESHAP Standards Established for Primers and Topcoats

There are additional requirements for performance tests and test periods; test methods and procedures to determine the organic HAPs content of the primers and topcoats, the efficiency of the carbon adsorber, and alternative application methods; monitoring and recordkeeping requirements; and reporting requirements.

COATING	EPA PROPOSED VOC [grams/liter]	AIA PROPOSED VOC [grams/liter]
Ablative	600	720
Adhesion Promoter	890	890
Antichafe	660	660
Clear Coating	530	720
Commercial Exterior Primer	350	650
Adhesive Primer	770	770
Corrosion Inhibiting Compound	700	700
Electric or Radiation Effect Coatings	800	800
Fire Resistant Coating	800	800
Flexible Primer	*635*	*635*
Flight Test Coatings	840	840
Flight Test Coatings - missiles or single use craft	420	420
Fuel Tank	*720*	*720*
High Temperature	850	850
Impact Resistant	600	600
Ink - screen print	840	840
Ink - part marking	850	850
Insulation Covering	710	770
Lacquers	*830*	*830*
Metallized Epoxy	*650*	*740*
Mold Releases	30	770
Optical Anti-Reflection	700	750
Pretreatment	750	780
Protective Oils & Waxes	840	960
Rain Erosion Resistant	347	850
Rain Erosion Resistant Compatible Primer	850	850
Solid Film Lubricant	526	960
Space Vehicle Coatings	890	890
Specialized Function Coatings	890	890
Temporary Protective Coatings	250	350
Thermal Control	770	770
Wing Coating	*750*	*850*

Figure 2. Volatile organic content limits proposed for coatings regulated under the Control Techniques Guidelines [CTG] AIA is the Aerospace Industries Association

A public hearing is scheduled for the NESHAP on 15 August 1994, with promulgation within 30 days. The CTG is currently under development by a joint task force composed of representatives from the EPA, Aerospace Industries Association [AIA], Department of Defense, and NASA. The italicized materials in Figure 2 are candidates for transfer to the NESHAP document, because of their high VOC and somewhat higher volumes of usage.

Elimination of Ozone Depleting Chemicals. The requirement to cease the manufacture of Class I ozone depleting chemicals [ODCs], as stipulated by the 1990 CAAA, is imposed concurrently with the requirements to comply with the NESHAP and CTG. Executive Order 12843, signed by President Clinton in June 1993, mandates the elimination of the use of ODCs at federal facilities and requires the elimination of contract language that requires government contractors to use or deliver contract deliverables which contain Class I ODCs in new or modified contracts.

Ozone depleting chemicals have historically been classified as "exempt" compounds, i.e., their emissions did not contribute to the VOC emissions from materials. Consequently, many organizations diluted their materials with "exempt" solvents to reduce the emissions to the regulatory-mandated limit. ODCs have been used quite widely throughout the aerospace industry for many processes which require non-aqueous solvents that are non-flammable and have high evaporation rates.

The concurrent elimination of ODCs will complicate the process of complying with the CTG and NESHAP, as these materials will no longer be allowed for use in aerospace materials and processes.

Pollution Prevention. Under federal regulations, all organizations are required to develop pollution prevention programs. However, the signing of Executive Order 12856 Pollution Prevention and Right-to-Know in the Government [October 1993] placed additional requirements on federal facilities and organizations that perform on government-issued contracts. Most government agencies have established a goal of the reduction by 50 percent of releases and off-site transfers of SARA Title III chemicals for treatment and disposal by 1999. This reduction is planned not only for the federal facilities, but will also be included in the acquisition process for new and existing aerospace programs.

The primary focus of the 50 percent reduction in the use of toxic materials is on the following chemical constituents, which are the largest volume use streams of the SARA Title III chemicals or pose significant health hazards:

Benzene	Methyl ethyl ketone [MEK]
Cadmium	Methyl isobutyl ketone [MIBK]
Carbon Tetrachloride	Nickel
Chloroform	Tetrachloroethylene
Cyanide	Toluene
Dichloromethane	Trichloroethane
Lead	Trichloroethylene
Mercury	Xylene
Methylene dianiline [MDA]	Diisocyanate
Freons	Chromium

In addition to the reduction requirements, government agencies have imposed the requirement for aerospace contractors to produce metrics on the volumes used of each product which contains these constituents and reduction status. The additional requirement in the Executive Order to revise Technical Orders and Military Specifications that require these materials is an enormous task.

Federal Acquisition, Recycling, and Waste Prevention. Executive order 19873 Federal Acquisition, Recycling, and Waste Prevention, signed October 1993, mandates the review and revision of specifications, product descriptions, and standards to enhance procurement of recycled or environmentally preferable products by government agencies. The order sets a minimum content standard for printing and writing papers and sets agency goals for waste reduction and procurement of environmentally preferable products.

Additional requirements are environmental factors must be considered in acquisition planning for all procurements and in contract awards. Federal agencies must identify, evaluate, and revise standards or specifications that present barriers to minimizing the emission of harmful by-products. Each federal agency is required to establish goals for solid waste prevention and recycling to be achieved by 1995. The requirements in executive order 19873 will be flowed to the aerospace contractor via contractual language on new and modified contracts.

Occupational Health and Safety [OSHA]. OSHA has also imposed more stringent industrial hygiene controls on some key aerospace materials: hexavalent chromium, cadmium, methylene dianiline, and methylene chloride. The increased controls, which include personal protective equipment, increased ventilation, specialized "set aside" control areas for use of these materials, add cost to fixed price production contracts which were not originally anticipated or included in the government contract or the final price of the product .

materials used. When cost control is desirable, the objective must be to spend the limited dollars on the materials which represent the highest risk, which includes volume and ranked regulatory risk.

Approach. The approach used by Northrop B-2 Division was to progressively eliminate the use of the *highest risk* chemical constituents which posed the *lowest technical risk and cost.* Each material is characterized by the automation described above, which matrixes all local, state, and federal regulations which impact the materials or processes. All known "pending" or probable regulations are included in this matrix. This provides an approximate five year forecast of new regulations. The SCAQMD has been most helpful in assisting in these forecasts. All materials and processes are then designed to the most stringent regulatory requirements and forecasts.

This five year forecast approach adds cost in the up-front design effort, but recovers the cost many times over by reducing the multiple qualifications of materials and processes as the regulations change.

Each regulated constituent used was ranked, as shown in Figure 3.

RANK	DEFINITION
1	Command and control regulatory requirements
2	Acutely Toxic: causes biological damage as result of single exposure to relatively small amounts
3	Reproductive toxicants
4	Carcinogens, Chronic Exposure [IARC 1>2>3]
5	Non-carcinogen, Chronic Exposure
6	Threshold regulations: control to an emissions level

Figure 3. Ranking of regulated constituents based upon regulatory and exposure risks.

An iterative decision process **[Figure 4]** was utilized to identify the highest-risk materials for replacement or implementation of control technology. The decision process incorporates both the engineering technical requirements with the regulatory requirements using a risk-based decision process.

This process has allowed a rational management of regulatory requirements with a reduced cost. Production schedule interruptions are minimized as the plan allows the forecast of material changes and places them on a schedule. Cost control is achieved by avoiding the use of the regulated constituents in the initial design and by preventing iterative qualifications of the same material caused by implementation of new regulations.

The long range strategic plan places the implementation of new regulatory requirements and the engineering closure plan to eliminate the material on the same time line. Each material is evaluated for total cost to use, i.e., hazardous waste, contingent liability, technical risk, health risk, regulatory risk, touch labor impacts, and capital asset replacement costs. Each project is assigned a process owner and metrics of progress on the project are reviewed regularly.

The benefit of this approach is the production program will soon move ahead of the regulations. The process will no longer be **compliance** driven.

Conclusions

Compliance with the rapidly changing environmental and health and safety regulations is about 10 percent science of material substitution and 90 percent managing the process to control cost, schedule and performance. It requires that non-traditional teams from the regulatory and the engineering departments within an organization be formed to develop common goals and approaches. Where applicable, minimization of high risk constituents, rather than elimination, is employed to reduce risk to the air vehicle

The cost of complying can be reduced significantly with automation, which also reduces the risk of non-compliance with a large and complex body of regulations. The goals of improving the environment and meeting the mission and performance requirements are not mutually exclusive - just a large management task which lends itself well to a systems engineering approach.

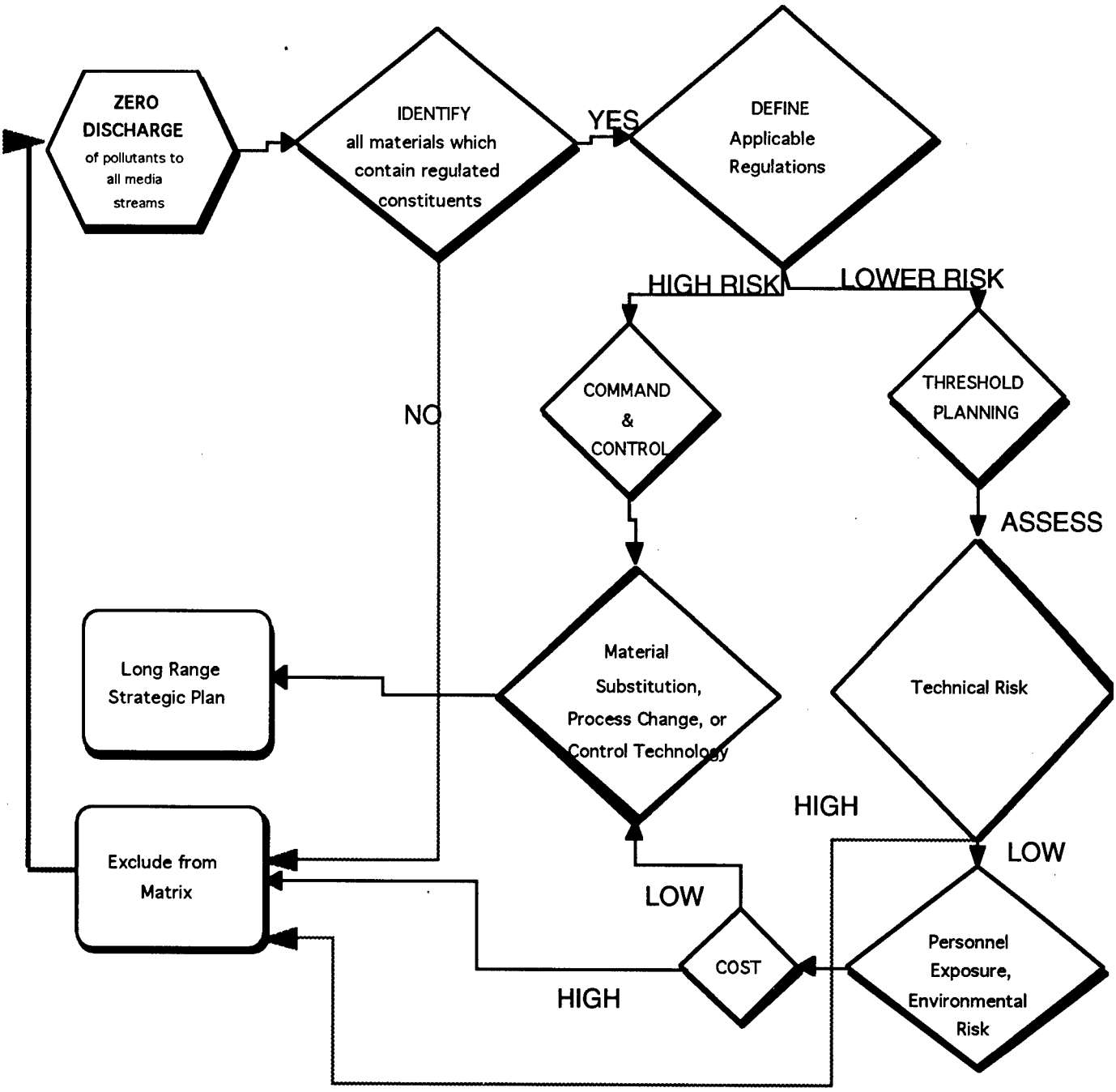

Figure 4. Risk-based decision process for process management and development of the long range strategic plan

CONVERGENT SPRAY PROCESS FOR ENVIRONMENTALLY FRIENDLY COATINGS

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ABSTRACT

Conventional spray application processes have poor transfer efficiencies, resulting in an exorbitant loss in materials, solvents, and time. Also, with ever tightening Environmental Protection Agency (EPA) regulations and Occupational Safety and Health Administration requirements, the low transfer efficiencies have a significant impact on the quantities of materials and solvents that are released into the environment. High solids spray processes are also limited by material viscosities, thus requiring many passes over the surface to achieve a thickness in the 0.125 -inch range. This results in high application costs and a negative impact on the environment.

Until recently, requirements for a 100% solid sprayable, environmentally friendly, lightweight thermal protection system that can be applied in a thick (>0.125 inch) single-pass operation exceeded the capability of existing systems. Such coatings must be applied by hand lay-up techniques, especially for thermal and/or fire protection systems.

The current formulation of these coatings has presented many problems such as worker safety, environmental hazards, waste, high cost, and application constraints. A system which can apply coatings without using hazardous materials would alleviate many of these problems.

Potential applications include the aerospace thermal protective specialty coatings, chemical and petroleum industries that require fire-protection coatings that resist impact, chemicals, and weather. These markets can be penetrated by offering customized coatings applied by automated processes that are environmentally friendly.

Introduction

Currently EPA is preparing regulations and gathering studies to meet rules set by the United States Congress in the Clean Air Act Amendments (CAAA) of 1990. EPA is proposing new Control Techniques guidelines (CTG's), developing rules to limit emissions of toxic air pollutants through two programs, National Emission Standards for Hazardous Air Pollutants (NESHAP's) and Hazardous Air Pollutants (HAP's).

Certain low-usage coatings were not addressed in the NESHAP. These coatings are adhesives, sealants, and 30 types of specialty coatings which

represent less than 6 percent of the total HAP emissions from the industry. Also, the EPA data analyses indicate that the maximum achievable control technology (MACT) floor for these coatings would be no control. The EPA is now requesting public comment on the need for a separate CTG providing guidance for the control of these types of coatings.

The overall objectives of the convergent spray project are to develop and demonstrate a convergent spraying process capable of applying a variety of high-solid coatings. Specific objectives are:

- To develop a solventless, zero-content volatile organic compound (VOC) Convergent Spray Technology (CST) to meet proposed EPA regulations
- To increase the transfer efficiencies of high-solids coating formulations, and
- To increase the application thickness per pass while maintaining the surface properties and coating characteristics.
- To address waste minimization through unique processing.

This project focuses on developing a state-of-the-art high-solids formulation and its associated application processes for thermal protection materials, insulative and structural restoration coatings. Work to date has centered on improving process characteristics while reducing costs and associated hazards.

System Design for Environmental Regulations

In order to address environmental issues such as VOC reduction and or elimination, waste minimization a convergent system was designed to meet the challenges of the 1990's for specialty coating applications. The system is designed as a spray on demand application system. Batch processing and associated wastes with pots and material transfer lines has been significantly eliminated along with the associated costs of material wasted due to short sudden equipment failures . Completion of convergent sprays is followed by a purging of the end effector resin mix system with some 200-300 ml of environmentally acceptable solvent after spray application. Resin and solid filler transfer lines are not purged because there is no mixed materials in lines. This reduces process waste to a same minimum, whether application to large or small parts or configuration.

The ergonomic design of the system also allows for efficient use and experimentation. Simple change out of resin materials, fillers with changes in material flows can lead to new coating development and optimizing performance.

On demand design also allows for more complex application techniques which reduce manual or hand close-out of more complex hardware configurations.

The aerospace industry has a unique problem in complying with changes in regulatory requirements. It can take up to 10 years to design a completely new aircraft. The production of complex aircraft, both commercial and military, relies on "long lead" procurement of assemblies, subassemblies and parts. Even though "rate manufacturing" can be between 5 to 50 units per year, many of the parts used were procured years earlier. Compatibility of reengineered materials with the "long lead" units already procured is a very large area of risk for this industry.

2.0 Strategies for Survival and Cost Control

Elements of the Strategy. The aerospace industry changes materials and processes in a very cautious manner, as these materials and processes must support a complex aircraft assembly which performs in a high risk environment. The pilot cannot pull the aircraft to the side of the road if an in-flight failure occurs which interferes with the ability the fly the aircraft safely. All aircraft have stringent performance requirements, which are defined by the aircraft mission, i.e., commercial [where passenger safety is critical]; military fight aircraft [where speed and agility are critical]; stealth aircraft [where low observability is a critical performance factor]. A simple material or process change can, in some cases, require the design allowables performance measurements be conducted again to verify the modified aircraft still meets the mission and flight safety requirements.

A key element in developing a strategy for incorporation of regulatory requirements into the design, manufacture, operation, maintenance and repair of the aircraft is the development of an integrated strategy, which includes both the engineering performance requirements as well as the regulatory requirements. Many organizations delegate their regulatory compliance responsibility to an administrative organization that has little visibility or understanding of the aerospace product performance requirements or the inherent risks of changing the materials or processes without a complete engineering evaluation of the subsequent impacts. The administrative organization will also be frustrated because the design, manufacturing, and logistical support community will not employ source reduction, where possible, to reduce the regulatory risk.

The second element in developing a successful strategy is the development of a long range strategic plan that will accommodate the advance planning for "long lead" procurements of components or assemblies for the aircraft.

The third element of a successful strategy is automation. Most of the regulations, both environmental and occupational health and safety, require the knowledge of all hazardous and VOC-emitting constituents

of each material and process used. It is atypical for the engineering design community to be knowledgeable of the chemical composition of the coatings, adhesives, sealants, and other materials used on the air vehicle. The design engineer is untrained in the basic chemistry of the materials and processes. The use of automation to marry the regulatory requirements to the regulated constituents in aerospace materials is essential in ensuring compliance and in cost control in the design effort. Automation also facilitates the preparation of the extensive reports required by the regulatory agencies.

Strategy Development. Most aircraft systems are unique in their design, i.e., each system will have a unique fatigue profile for the design and materials of construction. Therefore, the first step in the development of a long range strategic plan is recognition that, in general, there must be a plan for each aircraft system. A "common" plan for multiple aircraft systems is more probable for commercial aircraft. Military aircraft are at the other end of the spectrum and a unique plan is usually required for each system. Space vehicles fall more toward the military end of the spectrum.

Project or Integrated Product Team. The environmental, occupational health and safety, and engineering community must integrate their missions, usually by employing a teamed approach to material and process changes. Typically the team will be composed of the following organizations: Materials and Processes; Logistics; Test Flight; Contracts; Procurement; Design; System Safety; Research & Development; Environmental Management, Occupational Health & Safety, and the Program Office. The development of the long range strategic plan and all subsequent changes to the materials and processes are reviewed by this team for all potential impacts.

Automation. All regulated constituents in the air vehicle materials and processes can be scanned into or manually entered into a relational database. The data is extracted from the Material Safety Data Sheet and supplier data. All regulated constituents are identified by their chemical abstracts number [CAS#]. The multiple material safety data sheets that comprise a material system are grouped to identify all constituents in the "as applied" material system [i.e. a two-part coating which uses a thinner or reducer]. The material system is then linked to the command media, i.e., military or contractor specification, technical order.

Commercial software is available which links the regulated constituents to all state, federal and local regulatory requirements. The final linkage is from the regulatory database to the command media which specifies it. The command media is the document used by all aerospace programs to ensure that only "qualified" materials and processes are used on an air vehicle.

This type of automation allows users to quickly identify which materials are regulated by high risk or recently changed and new regulations. The automation also allows tracking of the volumes of the

Basic Convergent System

The Convergent Spray process is a means by which mixed resins are sprayed and entrained with solid filler materials outside the spray end effector to form a coherent coating material.

The resin system comprises two fluid transfer systems which supply the end effector with the resin polymer components separately maintaining proportional flow.

Two vibratory loss-in-weight units pneumatically feed a steady, measured stream of glass spheres and cork granules to a cyclonic mixer which then feeds the end effector (although solid, the eccospheres and cork flow much like a fluid).

The convergent spray end effector design consists a spray head in which the epoxy components are mixed and atomized, and a larger shroud, in which the glass/cork mixture is injected into an atomized resin air stream. The solids carrying air stream entrains into the atomizing resin spray (Convergence), and the resin/cork/glass sphere mixture is deposited to the substrate.

Mixing of resins does not occur until the very end of process at the resin mixing system at the specially designed end effector.

The resulting spray coatings produces high viscosity coating that can be applied to vertical surfaces without slumping.

Convergent Applications

Thermal Protection for SRB

A two-part room temperature or heat cure epoxy system, was selected as the resin side system material because it is a familiar adhesive used in the solid rocket booster (SRB) thermal protection system, and has excellent mechanical property characteristics. Granular cork and glass microspheres were selected as the dry system materials.

Tests of coatings comprising epoxy clear resin, granular cork, and glass eccospheres showed the best mix is 75 to 80 percent resin and 20 to 25 percent cork and glass eccospheres which results in densities ranging from 30 to 35 lbs/ft^3 and flatwise tensile strength generally from 150-250 pounds per square inch. Additional catalyst was shown to be to be an efficient way to speed the cure of the epoxy resin with no adverse effects.

In 1993, a production prototype was fabricated and installed in Marshall Space Flight Center's Productivity Enhancement Laboratory (building 4708) for detailed assessment and evaluation of a USBI IR&D developed thermal protection coating (TPS).

Equipment was specified and procured and facilities modified to accommodate the prototype. Programmable logic controller and host communications programs were developed to control the prototype. Finally, a spray test program was executed to produce test panels and demonstrate the end effector. As a result, in January 94 Marshall Convergent Coating (MCC-1) was selected for final development and qualification for use as a Thermal Protection System on the Solid Rocket Booster (SRB).

In 1993, USBI Materials and Processes designed, fabricated, and tested a more efficient convergent spray end effector. Improvements in the wet resin

spray system were designed and implemented. This new design was tested with great success in USBI's labs and later at MSFC's labs. Coating variation and surface finish were greatly improved. The coatings also performed well in aerodynamic heating tests in the MSFC Improved Hot Gas Facility. Coatings were also applied to small test articles like cable tunnels used on SRB.

It has also been demonstrated that the coatings will adhere to complex geometries such as stringers, risers, and bolt heads protruding from a structure.

Other lower recession formulations are being developed such as a unique polysiloxane/epoxy and epoxy/phenolic formulations which will potentially reduce recession and increase insulation characteristics.

Finally, the EPA toxic characteristic leaching procedure indicates heavy metal concentrations are well below acceptable limits, thus allowing disposal of cured material in a city landfill as non-regulated waste.

Other Potential High Performance Coatings

With the advent of increased processability and selection of a wide variety of polymer resin systems such as epoxies, urethanes, acrylics, and polyesters potentially new high solids coatings for use as structural, architectural and protective coatings can now be pursued. The capability of convergent spray to use a high degree of inexpensive filler loading can reduce cost of coating materials.

Unsaturated polyester resins can be convergently combined with traditional aggregate materials to be used as a low cost polymer concrete for resurfacing of highways and or support structures. Polyesters offer long endurance, skid resistance and short cure times.

Highly flame retardant epoxy based phosphate intumescent coatings have been developed for use in convergent spray systems. Flame retardants were added to achieve an Underwriters Laboratory (UL) rating of V-0.

Convergent Control Systems Development

Development of the convergent spray system for Thermal Protection involved a wet side (resin) and a dry side (granular cork). The feed and control integrity of each side of the materials system is crucial to ensure an accurate spray and mixing of the applied coating.

The On-Demand design of Convergent Spray puts more emphasis on process control in for materials coatings design. It also gives us the understanding and knowledge of really knowing what's occuring in different area's of the process. It allows the user to take a step back, look at the big picture and divide the process out into modules. In this way the control system can be designed from the top down and implemented and tested from the bottom up allowing us to meet the operational requirements from total quality management.(TQM)

Object oriented control systems and program logic control software (PLC) systems are being used on convergent spray systems. These control systems integrate data acquisition, supervisory control and management information functions and creates a single graphic window into the whole

process. In addition these systems perform alarming, trending and event detection. (See Figure 2)

A portable cart system is in design to address application of structural and architectural coatings. This system is being designed for field application of less critical coatings without the major cost involved with software control and PLC design.

Summary

A demonstration of a new convergent spray process that eliminates volatile, environmentally hazardous solvents has now been demonstrated and has been selected as a the next process to be used on the solid rocket booster (SRB) for application of Thermal Protection Coatings.

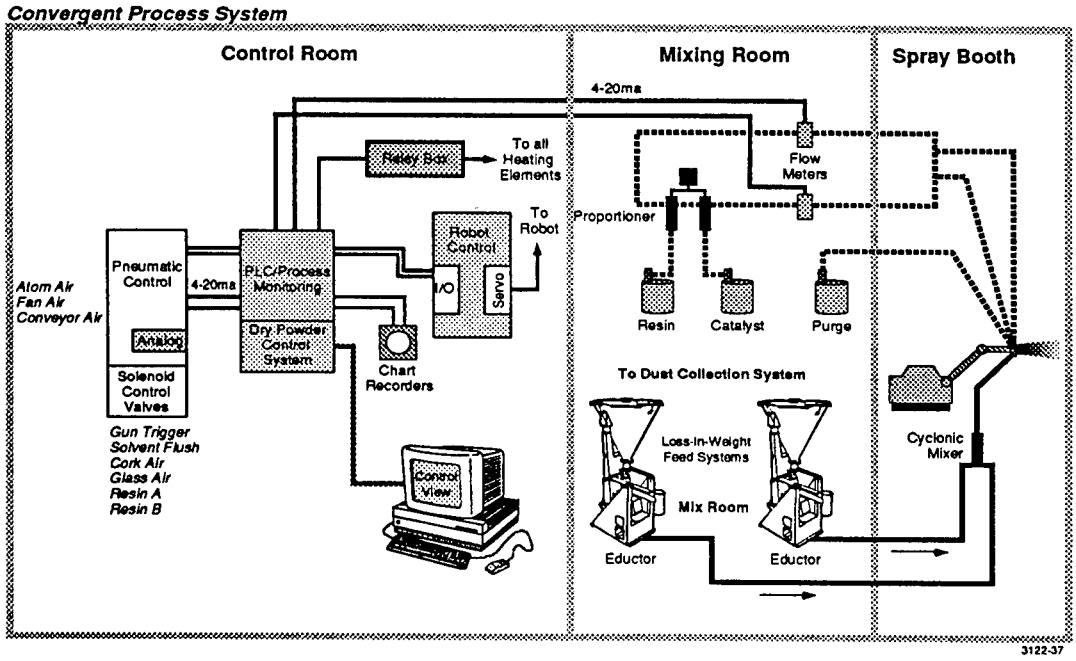

Figure 1: Schematic of solventless spray system. (3122-37)

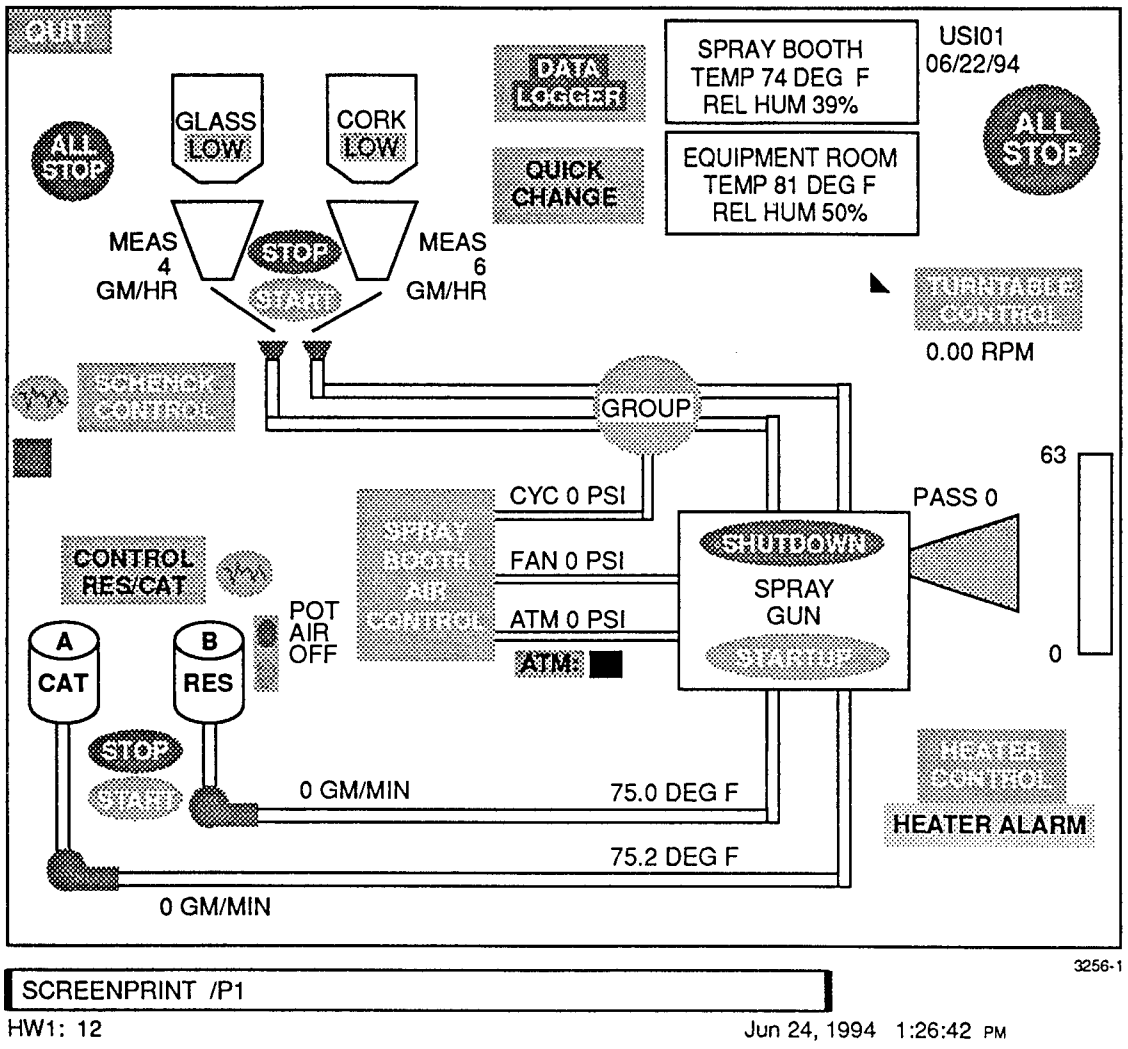

Figure 2 : Software Window Graphic Display

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SSME Main Combustion Chamber (MCC) "Hot Oil" Dewaxing

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Abstract

In an attempt to comply with the changing environmental regulations, a process was developed for the replacement of perchloroethylene in the dewaxing of the Space Shuttle Main Engine (SSME) Main Combustion Chamber (MCC) and other associated hardware filled with the Rigidax® casting compound. Rigidax® is a hard blue-dyed, calcium carbonate filled thermoplastic casting compound (melting point 77° C) that is melted and poured into hardware cavities to prevent contamination during material removal processes, i.e. machining, grinding, drilling, and deburring. Additionally, it serves as a maskant for designated areas during electroforming processes.

Laboratory testing was conducted to evaluate seven alternate fluids for the replacement of perchloroethylene in the dewaxing process. Based upon successful laboratory results, a mineral oil was selected for testing on actual hardware. The final process developed involves simultaneous immersion and flushing of the MCC channels using a distinct eight stage process. A nonvolatile hydrocarbon analysis of a solvent flush sample is performed to determine the hardware cleanliness for comparison to the previous perchloroethylene dewaxing process.

Introduction

The Space Shuttle Main Engine (SSME) Main Combustion Chamber (MCC) is a cylindrical, regeneratively cooled, structural chamber consisting of a coolant liner, a high strength structural jacket, coolant inlet and outlet manifolds, and a throat shell (see Figure 1a). The MCC contains the burning propellants with chamber cooling provided by hydrogen flowing through the coolant channels in the liner.

The liner is spin forged Narloy Z which is machined to the same contour as the inner diameter of the structural jacket. The outer surface of the liner (Figure 1b) has 390 milled axial coolant channels measuring approximately 24" linearly (from the aft to the forward end) with varying rectangular cross sectional dimensions ranging from 0.035" x 0.093" at the throat to 0.060" x 0.247" at the aft end of the liner. After the milling operation the channels are deburred, inspected and then readied for application of a wax maskant. The wax used is Rigidax®, a calcium carbonate filled thermoplastic compound with a melting point of 77°C. This particular compound is used because it is dimensionally stable when processed through the plating solutions.

Molten wax is poured into each of the 390 channels while the liner is continuously rotated horizontally. After cooling to room temperature, the liner is wet sanded by hand to expose the Narloy Z on the lands between the channels; and maintain a 32 surface finish. The required amount of copper (Cu) layer is then electrodeposited onto the liner to closeout the channels and to serve as a hydrogen embrittlement barrier followed by electrodeposition of the required amount of nickel layer. The electrodeposited nickel (EDNi) is then machined to the desired dimensional requirements. The dewaxing operation to remove the Rigidax® in the channels is performed following this step.

Previously, the dewaxing operation was performed by a combination of vapor degreasing and channel flushing with perchloroethylene following the process flow as shown in Figure 2. The chamber was then filled with perchloroethylene and allowed to soak for thirty minutes while suspended in the vapor zone of the degreaser after which the solvent was collected for verification analysis. The collected sample was evaporated and the residue analyzed for wax content using infrared spectrophotometry (IR). The cleanliness requirement is less than 0.50mg wax/200ml effluent. Following a drying step, an acetic acid and deionized water flush was performed to remove any residual calcium carbonate that may have been present after dewaxing. A final drying was performed, followed by borescope inspection viewing to inspect for any blocked channels.

Rocketdyne initiated an environmental task to eliminate the use of perchloroethylene for this operation due to the listing of perchloroethylene as a suspected carcinogen in California's list of air toxics, its regulation by rule AB2588 (Comprehensive Community Notification) and Proposition 65, and the inability to meet the stringent Occupational Safety & Health Administration (OSHA) allowable exposure limits (AEL) of 25 ppm. The focus of the replacement task was to develop a process that would be environmentally compliant, compatible with the hardware substrate materials, and yield cleanliness levels comparable to those achieved with the perchloroethylene process. To minimize the cost and time associated with extensive hardware trials, laboratory screening tests were performed to select the most feasible candidates followed by process scale-up.

Procedure

Identification Of Candidate Cleaners

Initial efforts focused on a literature review, an industry survey of Rigidax® users, supplier surveys, and recommendations by the in-house Environmental and Health & Safety departments. A list of candidate cleaners was compiled and the cleaners were reviewed for physical and chemical properties, cleaning effectiveness, material compatibility and integration into the existing manufacturing processes. Seven alternate fluids, as listed in Table 1, were evaluated during the laboratory test phase.

Laboratory Test - Dewaxing Effectiveness

Laboratory wax removal tests were performed using a 3" x 3" cut away segment of a scrap MCC. The test segments were pre-cleaned by vapor degreasing with perchloroethylene, weighed, filled with Rigidax® and reweighed. A 450-550ml sample of the test fluid was placed into a 600ml Pyrex beaker. The fluid was heated using a hot plate stirrer to the desired test temperature range as indicated in Figure 4. The Rigidax® filled segment was suspended in the test fluid which was agitated using a Teflon coated magnetic stir bar. The segment was periodically removed and visually inspected for wax removal. The time required to open the channels and remove the wax was recorded. When the MCC segment was visually clean, it was cooled to ambient temperature and reweighed to verify wax removal. If residual test fluid remained on the test segment, it was rinsed in hot deionized water at 60°C for one hour. The MCC test segment was then reweighed to determine any weight gain or loss. The same procedure was used for all of the fluids evaluated except as noted.

In the case of the hot oils (DXE and Turco 6802), an aqueous cleaning step was added prior to the deionized water rinse. The hot oil test required an additional alkaline cleaning step to remove the oil after dewaxing while the other fluids were tested as stand alone dewaxing fluids. Only rinsing was required with the Axarel and Brulin, and only evaporative drying was required with the KNI-2000 solvent and the kerosene.

Laboratory Test - Material Compatibility

General corrosion testing was performed with the Turco 6802 oil and Dupont Axarel 56 to determine the compatibility of these fluids with the hardware alloys. Five specimens each of nine metals were evaluated. The test panels included:

- Nickel Alloy 718
- Nickel Alloy 625
- Iron Nickel Alloy 903
- EDNi
- 21-6-9 Stainless steel
- A-286 Stainless steel
- Hastelloy® W
- Copper
- Narloy Z

Each panel was cleaned with Scotch-brite and deionized (DI) water to a water break-free surface, dried and weighed. One specimen of each alloy was set aside as a control. From each alloy set one panel was immersed in Axarel 56 at 49-54°C, one in Axarel 56 at 79-85°C, one in the Turco oil 6802 at 79-85°C and one in the Turco oil at 99-121°C for twenty minutes. The panels were allowed to stand in the cooling fluid for 24 hours. Upon removal from the fluids, the panels were lightly flushed with DI water; followed by a four minute immersion rinse in DI water. The panels were oven dried for one hour at 91-96°C. The panels were reweighed upon cooling and then evaluated visually and by use of a 30-100X microscope for any noticeable corrosion.

Pilot - Scale Tests

A pilot plant was assembled to allow testing of a full-size MCC. The final configuration of the pilot plant consisted of the following:

- A 4ft x 4ft x 4ft stainless steel tank containing the Turco 6802. The tank was equipped with a centrifugal filtration unit to filter out the calcium salt from the oil, and a 100 micron size rated cartridge filter to prevent particulate matter from entering the MCC channels.

- A 4ft x 4ft x 4ft stainless steel tank containing the 75/25 Axarel 56/water. The tank was equipped with a 100 micron size rated cartridge filter, two 15KW Chromalox external heating elements with safety interlocks to protect against any overheating. Agitation manifolds were added to ensure effective emulsification of the Axarel/water mixture. The agitation manifold consisted of four nozzles in each corner at the bottom of the tank.

- Two 4ft x 4ft x 4ft polypropylene tanks, one containing the Turco Vitroklene alkaline cleaner and the second containing acetic acid. Both tanks were equipped with 30 micron size rated cartridge filters.

- One 4ft x 4ft x 4ft polypropylene lined tank for intermediate water flushing and

- One stainless steel tank measuring approximately 4ft x 4ft x 4ft utilized for final rinsing with deionized water which was equipped with a 20 micron size cartridge filter.

Each tank was equipped with a 5hp magnetically coupled pump except the acetic acid tank which was equipped with a 1 1/2hp pump used at variable flow rates of 30-50gpm. Each pump was equipped with a safety interlock to shut down the pump if a loss of prime condition should occur. This ensures that the pumps do not run dry. Each tank was equipped with two 15KW immersion heaters except the Axarel as noted.

Testing in the pilot facility was conducted using a full-size scrap MCC (Figure 1). The MCC was first pre-cleaned by vapor degreasing with perchloroethylene and then filled with Rigidax®. Prior to wax application the MCC was heated to 177°C. Melted wax was then poured at 149°C into the channels from the forward end and allowed to gravity flow to the aft end. Once filled, the chamber was allowed to cool to room temperature. Dewaxing was initiated by first placing the MCC in an oven heated to 135-163°C for 2 ± 0.5 hours to remove the bulk wax as per the normal dewaxing process. The remaining wax was then removed using the experimental hot oil dewaxing flow process as shown in Figure 3.

Each cleaning stage involved an initial soak period by immersing the MCC in the fluid and filling the internal cavities after which the fluid was flushed through the channels (from the aft end up to allow observation of the effluent fluid). Gaseous nitrogen (GN2) was simultaneously injected into the fluid stream to enhance a scrubbing action in loosening and dissolving wax from the channel walls. GN2 was used with all the flushing operations except the acid flush. Process optimization including times, temperature, fluid flow rates and GN2 flow rate as well as upgrading of the 1/2 to 3/4 hp pumps to 5 hp pumps were performed as testing progressed. Verification for the effectiveness of wax removal, was performed using TCA (1,1,1, trichloroethane). The MCC was filled with TCA and allowed to soak for 30 minutes at 66°C. The TCA was collected and the wax content determined by IR spectrophotometry after solvent evaporation.

Production - Scale Testing

Production scale testing was conducted primarily using the scrap MCC and the dewaxing flow process (Figure 3) with implementation of the optimized parameters. Several tests were conducted to evaluate the repeatability of the process. Process specification approval from the customer was obtained and facility modifications were completed to permit use of the process on production hardware. Production hardware continues to be dewaxed using the hot oil process.

Results & Discussion

Laboratory Rigidax Removal

Laboratory test results are presented as the amount of time, at a particular fluid temperature, required to remove the wax from the channels of the test segment (Figure 4). NVR evaluation was not necessary since the test segment channels were visually inspectable for any blockages or residual film on the channel walls. The results from the initial laboratory experimentation using the DXE oil showed that the test fluid was capable of dewaxing the MCC test segments based upon the selected time and temperature parameters. Following the completion of seven successful laboratory tests, a primary process set up consisting of the DXE hot oil dewax, alkaline clean, acid flush, DI water rinse, dry, and a TCA verification was proposed for trial at the pilot scale testing.

Pilot & Production Scale Rigidax Removal

Test results at the pilot & production scale levels are presented as wax content of the TCA solvent sample obtained from the MCC subsequent to the cleaning cycle. The results are classified as pilot-scale and production-scale. The pilot-scale refers to the original plant with minimal processing

capability and the production-scale refers to the upgraded facility with the more robust processing capability. NVR hydrocarbon analysis was used since the channels are not visually accessible. Results from both the pilot and production scale tests are graphically represented on Figure 5.

In the pilot-scale testing, it was determined that the primary process was inadequate in the dewaxing of the MCC. Additionally, the DXE oil vapor was offensive to the employees. Furthermore, each process step lasted 8 hours, requiring one week to completely dewax an MCC. This process also lacked intermediate water flushing, resulting in severe contamination of the process tanks (from excessive carry-over) and subsequent incomplete cleaning. Test A (Figure 5), was performed using perchloroethylene. Test B, in Figure 5 is the average of five tests performed with the DXE process.

A complete re-evaluation of the dewaxing process which included evaluating test fluids other than the DXE oil was performed (Figure 4). Turco 6802 oil was selected at the conclusion of the laboratory testing. Turco 6802 contains a surfactant and with its improved rinsability exhibited a higher potential for effective dewaxing. Both the Axarel 32 and 56 showed effective dewaxing potential but the low flash points (93-99°C) diminished their viability as substitutes. The KNI-2000 solvent, kerosene and Brulin Exp. 492-1 were ineffective and no further tests were conducted with these fluids.

Use of the Turco 6802 oil to replace the DXE in the preliminary process set eliminated the odor encountered with the DXE but the parts still failed to meet the NVR requirement. The results showed the oil effectively dewaxed the MCC but the alkaline cleaner (Turco 3878) could not effectively remove the residual oil/wax mixture from the liner walls. Vitroklene cleaner was substituted for the Turco 3878 due to its higher operating temperature but did not enhance the cleaning effectiveness either. It was critical that all processing fluids in the dewaxing process were operated above the melting point of the Rigidax® to avoid any form of re-solidification of the wax.

The inability to meet the NVR requirement resulted in evaluating the use of GN2 during the flushing process and an Axarel 56 closed loop soak and flush step at the end of the hot oil flush. The GN2 was intended to enhance the scrubbing action during flushing and the Axarel 56, being a mixture of aliphatic hydrocarbons, aliphatic esters, and a nonionic surfactant, would effectively remove the residual oil/wax mixture and followed by an alkaline clean (Vitroklene). This combination; Turco 6802 oil ➡ Axarel 56 ➡ Alkaline clean(Vitroklene) ➡ Acetic acid ➡ DI water rinse ➡ TCA verification, finally yielded passing NVR results (Figure 5, test C) and thus provided the basis for a permanent replacement for perchloroethylene dewaxing process.

Due to the low flash point of the Axarel 56, follow - up laboratory tests were designed to test the Axarel in an emulsion concentration at various temperatures in an attempt to eliminate the hazard. The tested emulsion ratios were effective in dewaxing the MCC test segments and the fluids would not flash when tested. Testing following the addition of the Axarel in the dewaxing process improved the potential for yielding passing cleanliness results (Figure 5) thus proving the process production ready. Pilot tests D, E and G were also conducted with test C combination but did not pass the cleanliness requirement test due to parameter changes. In tests D and E, the operating temperature of the Axarel was lowered and in test G, a shortened processing time for the overall process was used. Tests F and H were conducted with combination C parameter and both yielded passing results. Production scale tests that followed (Tests 1 through 5, Figure 5) were conducted on a continuous basis (using the same parameters as test C but with the 75/25 Axarel/water emulsion) to collect data and determine the repeatability of the process. Results show consistency in meeting the cleanliness requirement and so have the production hardware processed to date.

The following events occur during the dewaxing process. The hot oil first dissolves the wax while the calcium carbonate filler material drops out of solution. The Axarel, in turn, dissolves the residual oil/wax film left on the channel walls and an aqueous alkaline cleaner then removes the Axarel. The acid flush eliminates any residual calcium carbonate salts that may be left in the channels. A final DI water flush is performed to remove any cleaning solution residues.

Material Compatibility

All the tested alloys exhibited compatibility with the tested fluids. There were no evidence of surface corrosion or intergranular attack (IGA) when the coupons were examined visually or using a 30X to 100X microscope.

Conclusion

It can be concluded from the extensive testing performed thus far that:

- The hot oil dewaxing process is a technically acceptable process for production implementation and is a viable replacement for perchloroethylene dewaxing.
- The Axarel emulsion eliminated flash point concerns.

Acknowledgment

The author would like to acknowledge especially Marilyn Fritzemeier, for her technical and editorial contributions, the equipment laboratory personnel at the Santa Susana Field Laboratory (SSFL), especially R. Leonard & L. Goff, for their facility design inputs, and personnel at the chemistry lab (Canoga) who contributed immensely to the success of Hot Oil Dewaxing project. Their tremendous support and dedication during the development period is greatly appreciated.

TEST FLUIDS	MANUFACTURER	FLASH POINT	BOILING POINT
DXE ($C_{18}H_{22}$) Dixylylethane	AllCo Chemical Corporation	163°C (325°F)	335°C (635°F)
Re-entry-KNI Solvent 2000	Envirosol Inc.	64° C (148°F)	190-215°C (375-420 °F)
Turco 6802 Oil - Petroleum distillate w/Octylphenoxypoly (Ethyleneoxy) Ethanol Surfactant	Turco Products Inc.	149°C (300 °F)	260°C (500 °F)
Axarel 32	Du Pont Company	94-99°C (200- 210° F)	221-295°C (430-563°F)
Axarel 56	Du Pont Company	94-99° C (200-210°F)	216-260°C (420-500°F)
Kerosene	J.T. Baker	65-85°C (150-185°F)	79-163°C (175-325°F)
Brulin Exp 492-1	The Brulin Corporation	N/A	N/A

Table 1: Description of Test Fluid

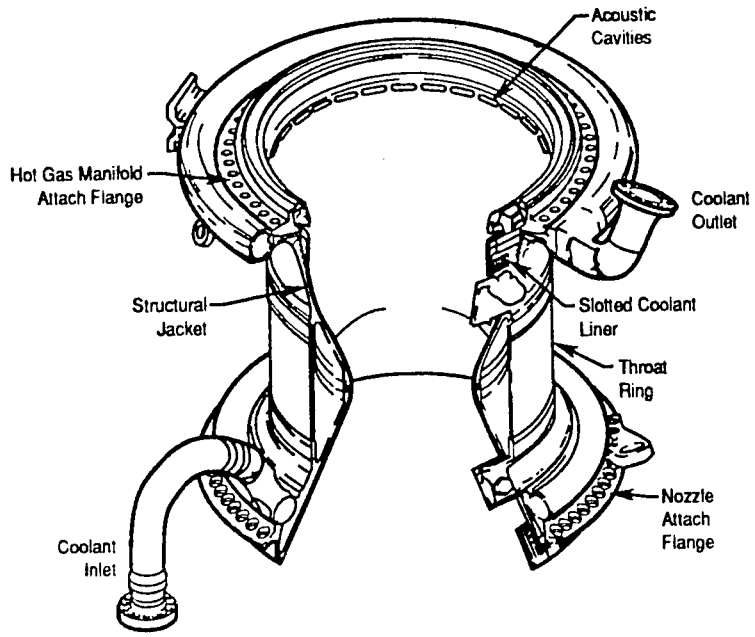


Figure 1a: Main Combustion Chamber

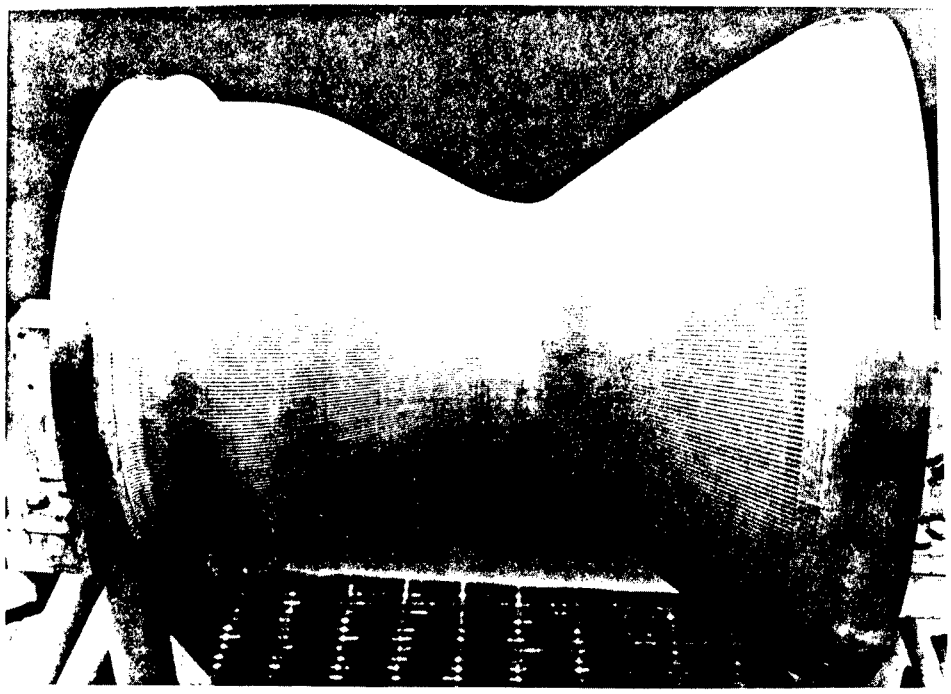


Figure 1b: MCC Liner With Slotted Channels

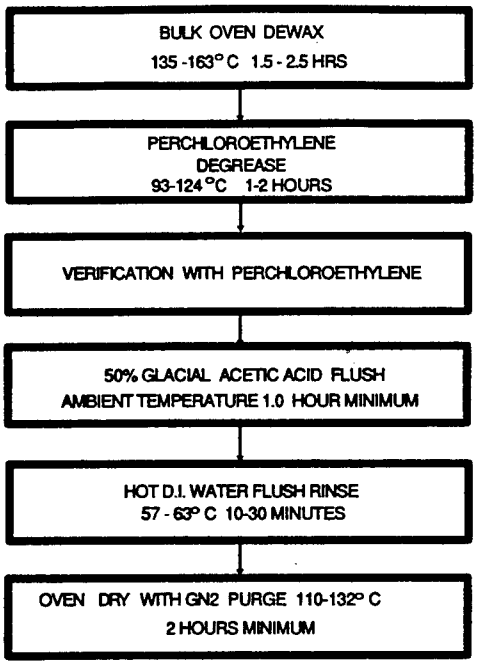
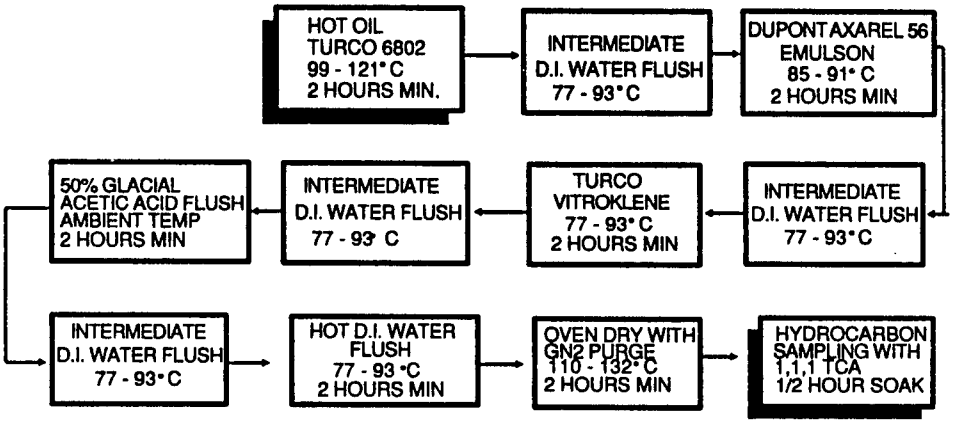


Figure 2: Perchloroethylene Dewaxing Process



NOTE: ONLY ONE TANK IS UTILIZED FOR THE INTERMEDIATE FLUSHES SHOWN

Figure 3: MCC Dewaxing Flow Process

Bicarbonate of Soda Paint Stripping Process Validation and Material Characterization

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Abstract

The Aircraft Production Division at San Antonio Air Logistics Center has conducted extensive investigation into the replacement of hazardous chemicals in aircraft component cleaning, degreasing, and depainting. One of the most viable solutions is process substitution utilizing abrasive techniques. SA-ALC has incorporated the use of Bicarbonate of Soda Blasting as one such substitution.

Previous utilization of methylene chloride based chemical strippers and carbon removal agents has been replaced by a walk-in blast booth in which we remove carbon from engine nozzles and various gas turbine engine parts, depaint cowlings, and perform various other functions on a variety of parts.

Prior to implementation of this new process, validation of the process was performed, and materials and waste stream characterization studies were conducted. These characterization studies examined the effects of the blasting process on the integrity of the thin-skinned aluminum substrates, the effects of the process on both air emissions and effluent disposal, and the effects on the personnel exposed to the process.

Paper Content

San Antonio Air Logistics Center is responsible for the maintenance of the C-5 fleet. This maintenance involves among other things, corrosion control which includes depainting. In the past, we have always relied on the use of methylene chloride based chemical strippers for both aircraft and components. This method generated great quantities of waste which had to be drummed and disposed of as hazardous waste. The effluent itself was sent down the industrial waste lines to dedicated phenolic basins in our industrial waste treatment plant.

We began exploring various alternatives to chemical strippers in 1986. Many substitute processes emerged and two seemed viable for our requirements. Plastic Media Blasting (PMB) developed as an alternate method for depainting aircraft. We have since incorporated PMB in our aircraft depainting facility. The second alternative to chemicals which we considered viable was a similar abrasive process, bicarbonate of soda paint stripping. Having met various requirements for a paint removal process, we subjected the process to a series of vigorous tests. Proving successful through all the initial testing, we initiated a formal testing program to optimize the bicarbonate of soda blasting process parameters and characterize the effects of the blast stream on the substrate materials commonly used as aircraft skins. A separate test program was initiated to determine the environmental effects of the process on the worker, our existing industrial waste treatment system, and the ambient air quality.

The optimization and material characterization effort was contracted to Battelle out of Columbus, Ohio. The objective of the program was to determine if this particular process could meet or exceed Air Force criteria for productivity versus possible blast-imparted substrate damage. The process was tested in a fourteen foot wide by fourteen foot high by thirty-four foot long walk in blast booth installed in an existing chemical stripping room. The booth itself is basically a modified water wash paint booth. The

booth has a cross draft ventilation pulling the exhaust air through a water curtain and into the exhaust chamber, where it passes through a series of sheet baffles prior to exiting the stack. Used media and material removed from aircraft parts fall through a grated floor into a sloped trough filled with water. A series of pipes traverse the trough, each with 10 nozzles directed to maximize the agitation and mixing effect of the used media and water. The water is pumped through the agitation pipes and the exhaust chamber and recirculated throughout the system. A gravity drain weir accommodates the effluent discharge. The effluent travels through a wire mesh trash screen, over the weir, and finally out through a five micron sock filter. From there, the effluent mixes with the chemical waste from our component cleaning room and enters a sump outside the facility. A motorized trash screen and a rotary drum remove solids from the liquid. The liquid is then pumped through a force main to the industrial waste treatment plant. The blasting system utilizes a twenty cubic foot, two nozzle blast pot and is loaded via a two thousand pound super sack loading system.

In order to conduct the materials characterization testing, an optimum set of operating parameters had to be established. To accomplish the optimization we utilized an x-y positioning system to control the traverse rate, angle of impingement, and stand off distance. Additional parameters which were varied in a matrix format were: nozzle pressure, water pressure, and media flow rate. Almen arc height data was established for each combination of blasting parameters. The material used for optimization testing was 0.032 inch 2024 T3 Bare Aluminum. The optimum set of operating parameters evaluated and subsequently used in conditioning of all specimens in the materials characterization portion are:

Blast Medium: Armex Maintenance Grade XL
Stand off Distance: 18 inches
Impingement Angle: 30 degrees
Nozzle Pressure: 60 psi
Water Pressure: 150 psi
Traverse Rate: 0.8 inch/second
Media Flow Rate: 3.0 lb/min

The combination of these optimized parameters yielded a paint removal rate of 0.29 sf/min and 5.11 +/- 0.61 mils of almen arc height deflection. Conditioning of the specimens was conducted in preparation for tests to assess the effects of the blasting process on clad erosion, surface roughness, residual stress, fatigue crack growth rate, and fatigue life (notched). The materials characterization tests were performed on 0.032 inch specimens of 2024 T3 and 7075 T6 bare and clad aluminum.

Cladding erosion evaluations were made by a determination of cladding loss by weight per blast cycle. Six cycles of blasting on unpainted clad surfaces yielded a high rate of clad erosion for both alloys. The erosion percentage data were calculated on the basis of a nominal cladding thickness of five (5) percent per side of the total sheet thickness. Since the densities of the alloy and the cladding were nearly the same, weight loss was correlated to volumetric loss by assuming the nominal thickness was 5 percent of the 0.032 inch sheet thickness. Three sample sets of each material were subjected to the blasting process and measured for weight loss after each blast cycle. The mean percent cladding loss for 2024 T3 clad material ranged from 1.54 % for one cycle to 4.03 % for 6 cycles and the loss on the 7075 T6 clad material loss ranged from 1.44 % for one cycle to 3.48 % for 6 cycles.

Surface roughness measurements were made on unpainted Almen specimens of both alloys, bare and clad. These specimens were grouped by alloy type and each of 6 specimens per set were blasted from one to six cycles to determine cumulative changes to surface roughness. As expected, the bare surfaces after one blast cycle were much smoother than the clad surfaces. Subsequent blast cycles increased the roughness on the bare alloys, while the clad alloys tended to become smoother.

Residual stress was measured by two different means. The saturation response of the substrate to the bicarbonate of soda blasting process by the system used in the study was determined as the delta almen arc height as a function of elapsed blast time for unpainted 2024 T3 and 7075 T6 bare specimens. The delta almen arc height is not a direct measure of blast induced cold work strains, but a change in the bending moment of the unrestrained specimen produced by the residual stresses associated with the cold work process. The overall response for 2024 T3 bare was higher than the 7075 T6 bare response by a factor of 2 or more. However the point at which saturation occurs is about the same for both materials.

Residual stress was also measured by XRay diffraction testing on 5 specimens each of 2024 T3 and 7075 T6 bare almen strips sheared from painted panels, measured for baseline, and constrained by epoxy to a 1/4 inch steel backing plate. They were then conditioned by one blast cycle of paint stripping, plus three additional blast cycles at the same rate to simulate a total of four blast cycles. Each of two sets of specimens included two Almen specimens which were unrestrained at the time of baseline strain measurements. All strain measurements were made after the conditioning was conducted with the Almen specimens in the constrained state. Both alloys exhibited an increase in surface compressive stress decreasing to a depth of 0.003 inch. Beyond the 0.003 inch depth, the distributions remained fairly constant. The 311 peak width distributions for both alloys indicated a surface maximum which may be a result of a more cold worked surface and near surface material.

Fatigue specimens were initially sheared from as received panels and from painted panels after bicarbonate of soda stripping. The individual specimens were then machined to final dimensions. A 60 degree angular notch was pressed 7 thousandths of an inch deep in the center of the specimen over 1/4 inch length. The notch was used to simulate surface flaws on the substrate (both front and back). The fatigue specimens were then tested following guidelines of ASTM E466 (with the exception of the notch). All specimens were cycled under load control with a sinusoidal waveform at 10 hertz. Tests were constant amplitude with a +0.1 stress ratio. The nominal maximum stress for the 0.032 inch material was 33 ksi. Results indicated no appreciable change in fatigue characteristics and in fact the front notched specimens showed an improvement in fatigue life.

Fatigue crack growth rate specimens were 2024 T3 bare aluminum material sheared from as received panels and from painted panels after bicarbonate of soda blasting. These specimens were machine finished to final dimensions. An 1/8 inch hole was drilled through the center of the specimen and an initial 0.040 inch starter notch was machined by electrical discharge machining using a 6 mil traveling wire cut. The test followed guidelines of ASTM E647 and cycled under load control with a sinusoidal waveform at 10 hertz. Test loads were constant amplitude with a +0.1 stress ratio and a maximum load of 1120 pounds. The nominal maximum stress for the 0.032 inch material was 8,750 psi. Crack growth measurements were made with cast epoxy Krak gages and showed no appreciable change in crack growth characteristics.

The second portion of the testing performed at SA-ALC was to verify that the bicarbonate of soda blasting process conformed with the Pollution Prevention Act of 1990. The Act emphasizes that the preferred method of preventing pollution is to reduce, at the source, the volume of generated wastes and that reuse should be performed whenever possible. Air Force Directive 19-4 went a little farther by making a commitment to "... prevent at the source, to the greatest extent possible, environmentally harmful discharges to the air, land, surface water, and ground water."

This portion of the testing was contracted to Pacific Environmental Services in Mason, Ohio. They were tasked to evaluate effluent samples, air emissions for total particulates and metals, analyze stack gases and determine worker exposure effects.

During the testing phase, a variety of aircraft parts were used and tasks were performed. Tasking involved depainting, parts cleaning, and a combination of paint stripping and parts cleaning. One operator was used in the booth for the purposes of the report.

Average stack gas velocity for the sampling runs was 52 feet per second with an average temperature of 60 degrees F. The average flow rate was 30,831 dry standard cubic feet per minute. The stack gas averaged a particulate mass emission rate of 1.855 lb/hr. Particle size analysis of the air emissions showed that more than 98% of the particulate mass emitted was comprised of particles smaller than 10 microns. The absence of large particles suggests that the larger particles settled out or were captured in the water curtain. Analysis of the metals present in the emissions were also conducted during the runs. Sodium accounted for 99+% of the total mass of all metals detected. Other metals detected included: iron (0.0033 lb/hr), zinc (0.0020 lb/hr), total chromium (0.00093 lb/hr), and cadmium (0.00080 lb/hr).

Workspace air samples were collected and analyzed for alkaline dusts, nuisance dusts, and multiple metals. Dust samples were collected between the blast stream and the exhaust chamber, to simulate worst case of one operator working directly downstream of the other. Workspace air sampling resulted in measurable quantities of total nuisance dusts, alkaline dusts, and elemental sodium, and detectable quantities of calcium, zinc, aluminum, and chromium.

Measured concentrations of total dust were in excess of OSHA's Permissible Exposure Limit of 15 mg/cubic meter. The American Conference of Governmental Hygienists have a Threshold Limit Value of 10 mg/ cubic meter for exposure to total particulate matter. The concentrations of detectable metals did not exceed any TLV or PEL standards. With these concentrations in mind, worker exposure limits are negligible. As a comparison, air-supplied hoods can be used in nuisance dust concentrations up to 375 mg/cubic meter. The half faced respirator with a protection factor of 10 can be used in an environment up to 150 mg/cubic meter.

Analysis of the effluent included samples of the rinse water, sump suspension, filtered solids, and filtered effluent. The Total Suspended Solids (TSS) in the sump suspension was 4,850 mg/l. This is 0.00485 kg of solids per liter. The liquid effluent from the process has a pH of about 8.9 and is high in both alkalinity and total dissolved solids, indicating that the effluent contains primarily dissolved NaHCO3. Results indicated that the NaHCO3 concentration in the effluent was no higher than 15 g/l, well below its solubility limit of 96 g/l. The effluent contained, on the average, 50 mg/l suspended solids and had a low content of metals and other contaminants.

The solid material collected in the filter sock had a high oil and grease content as well as a high metals content. The concentrations of antimony, cadmium, chromium, lead, and zinc were sufficiently high that the waster would be classified as hazardous. Less than 1% of the solids in the sock was spent blast material.

To summarize the results of the effects of the bicarbonate of soda stripping process as an alternative paint removal process, utilizing the process parameters developed by this program; it exhibits minimal blast imparted substrate damage. The major exception being that this process tended to erode cladding on the aluminum at higher than preferred rates. The production stripping rate associated with the test panels was only 0.3 sf/min however, in normal production coating removal, rates in excess of 1 sf/min are common. Bicarbonate of soda is a viable alternative for paint stripping as well as a great carbon remover, degreaser, and overall cleaning agent.

We currently utilize the process to remove carbon from F100 engine nozzles and gas turbine engine deswirlers, depainting of fiberglass and fiberglass/aluminum panels as off the T-38 aircraft or TF39 engine, and depainting of fighter aircraft accessories, all resulting in considerable savings in time

and materials. The bicarbonate of soda blasting process has successfully demonstrated that it cleans surfaces in preparation for welding operation significantly better that previous nitric acid processes and has proven to be very effective on cleaning and depainting aircraft wheels, struts, reverse thrusters, and brakes. The process has performed very well for us and, depending upon the application, could work very well as an alternative to chemicals in any industrial operation.

WATERJET PROCESSES FOR COATING REMOVAL

by

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ABSTRACT

USBI and NASA have been testing and investigating the use of high pressure water for coating removal for approximately the past 12 years at the Automated TPS(Thermal Protection System - ablative materials used for thermal protection during ascent and descent of the solid rocket boosters) Removal Facility located in the Productivity Enhancement Complex at Marshall Space Flight Center. Originally the task was to develop and automate the removal process and transfer the technology to a production facility at Kennedy Space Center. Since that time more and more applications and support roles for the waterjet technology have been realized. The facility has become a vital part of development activities ongoing at MSFC. It supports the development of environmentally compliant insulations, sealants, and coatings. It also supports bonding programs, test motors, and pressure vessels. The most recent role of the cell is supporting Thiokol Corporation's solid rocket motor program in the development of waterjet degreasing and paint stripping methods. Currently vapor degreasing methods use 500,000 lbs. of ozone depleting chemicals per year. This paper describes the major cell equipment, test methods practiced, and coatings that have been removed.

Introduction

The use of high pressure water as a means of coatings removal was used in the late 70's to refurbish the Solid Rocket Boosters (SRB) used in the space shuttle program. After recovery of the SRB's following a shuttle launch the TPS is removed from the booster components and prepared for future flights. Until this process was automated, it was a manual operation where personnel wearing protective suits and using high pressure waterjet wands would spend countless hours stripping the TPS. The results were acceptable but it was a very tiresome, tedious, and personally hazardous task.

USBI and NASA jointly developed a system to automate and optimize the TPS removal process using robotics. This system removed personnel from the hazardous environment and reduced the SRB processing time due to the precision stripping the automated TPS removal system is capable of delivering. Through emperical testing, the optimum waterjet stripping parameters for each TPS material were determined. All the testing and developmental work was done at MSFC in the Productivity Enhancement Complex and then the technology was transferred to Kennedy Space Center in Florida where it is currently used in the production facility.

Equipment

Robot - A Cincinnatti Milacron HT^3 ™ Industrial hydraulic six axes pedestal mounted robot. Five axes are actuator driven and one is cylinder driven, all axes are controlled by servo valves. The normal hydraulic operating pressure is 2250 psi. The robot is mounted on a lift table that provides an extra 4 foot of travel on the Z axis. All axes are fed with with a low positive air pressure to prevent water intrusion into the actuator units and control boxes. The robot is capable of a 200 pound payload, this is necessary with the back thrust created by the high pressure water at high flow rates.

Computer - All system equipment interfaces with a Digital Equipment Corporation 11/73+. An Industrial Processor allows for discrete I/O, D/A and A/D interfaces. The turntable and robot interface through RS-232 communications.

Pumps - The cell contains three pumping systems. The first system is a Hammelmann HDP650. As its model number implies it has a driving output capability of 650 horse power. The HDP650 has five 30 mm cylinders and can operate up to 2100 rpm's. The pump can deliver pressures up to 20,000 psi at a flow rate of 32 gallons per minute. The second system is a Hammelmann HDP334. The HDP334 has three 25 mm cylinders and with a 450 horse power output capability can deliver 36,000 psi at a flow rate of 12 gallons per minute. The third pumping system is a Flow Systems Model 11X intensifier. It is capable of delivering ultra high pressures up to 55,000 psi at flow rates up to 1.25 gallons per minute. The Flow Systems Waternife pump is used strictly for cutting processes and not coatings removal. The Waternife is capable of cutting all types of metals and composites without thermal distortion or delamination.

Frequency Drive - An Allen Bradley 1352 frequency drive is used to drive the 500 horsepower motors that drive the Hammelmann pumps from zero up to their maximum outputs of 20ksi or 36ksi. Only one pumping system can be operated at a time depending on which is selected at the frequency drive console.

Diversion Valves - Three Autoclave Engineering electrically controlled hydraulic operated valves are used to divert the high pressure water to the desired stripping nozzle. Up to three nozzles can be run at once but normal operation is done with either one single stream nozzle or a rotary nozzle. The third valve is normally used as a dump valve to divert the water during system setup or dump the pressure if an emergency situation should arise. The diversion valves are only used with the 20ksi pumping system.

Turntable - The turntable is 12.5 foot in diameter and is equipped with outrigger attachments and supporting hardware that allows it to accomodate each SRB component. This includes the nose cap, frustrum, forward skirt, and aft skirt. The table is capable of speeds up to six revolutions per minute. The table platen floats on air bearings which are capable of handling heavy loads. The entire table is also mounted on air bearings which allows the table to be easily positioned anywhere in the spray cell. It is also equipped with jacks, wheels, and a tow bar so it can be completely removed from the spray cell or used for transporting hardware short distances.

Nozzles - A variety of different styles and types of nozzles have been tested. The most efficient and effective nozzles were found to be the single stream stripping nozzles developed by USBI and rotating nozzles developed by Hammelmann Corp. and Flow International Corp. The single stream Full Tapered Stripping(FTS) nozzles were developed early in the program after it was found that off the shelf nozzles exhibited wear after several hours of operation at pressures up to 20,000 psi. The FTS nozzles were designed and patented by Messrs. Steve Cosby, a senior USBI Process Engineer; and Robert M. Rice, a senior Robotics Engineer (currently working with Pratt & Whitney Waterjet Systems). The FTS nozzles are easily installed in a 3/4" Autoclave Slimline fitting and will also readily adapt to a mixing chamber that was designed along with the FTS nozzles that allows abrasives such as crushed walnut shells and plastic media to be injected into the high pressure water stream to improve stripping rates. The mixing chamber is designed such that the abrasive is pulled in due to the venturi effect created by the water passing through the chamber.

The Hammelmann twin jet rotating nozzle is the most effective at pressures up to 20,000 psi. The twin jet nozzle is capable of speeds up to 1200 rpm. The two orifices are configured so that the back force of the water itself causes the nozzle rotation - the higher the pressure and flow through the nozzle, the faster the nozzle rotation. The twin jet nozzle also has an adjustable braking system that gives the user a limited control over the speed of the nozzle. The braking system uses an internal magnet, the more the magnet is engaged, the slower the rotational speed.

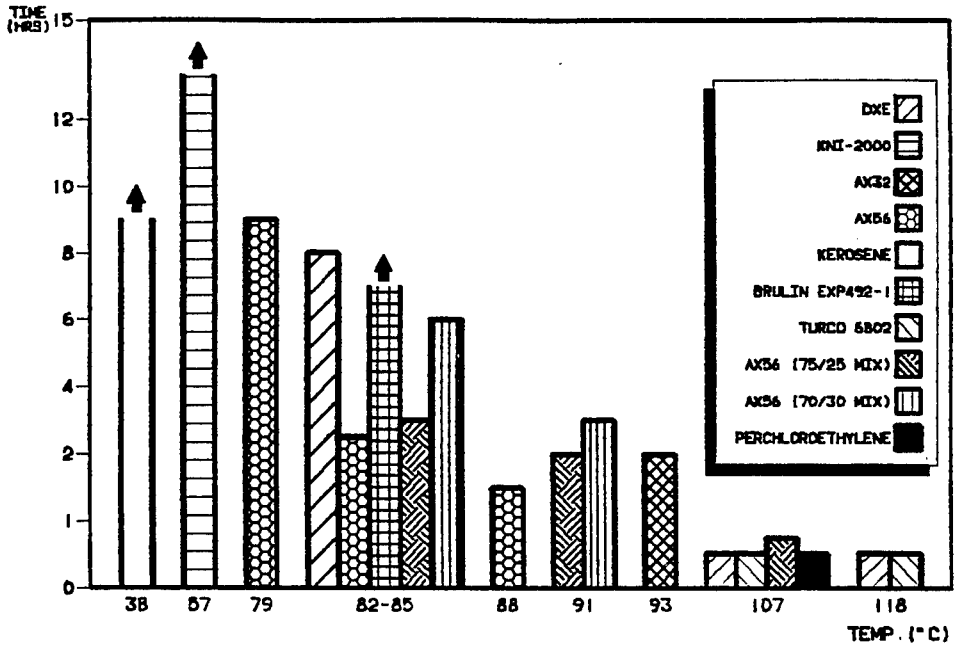

Figure 4: Dewaxing Time And Temperature

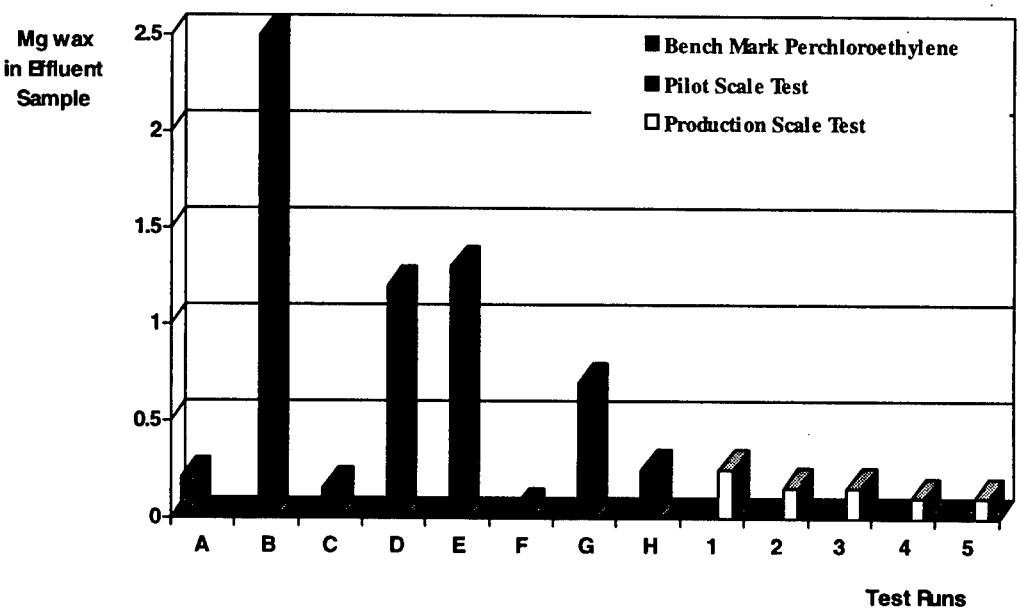

Figure 5:Results from Pilot and Production Scale Tests

Hammelmann also designed two rotating nozzles that are used with the 36,000 psi pumping system. One will accomodate four orifices that are positioned at radii of 32.5mm, 37.5mm, 42.5mm, and 47.5mm. The other nozzle will accomodate fourteen orifices and they are located 2.5mm apart starting at a radius of 15mm and ending at a radius 47.5mm. The two nozzles are interchangeable with the same hydraulic drive unit. The drive system is capable of rotating the nozzles up to 2300 rpm. The orifices are also interchangeable and are sized to achieve the desired flow rate. The orifices mount at a 90 degree angle to the face of the nozzle.

Test Methodology

There are a number of hydro stripping parameters that play a role in coating removal rates. These parameters include water pressure, flow rate, stand off distance, stripping velocity, attack angle, sweep angle of attack, and with the rotary nozzles include orifice size and placement as well as the nozzle rotational speed. It was found that by controlling these parameters a piece of hardware could be stripped to selected levels. The insulation could be removed leaving the topcoat of paint undamaged, the paint could be removed leaving the primer intact, and finally the primer could be removed leaving the bare substrate.

Most of the tests are conducted on flat 24" x 24" test panels with the coating to be tested applied at the nominal thickness. The test panels can be mounted on support structures that are mounted on the turntable. The robot end effector is configured with the nozzle to be tested and the robot is "taught" the motions needed to conduct the desired testing. Normally a "rough and dirty" test is done to determine what range of the variable parameters will be tested. Once test runs have been made with the range of test parameters, each test pass or panel is assessed and the level, width, and rate of coating removal are determined. Test results are used to determine the optimum coating removal parameters.

The major focus of testing is identifying the orifice diameter that maximizes the available energy, i.e., the nozzle that removes the coating most effectively with the available pressures and flows.

After the installation of the Hammelmann 36ksi pumping system and the multiple orifice nozzles were tested it was found that the orifice size and placement on the nozzle were very critical in order to achieve an even energy distribution throughout the stripping width of the nozzle. Random orifice selection normally yielded visible energy bands on the substrate where there was obviously concentrated levels of pressure and flow. To improve the energy distribution, theoretical flow rates/orifice distance traveled, based on the orifice location on the nozzle(radius) were determined. The orifices were sized so that there is an equal flow of water per orifice distance traveled regardless of the orifice location on the nozzle. In other words, if the orifice located at a radius of 15mm flowed one gpm/revolution of the nozzle which equates to:

@r = 15mm

$$circumference = \pi d = \pi 30mm = 94.25mm$$

@ 1rpm

$$\frac{1gpm}{94.25mm} = .0106gpm/mm$$

then the orifice located at a radius of 30mm would be sized so that its flow would be equal to .0106 gpm/mm traveled by the orifice.

Example:

$$circumference = \pi d = \pi 60mm = 188.49mm$$

$$\frac{xgpm}{188.49mm} = .0106gpm/mm$$

$$x = 1.99gpm$$

This approach was used to determine orifice size regardless of how many orifices were used, whether it be four or fourteen. Along with equalizing the flow per distance the orifice traveled, the nozzle rotational speed and the stripping velocity were very dependent on each other and were critical stripping parameters to determine. With the help of a user friendly computer simulation program developed by Mr. David Hoppe (NASA Engineer) the optimum rotational velocity and robot stripping velocity could be determined to achieve the most efficient coverage of the stripping width. The computer program allowed the desired orifices, the rotational speed, and the stripping velocity to be entered and a graphic display is generated showing the coverage. The program also provides a quantitative analysis of the coverage by counting the number of pixels on the computer monitor not hit by the orifices selected. It was also found that the direction of travel across the test panel whether it be left to right or vice versa also played a role in the coverage and removal rates.

Coatings Removed

Over the years a number of insulations, adhesives, paints, and coatings have been stripped at the MSFC Automated TPS Removal Facility. The following matrix list most of those along with a brief description of the coating, approximate stripping rates, and the nozzles used. Most of the coatings were applied to aluminum substrates, either 2219-T87, 6061, or 7075 Alclad. The rubber insulations and propellants have been removed from D6AC steel and NBR has been removed from a filament wound case - shallow stripping angles were used to prevent delamination of the case from occuring. The high pressure water does have the capability to damage any surface if steps are not taken to ensure the waterjet does not dwell in the same spot too long.

Coating	Description	Nozzle	Removal Rate
1/4" MSA-1	SRB thermal protection insulation	rotary&FTS	57-75 in^2/sec
1/2" MSA-2	SRB thermal protection insulation	rotary&FTS	30-40 in^2/sec
1/8"-1/4" MSA-3	SRB thermal protection insulation	rotary	52-61 in^2/sec
3/8"-1" K5NA	SRB closeout material	rotary	4-6 in^2/sec
3/8"-1" MTA-2	SRB closeout material	rotary&FTS	16-30 in^2/sec
1/4"&1/2" CORK	SRB thermal protection & closeout material	rotary&FTS	11-14 in^2/sec
3/8"-1" BTA	SRB closeout material	FTS	7-15 in^2/sec

Coating	Description	Nozzle	Removal Rate
1/8"-1/4" USI	SRB & Titan IV thermal protection insulation	rotary	8-13 in^2/sec
1/8"-1/4" MCC-1	SRB & Titan IV thermal protection insulation	rotary	18-26 in^2/sec
1"-1.5" SOFI	External Tank insulation	rotary	60-70 in^2/sec
1.5" INSTAFOAM	SRB thermal protection insulation	rotary	80 in^2/sec
1/32" ZINC COATING	Thrust Vector Control Cover corrosion protection	rotary	5-7 in^2/sec
2"-4" NBR	MNASA motor insulation	FTS	.3-.5 in^2/sec
2"-3" INERT PROPELLANT	Hybrid motor propellant	FTS	removed in sections
HYSOL 901	test sample bonding adhesive	rotary	*10 in^2/sec
HYSOL 934	test sample bonding adhesive	rotary	*10 in^2/sec
HYSOL 913	test sample bonding adhesive	rotary	*6-7 in^2/sec
HYSOL 946	test sample bonding adhesive	rotary	*10-17 in^2/sec
HYSOL 615	test sample bonding adhesive	rotary	*10 in^2/sec
HYSOL 9689	test sample bonding adhesive	rotary	*10 in^2/sec
HYSOL 608	test sample bonding adhesive	rotary	*10 in^2/sec
3M 2216A/B GRAY & TRANSLUCENT	test sample bonding adhesive and component of MSA1&2, BTA, USI, & MCC1	rotary	*10 in^2/sec
3M CA5	test sample bonding adhesive	rotary	*10 in^2/sec
3M CA9	test sample bonding adhesive	rotary	*10 in^2/sec
LOCTITE 410	test sample bonding adhesive	rotary	*10 in^2/sec
CREST 212	test sample bonding adhesive	rotary	*10 in^2/sec
RTV 133	sealant	rotary&FTS	5.5 in^2/sec
PRC 1770	high temperature sealant	rotary	5.5 in^2/sec
PRC 1422	high temperature sealant	rotary	5.5 in^2/sec
URETHABOND 3015	TPS topcoat	rotary&FTS	removed with TPS
HYPALON HFR2200	TPS topcoat	rotary&FTS	removed with TPS

Coating	Description	Nozzle	Removal Rate
AKZO PAINT & PRIMER	Aluminum substrate corrosion preventive	rotary	*10 in^2/sec
DEFT PAINT & PRIMER	Aluminum substrate corrosion preventive	rotary	*10-12 in^2/sec
CONOCO HD2 GREASE	solid rocket motor case corrosion preventive	rotary	*52 in^2/sec
SHELL DIALA OIL	solid rocket motor static pressure test	rotary	*80-90 in^2/sec
MAGNAFLUX MAGNAGLOW 20B & WA4	magnetic particle solution and rinse used for motor case inspection	rotary	*80-90 in^2/sec
RUSTOLEUM PAINT & PRIMER	D6AC steel motor case corrosion preventive	rotary	*10-12 in^2/sec
CHEMLOK 205/233	motor case preparation before insulation bonding	rotary	*9-10 in^2/sec
CHEMLOK 205/220	motor case preparation before insulation bonding	rotary	*7-8 in^2/sec
CHEMLOK 205/236A	motor case preparation before insulation bonding	rotary	*12-13 in^2/sec

* These represent removal rates that were achieved with the 36ksi pumping system using either the Hammelmann or Flow International nozzles. All other rates were accomplished with the 20ksi system.

Current Investigations

Testing is being done with multiple orifice rotating nozzles to improve stripping rates. Orifice size, design, and location on the nozzle are parameters that are being investigated. Several orifice designs by Hammmelmann have gone through some limited testing. The first is a sapphire orifice, which has the same design as orifices used with the waterjet cuttting system, but require a sealing lens when installed in the nozzle. The sapphire nozzles have an efficiency rating of 63%. Other orifices tested are stainless steel and much more easily installed and aligned in the nozzle(no sealing lens). The stainless steel nozzles have an efficiency rating of 92%. The higher efficiency orifices keep the water stream collimated longer allowing larger stand off distances and improved stripping rates. Collimation is critical for nozzle efficiency, therefore other nozzles with collimated channels feeding the orifices are being investigated. The more laminar the flow when it reaches the orifice, the longer the waterjet stream will stay collimated. Efficient nozzles are the key to coating removal and will continue to be a focus of the Automated TPS Removal Facility.

Ultra-High Pressure Water Jetting for Coating Removal and Surface Preparation

By

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ABSTRACT

This paper shall examine the basics of water technology with particular attention paid to systems currently in use and some select new applications. By providing an overview of commercially available water jet systems in the context of recent case histories , potential users may evaluate the process for future applications.

With the on going introduction of regulations prohibiting the use of chemical paint strippers, manual scrapping and dry abrasive media blasting, the need for an environmentally compliant coating removal process has been mandated. Water jet cleaning has been a traditional part of many industrial processed for year, although it has only been in the last few years that reliable pumping equipment capable of ultra-high pressure operation have become available.

With the advent of water jet pumping equipment capable of sustaining pressures in excess of 36,000 psi. there has been shift away from lower pressure, high water volume systems. One of the major factors in driving industry to seek higher pressures is the ability to offer higher productivity rates while lowering the quantity of water used and subsequently reprocessed. Among benefits of the trend toward higher pressure / lower volume systems is the corresponding reduction in water jet reaction forces making hand held water jetting practical and safe.

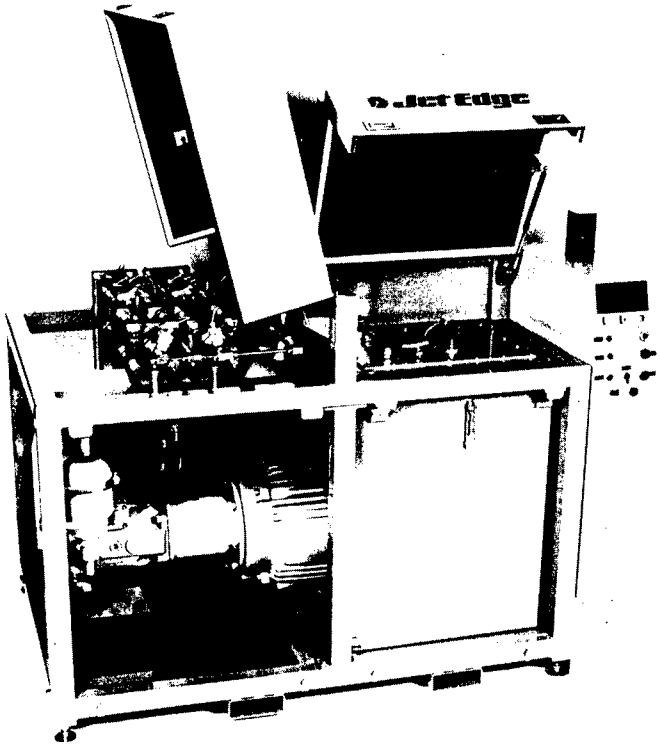
Other unique applications made possible by these new generation pumping systems include the use of alternative fluids including liquid ammonia for specialized and hazardous material removal applications. A review of the equipment used and the required modifications will be presented along with the conclusions reached reached during this test program.

EQUIPMENT BACKGROUND AND HISTORY:

Water jetting is a technology that can trace it's roots to the Gold Rush era of the early 1900's. and placer mining. In the quest to uncover alluvial deposits of gold, miners found that by redirecting small creeks through a rudimentary piping system a concentrated stream of water could be utilized to speed erosion, exposing greater quantities of material. These early miners soon adapted the water pumps designed to keep under ground mines dry to the task of accelerating that water to higher and therefore more productive velocities.

Many of the pump designs in use today were originally developed to meet the demands of deep rock drilling , petroleum extraction and refining. Even today the US Bureau of Mines has an active water jet research program looking to increase safety while replacing conventional drilling and crushing technology.

In the petroleum industry the quest to maximize oil production spurred the development of pumping systems able to hydraulically fracture the well casing and surrounding rock to force more oil out of low producing fields. The most important offshoot of this "fracking" process was the development of the intensifier style pump.(Fig. 1) The intensifier pump is capable of generating enormous pressures with a minimum of moving parts and with significant safety features.

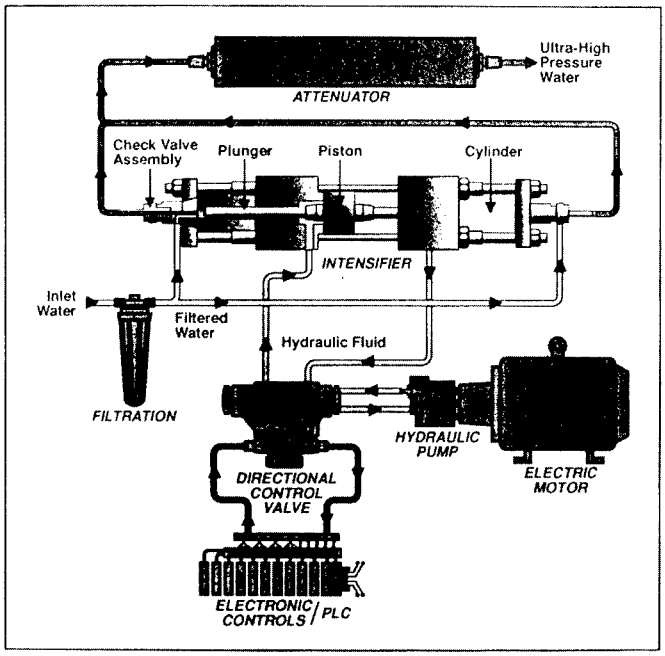


Intensifier Pump
Fig. 1

This design concept was routinely available by the late 1960's for use in static pressure generation systems and the aforementioned well fracking. Industrial contractors using lower pressure crankshaft driven water pumps had recognized the increased cleaning potential offered by higher pressures and seized on the intensifier design as a likely candidate for their applications. Taking into account available materials. high pressure hose technology and desired reaction forces, 35,000 psi. and 6 gpm. flowrates were determined to be a practical set of parameters to design for in the early 1970's. As it has turned out these parameters have remained very nearly unchanged for 15 years in which time the equipment has become very reliable. A typical current generation pump delivers water jet outputs of 36,000 psi at 7.2 gpm. Early systems counted operating time in hours while today's pumps routinely deliver months of running time between scheduled maintenance.

It should be noted that the two largest domestic manufacturers of 36,000+ psi water jet cleaning and coating removal equipment have extensive experience in the design and manufacture of 60,000 psi. intensifier pumps. While those pressures are currently only being used in a few very specialized coating removal applications the technology is already well developed should the need arise.

In practice the intensifier pump consists of a piston driving a plunger. The piston has a large surface area and is driven by low pressure (3000 psi.) hydraulic fluid. (Fig. 2) Coupled to it, is a plunger with a much smaller surface area that acts against the water contained in a heavy walled cylinder. The piston / plunger surface area ratio is typically either 12:1 and 20:1 , yielding output pressures of 36,000 to 60,000 psi., respectively. By attaching a plunger to either side of the hydraulically driven piston and installing simple check valves a continuos pressure output pump is achieved.

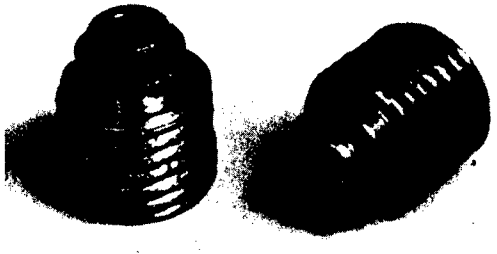


Intensifier Schematic
Fig. 2

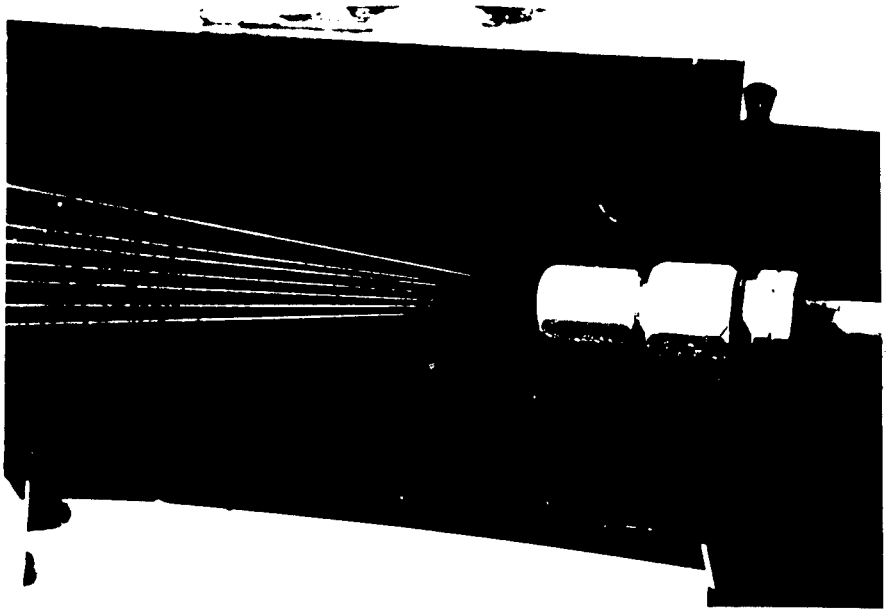
It therefore becomes a simple matter to regulate water output, flow and pressure by modulating the hydraulic fluid pressure. The variable displacement, pressure compensated hydraulic pump are designed for the specific task of maintaining a set pressure at varying fluid flow demand levels. This pressure compensation ability allows the intensifier pump to operate with dry shutoff blasting devices and to minimize water consumption.

After the water (or other fluid) is pressurized it is directed to the point of use via stainless steel tubing or braided wire reinforced hose. For pressures of 36,000 psi. and above the tubing typically has an outside diameter three times that of the inside diameter. When hose is used, a minimum of seven spiral wrapped layers of wire are applied around a Delrin or Nylon core in addition to an outer abrasion resistant jacket. In situations involving long supply line distances or extreme pressure fluctuations, the stainless steel tubing is preferred due to lower flow restrictions and resistance to cyclic fatigue.

Once the high pressure fluid has reached the point of use a nozzle or manifold is required to generate individual coherent streams of water. These nozzles are then attached to the end of the tubing or hose using specially designed threaded fittings. At pressure below 20,000 psi holes drilled into a block of stainless steel will suffice for a nozzle. Due to the higher fluid velocities achieved at pressures above 30,000 psi. , erosion of the nozzle material becomes unacceptable using the drilled hole design. In the majority of applications it has been found that a synthetic sapphire jewel works well in withstanding the erosive effects of the high velocity fluid stream. These jewels are available in .001" diameter increments and are pre-mounted in replaceable threaded mounts. (Fig. 3) Since fluid flow rate is directly related to the net area of the orifice through which it passes, an extreme level of precision and control can be applied to the sizing and layout of multiple orifice water jet nozzles. By varying the size and location of the orifices within a given manifold ,material removal patterns and substrate preparation can be tightly controlled. In practice it has been found that by rotating a multiple orifice manifold (Fig. 4) at a controlled rate generates optimum coating or material removal rates while significantly reducing the chance of base material damage.



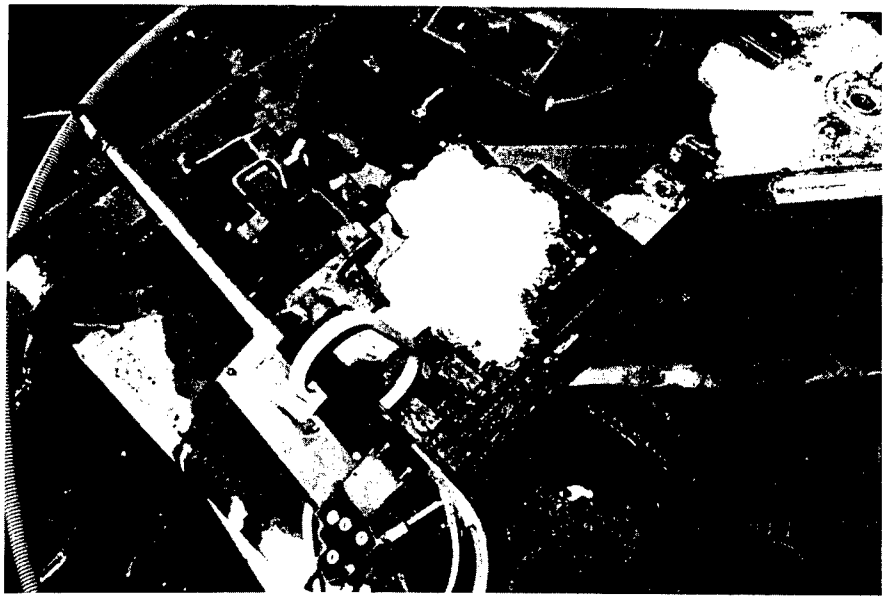
Pre-mounted Orifice, 3X scale
Fig. 3



Muliple Orifice Nozzle
Fig. 4

Water jetting first found favor in the industrial maintenance sector for the removal of accumulated deposits found in boilers and heat exchangers. Other popular applications include storage tank and processing equipment cleaning. In each case a rotating nozzle is utilized. For boiler tube cleaning a rigid length of stainless steel tubing is threaded at one end to accept a nozzle tip containing one or more orifices. This "lance" is then attached to a powered rotary joint mounted on a sliding carriage. The lance and carriage are then advanced through the tube to be cleaned and then retracted. This process is repeated until all tubes in a boiler or heat exchanger are cleaned. The most widely used water jet cleaning method found involves the use of hand held "guns" attached to flexible hose. (Fig. 5) A typical hand tool contains an on / off valve, safety detented trigger and an air or hydraulically powered rotary joint. Depending on the martial to be removed and the condition of the substrate any of several nozzle configurations are attached to the end of the rotating barrel. Tools designed for use at 36,000 psi. have 2 to 3 times working pressure design factor ratings and employ guards and shields for operator safety.

In the majority of 36,000 psi. hand held operations overall flowrate is limited by orifice selection to approximately 3 gpm. To achieve similar water jet energy transfer at lower pressures such a large increase in discharge volume is required that reaction forces become unmanageable and unsafe.



Gyra-Jet , 36,000 psi rated hand tool & APC Rear Hatch
Fig. 5

APPLICATIONS:

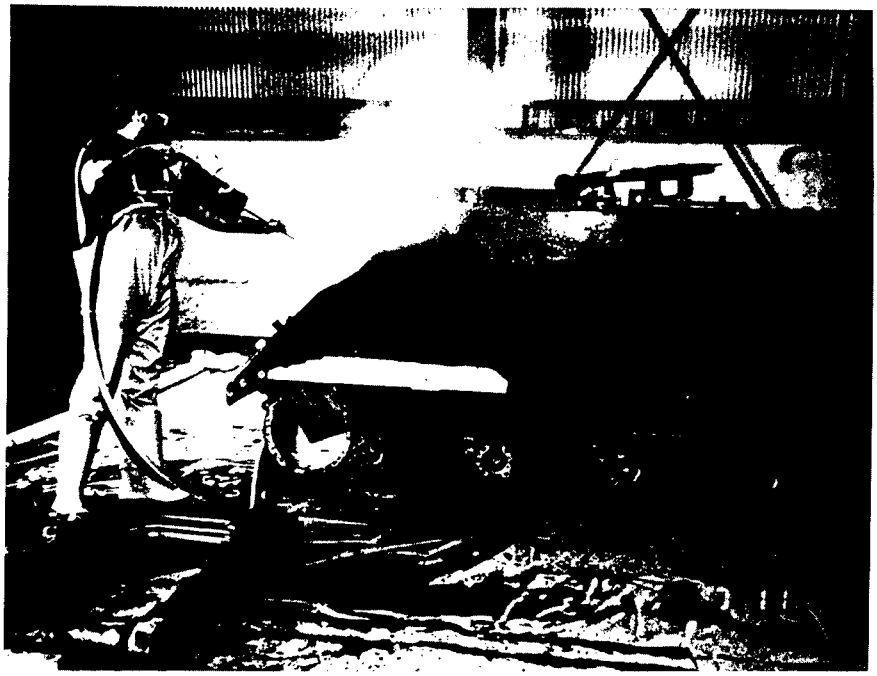
A typical hand held coating removal application is currently in use by a major defense contractor refurbishing M113 series armored personnel carriers(APC 's). Many of these units are nearly 20 years old and have been repainted and modified numerous times. Prior to refurbishment and upgrading the majority of existing coatings must be removed from the aluminum hulls with minimal base metal damage. In certain locations it is also required that the alodine wash primer be removed to facilitate welding.

Due to the cost of media collection and disposal grit blasting was rejected for such a large project. The large number of threaded holes and the inherent difficulty in removing all grit material from the confined interior spaces also weighed heavily in the decision to use water jets.

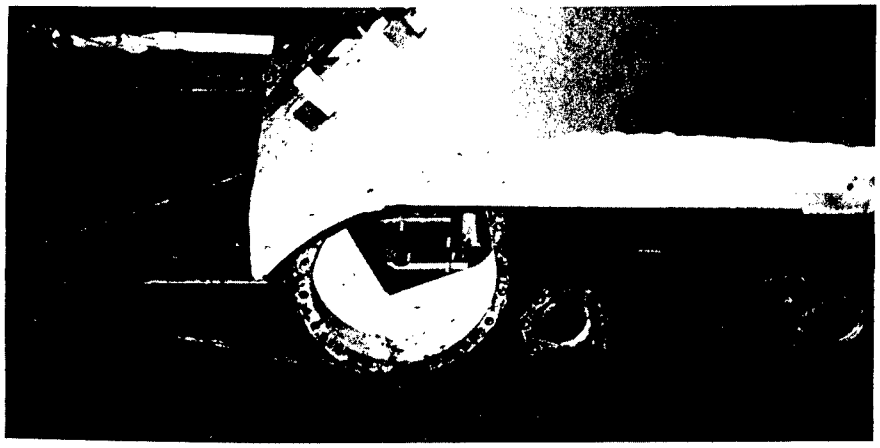
The water jet process is preceded by initial disassembly in which all component parts are removed leaving a bare hull which is essentially an aluminum box. This hull is then placed on a work stand in in a contained area dedicated to the water jet cleaning process. Included in this facility are water collection and filtration systems, air filtration, and the high pressure water jet pump and hand tools. The pump used is a 36,000 psi. 4 gpm. unit manufactured by Jet Edge to which are plumbed two hand held rotary nozzle tools called Gyra-Jets from the same vendor. Each hand tool is equipped with 4 orifice nozzle with the .011" diameter orifices arranged in a staggered pattern. Water flow rate though each tool is limited to 2 gpm.

In use the operator wearing a rain suit and eye and ear protection moves about the vehicle removing paint and other residues from marked areas.(Fig. 6) The coating system being removed consists of an alodine wash primer over which a zinc chromate paint primer is applied. The top coat(s) consist of a Chemical Agent Resistant Coating (CARC) paint. In many cases there may be as many as four addition layers of top coat material to remove. On average the operator is able to remove all paint and primer down to the alodine wash at rate of over one square foot per minute.

Due in part to minimal preparation during the previous repaints the water jet was able to yield even higher productivity rates on the more heavily coated surfaces. This is a marked contrast to the grit blasting method where coating thickness decreased productivity.



Water Jet Paint Removal
Fig. 6



RTV removal and Bolt hole cleaning
Fig. 7

An additional benefit was realized in terms of eliminating masking of threaded holes. It was found that the threaded holes used to mount drive train components could be completely cleaned without damage using the Gyra-Jet.(Fig. 7) The ability to completely remove the alodine conversion coating, RTV sealants along with grease and oil was also proven and has greatly improved the weld quality during subsequent operations.

APPLICATION 2:

As a counterpoint to the previous conventional application an In the instance equipment originally designed for 36,000 psi. water jet cleaning was modified and adapted to use liquid ammonia as the fluid for material removal.

The recognized need to dispose of obsolete, over-aged and treaty limited solid rocket motors while meeting increasingly stringent environmental constraints lead to the initiation of this project. In the past these motors were destroyed by open burning or detonation both of which are incompatible with environmental concerns and preclude the recovery and reuse of the raw materials.

Global Environmental Solutions a division of Hercules Aerospace and Rust Engineering are planning a solid rocket motor decommissioning pilot plant system for Hercules' Magna Utah facility. This system is based on test work recently completed at the Bacchus Plant location.

The test system utilizes a slightly modified Jet Edge 36,000 psi water jet pump and a highly modified Gyra-Jet Hand tool. Due to the extensive use of stainless steel in ultra-high pressure water jet equipment few modifications other than a change in o'ring material in the high pressure seals was needed within the pump unit. It was discovered that the liquid ammonia required additional cooling to avoid boiling within the pump and therefore a primitive alcohol and dry ice heat exchanger was installed on the inlet side of the pump.

In order to facilitate the use of the rotating jet tool originally designed for hand held use in a remote control setting a great number of modifications were made to the Gyra-Jet. Changes included the relocation of the water on / off valve and the integration of the rotational drive with a remote control station.(Fig. 8-9) The pump used featured a 40 Hp. motor driving both the intensifier and providing hydraulic pressure to operate the rotary nozzle.

A series of test were conducted on both MLRS and Chaparral (GCU-1) propellant with variations made in nozzle configuration and ammonia pressure. Hazard evaluation tests were conducted under conditions worse than expected in production and no ignition threshold levels were observed. The optimum configuration was found to be a 36,000 psi working pressure and a .8 gpm fluid flow rate. It was determined that propellant removal rates of 234 lb / hr using 36,000 psi. were possible with all propellants tested. The test method involved pumping pressurized ammonia though a rotating multiple orifice nozzle that was then advanced into the test sample.(Fig. 10)

REFERENCES:

Large Rocket Motor Demilitarization / Disposal Technology Program
Task A-2 / B-2, Propellant Removal, Final Report, Data Item A006
Authors; R.A. Patterson, Jeff Nelson ,Hercules Aerospace

Automated High Pressure Water Jet - A Technology for Aviation Maintainance
Cleaner Times, May 1992
Author; Dr. Jim Shunk , USBI / Pratt and Whitney Water Jet Systems

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Photographs: Jet Edge, Minneapolis MN
FMC/BMY/United Defense, Anniston AL
Hercules Aerospace,Bacchus Works, Magna Utah

ALTERNATIVE CLEANING TECHNOLOGY SYSTEMS

Aqueous Cleaning Design Presentation

Presentation By: Peter F. Maltby, Vice President of Operations, Forward Technology Industries, Inc., Minneapolis, MN

INTRODUCTION

The phase-out of CFCs and other ozone depleting chemicals has prompted industries to re-evaluate their present methods of cleaning. It has become necessary to find effective substitutes for their processes as well as to meet the new cleaning challenges of improved levels of cleanliness and to satisfy concerns about environmental impact of any alternative selected.

One of the most popular alternatives being selected is aqueous cleaning. This method offers an alternative for removal of flux, grease/oil, buffing compound, particulates and other soils while minimizing environmental impact.

What I will show are methods that can be employed in an aqueous cleaning system that will make it environmentally friendly, relatively simple to maintain and capable of yielding an even higher quality of cleanliness than previously obtained. I will also explore several drying techniques available for these systems and other alternatives along with recent improvements made in this technology.

OVERALL SYSTEM CONSIDERATION

When considering any type of cleaning system, a number of variables should be determined before selecting the basic configuration. Some of these variables are:

- Soil or contaminants being removed from your parts.
- The level of cleanliness required.
- The environmental considerations of your area.
- Maintenance requirements.
- Operating costs.

- Throughput requirements.
- Dryness requirements.
- Space and cost constraints.

SOIL, CONTAMINANTS, AND CLEANLINESS

When considering the basic configuration, the type of soils /contaminants and the level of removal must be factored into the equipment's basic design. Some of the key factors are:

The types of surfactants used are determined by the types of soils, the amount of contaminant, material of the parts and the cleanliness requirement.

- The types of soils help determine the amount of and type of filtration required. For example, if oils are the major contaminants, some type of oil removal system should be considered in the wash station. The amount of oil and parts cleanliness requirements will help determine the type of oil removal system. A simple decanter separator will remove large amounts of oil, but the level of removal is less than a more expensive membrane system. However, if the cleanliness requirements are very high, a membrane system may be the most effective approach. Of course, there are other degrees of oil removal, such as coalescing filter systems. Coalescing filters will meet requirements in the middle of the decanter and membrane systems.

If, however, the contaminants are mainly particles, only a simple recirculating filter system would be required. The type of filter best suited for the application will again be determined by the amount of contaminant and the cleanliness requirements.

- The amount of contamination and the cleanliness requirements will also help determine the number of wash and rinse stations needed as well as water level requirements. Generally, the larger the amount of soil that must be removed and the higher the level of cleanliness required, the more wash and rinse stations that are needed. Also, as the cleaning requirements increase, so must the quality of the water being used.

- Over-specifying any of these levels only increases the amount of equipment and cost unnecessarily.

ENVIRONMENTAL CONCERNS

When considering the environmental impact of cleaning systems, one should look at the process in terms of its ozone depletion potential (ODP), global warming effect, energy usage, use of consumable resources, toxicity and safety. All of these factors should be carefully evaluated when selecting a cleaning process. An aqueous cleaning system has no ozone depletion potential, minimal global warming effect, low toxicity, and it is safe. It can be designed for reasonable energy usage while minimizing the amount of considerable resources (water) that are used.

The system designed to conserve energy should have as many of the following features as possible:

- Recirculated hot air drying, which can reduce energy usage as much as 75 percent over a nonrecirculating system.
-
- Minimize compressed air for blow-off and/or drying.
- Improved surfactants that allow easier rising in cooler water.
- Rinse agents that can speed up drying times.
- Improved rinsing by using ultrasonics and filtration, thereby reducing overall water flow.
- On many metal parts, the use of rust inhibitor minimizes the usage of energy and water.
- Filtration and oil removal to extend wash tank life.
- Multiple wash tanks to reduce soils loading on the rinse tanks.
- A heat recovery system on overflow of any water to drain.

It is important not to over specify requirements and, therefore, create additional and unnecessary energy and water usage. Consideration should be given to water reduction techniques such as:

- A gross tank to reduce detergent carry-over.
- Ultrasonic agitation to reduce overall process time and rinse water flow rate.
- Closed-loop process that allows overflow water to be reused.
- Improved fixturing to reduce water drag-out, to improve rinsing and to speed drying.

EASE OF MAINTENANCE AND OPERATION

Another important area is ease of maintenance and operation. Issues to be considered should include:

- Convenient access to routine maintenance items such as filters.
- How are detergents dispensed to the system? Should detergent injectors or a metering pump system be added for automated dispensing of detergents?
- Should an automated handling system be used to process parts?
- Does the system use auto drains and fills versus manual valves?
- Is the de-ionized (DI) rinse water continuously monitored and is auto makeup available?
- What type of plumbing is used (compression fitting versus NPT pipe)?
- Is high flow filtration continuously used?
- Have the cleanliness level and the amount of soil to be removed been considered when selecting the filter?
- What other instruments should be considered? Options include pressure gauges, temperature controllers, pH monitors, resistivity monitors and turbidity monitors.

THROUGHPUT AND DRYNESS REQUIREMENTS

When selecting a basic design, a major consideration should be the amount of parts that are to be processed through the system in a given period of time. This will affect:

- The size and configuration of the system.
- Overall equipment and operating costs.
- Type of automation, if required.

Since drying comprises a significant portion of time in any process, specifying only the level required is fairly important. In some cases, you may not require drying even though it may have been done in the past. If drying is essential, specifying it correctly impacts the type of equipment used and the amount of time required.

SPACE AND COST CONSTRAINTS

Available space and overall cost will impact the type and design of the equipment. However, in both cases, using artificially low values may cause the equipment design to be negatively impacted to a point that prevents you from meeting many of your other objectives in a prudent manner.

However, if all the previously mentioned factors are carefully balanced against your ultimate goal, an aqueous system can be configured to meet your needs.

BASIC ULTRASONIC AQUEOUS CLEANING SYSTEM

Now that many of the basic variables have been considered, let's build an ultrasonic aqueous cleaning system that would meet many of the fundamental needs. First we must look at three basic building blocks of the system: WASH, RINSE and DRY.

As we discuss these system components, remember that the system being described will actually yield parts that have a higher level of cleanliness than that of a roughly comparable solvent cleaner. Our theoretical system will also incorporate many of the features discussed earlier.

The wash station is designed to remove complex soils and particulates completely from a wide variety of parts utilizing biodegradable detergents. The major features of this station are: ease of use, prolonged bath life, minimal drag-out, effective removal of all soils and minimal waste. A typical two-tank configuration is shown in Figure 1.

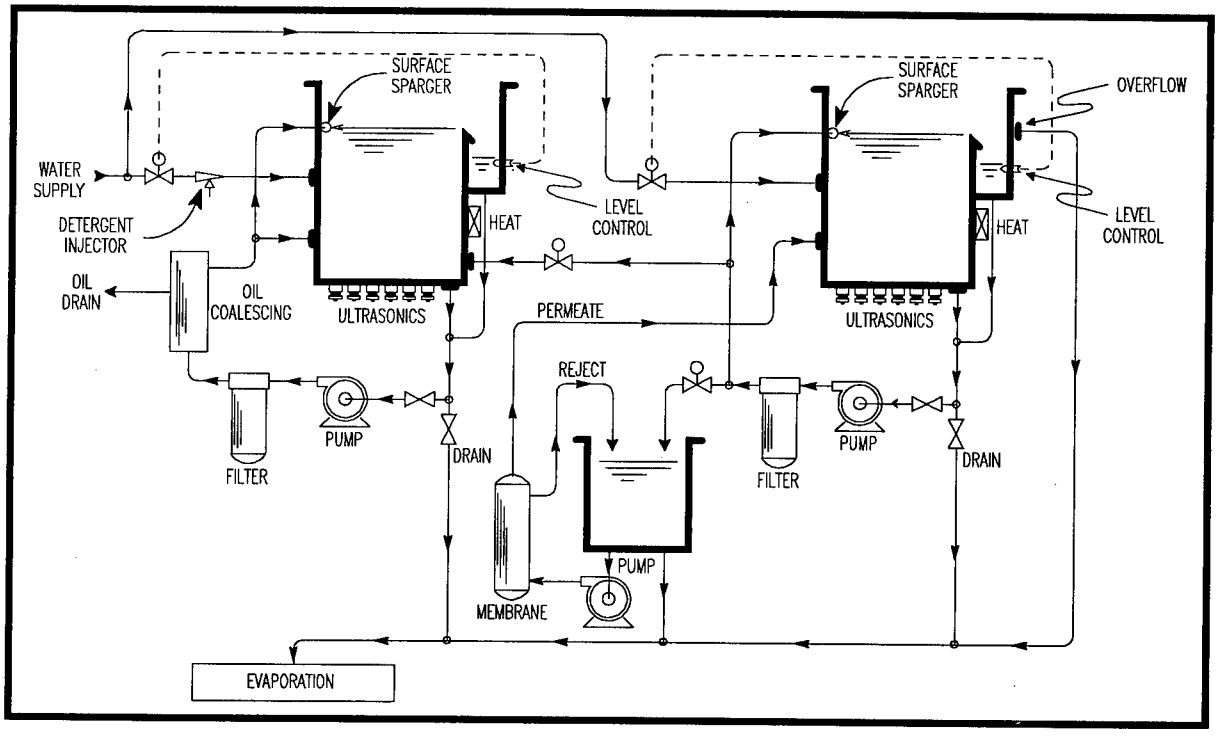


Figure 1: Cleaning Tanks.

Both tanks utilize bottom-mounted ultrasonics to assist in the thorough removal of all soils. Tests have shown that with proper power controls most parts can be effectively cleaned utilizing ultrasonics.

The tanks illustrated above also incorporate a high flow recirculation filtration system with multiple return ports. Recirculation filtration is important to minimize the redepositing of particulate on components and to extend the bath life. With proper control of the flow return to minimize turbulence and provide a proper

sweeping action, flow rates covering 50 percent of the tank volume per minute can be utilized with no impact on the ultrasonic activity.

The first tank of the wash section will frequently have a detergent injection and automatic water makeup system to maintain a constant level of water and detergent in the bath. The detergent level in the second tank is allowed to fluctuate as the detergent is dragged in the first tank.

Through the use of an oil coalescing system and a surface skimmer, oils can be removed easily from the wash tank if an appropriate non-emulsifying detergent is used. To prolong the life of the second wash and to provide a higher level of cleanliness, a membrane system may also be incorporated. The savings realized are a function of water usage plus disposal cost and can range from $10,000 to $100,000 per year.

The two cleaning tanks must be dumped when either the effectiveness of cleaning has dropped below acceptable levels or the concentration of detergent in the second tank is too high. This is accomplished by first dumping Tank 1 into an evaporator holding tank. The evaporator flashes off the water, leaving a small volume of solid waste that must be disposed of. It should be noted that the average operating cost of an evaporator is 6 cents to 10 cents per gallon evaporated. These figures can be used to determine if such a system is an effective method of minimizing your disposal cost per year or if some other method should be considered.

Tank 1 is refilled by dumping Tank 2 into Tank 1. Tank 2 is then refilled with clean water or with water from the first rinse station. The use of a two-wash tank configuration reduces the frequency of tank solution changes, minimizes the detergent carried over into the rinse tank and increases the consistency of cleaning achieved with the system.

RINSE

The rinse station is designed to thoroughly rinse the detergent and remaining particulates from the components utilizing the minimum volume of water possible.

The rinse station has been divided into two parts: Gross detergent removal and final rinse. The gross detergent removal tank is designed to remove the majority of the detergent utilizing a combination of spray and immersion with a closed-loop water supply. The tank consists of a one-sided ultrasonic overflow tank with

a two-sided spray system above it and a high-flow recirculation pump and filter system (Refer to Figure 2).

The oversized overflow trough is utilized as a reservoir for the pump and filter system. The filtered water is returned either to the bottom of the rinse tank or to the sprays. The system operates as a closed-loop until the maximum conductivity limit is reached. The water from the final rinse stage is then fed into the tank that overflows into the second wash tank. The entire tank is dumped into the second wash tank where the wash tank solutions are changed. The tank design allows the majority of the detergent to be removed with minimal fresh water input (Refer to Figure 2).

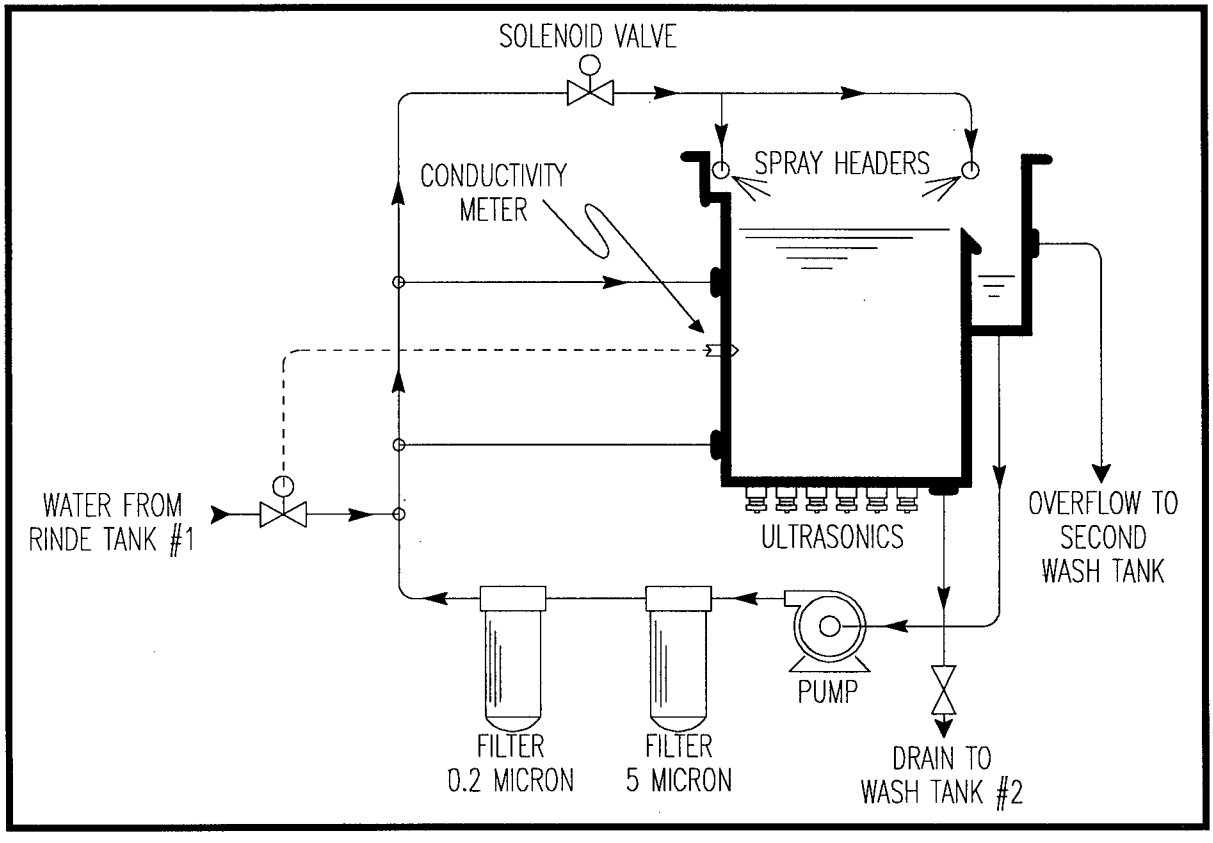
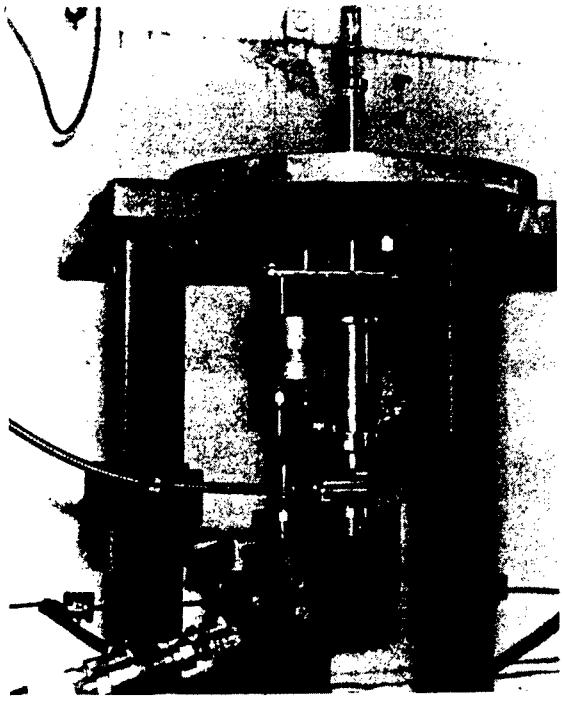
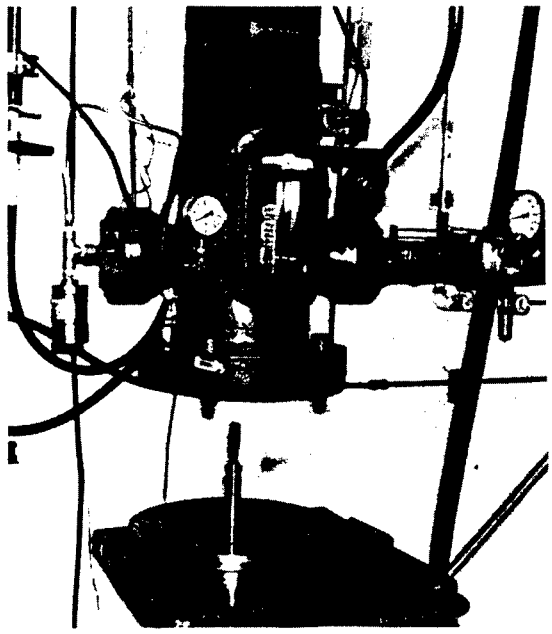


Figure 2: Gross Rinse Tank.

The final rinse stage consists of two cascading overflow rinse tanks with ultrasonics in both. The rinse tanks have spray rinses above them for final

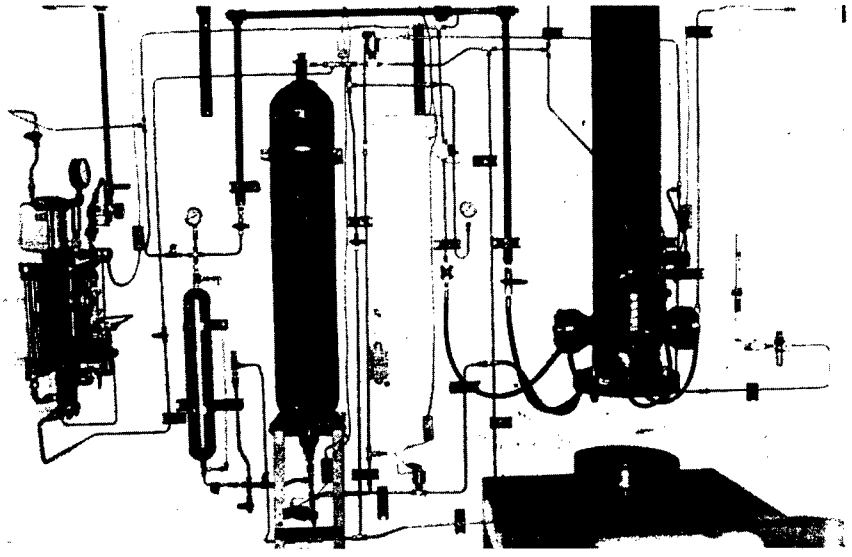


Modified Gyra-Jet Installed in Test Stand
Fig. 8



Rotating Nozzle Fixtured in Base Plate
Fig.9

In comparative testing ,conventional milling it was found that to ensure safe operation that the milling process would have to be slowed down greatly when operating near the motor case. Based on preliminary experience capital equipment cost appear similar for either method. This therefore gives an advantage to the ammonia jet method in terms of overall productivity and in motors having high case to propellant area ratios.



Amonia-Jet Test Facility
Fig. 10

CONCLUSION:

As has been described the use of water under pressure as a cleaning method is hardly a new concept. In reality what the last ten to fifteen years have done is provide the time needed for the technology to catch up with the concept. By the manufacturers focusing on reliability and incremental product design improvement the hardware of ultra-high pressure water jetting has reached a point where the pumping and delivery equipment is not the limiting factor in a particular application. Most manufacturers and end users would agree that the equipment available today is well qualified to operate well into the next century without being obsoleted. This allows the end user to explore innovative nozzle designs and alternative fluids for specific cleaning and coating removal projects. In the case of the APC's mentioned the majority of evaluation and configuration time was dedicated to selecting a nozzle design that generated the best paint removal pattern while simultaneously allowing for selective layer by layer coating removal from a soft substrate. Those involved in the rocket motor demil project were similarly able to focus development effort on the handling of the ammonia and the disposal of the waste material rather designing a pumping system.

That the technology to go to much higher pressures with the same basic pump design already exists ,the room for growth is virtually unlimited by the availability of hardware.

It can be anticipated that we have entered a new phase of high pressure fluid jet cleaning and coating removal development where the majority of time and effort is dedicated to perfecting existing concepts and applying that experience to the multitude of environmental cleanup challenges the future holds.

rinsing. The first rinse tank is fed from the overflow of the second rinse tank. The first tank overflows into a holding reservoir that feeds a pump that pumps the water to a surfactant-stripping and water-polishing system for recycling. The return from this recycling system feeds the second rinse tank (Refer to Figure 3). Fresh water is fed into the reservoir tank. The last rinse should be hot to expedite drying.

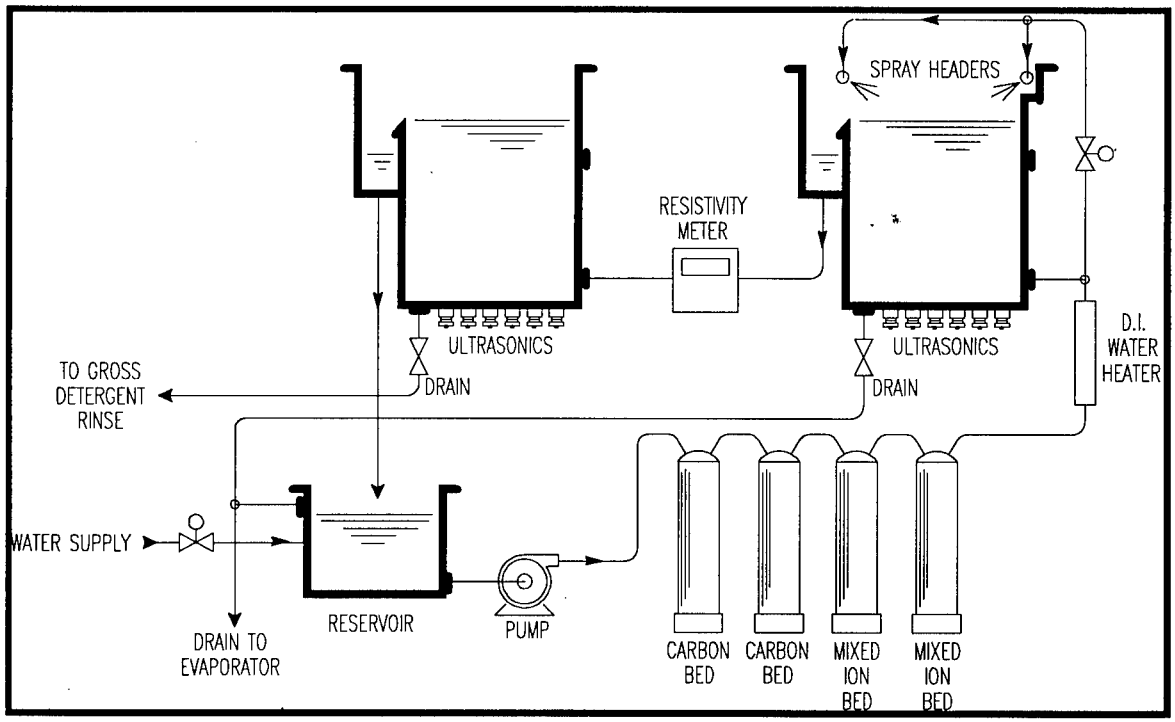


Figure 3: Final Rinse.

The closed-loop design allows the system to operate with very low water requirements while providing thorough rinsing before the drying stage. No detergent residues can be present if spot-free drying is to be achieved.

A closed-loop water system used in this manner with a 2 gal/min flow rate and a drag-over of approximately 1000 grams of a pH neutral surfactant per day would have an approximate operating cost of $ 4,600 to $6,300 per year. Most systems are being designed so that closed-loop rinse water recycling can be added at a later date.

DRYING

There are many new non-CFC drying techniques available, but the most widely used is high efficiency recirculating hot air. The high efficiency design utilizes large volumes of moderate temperature recirculating air to remove water from a wide variety of components. The air distribution plenums are usually located on opposed sides with a bottom return for even air flow. The air recirculating system includes HEPA filters, inline air heaters and adjustable air discharge and makeup ports to control the humidity in the recirculating air. The recirculating hot air design is much more energy efficient than conventional blow-off designs and more versatile in the variety of components that can be used.

The limitation of hot air is that it cannot remove water from deep blind holes, cupped pans or surface adsorbed water. If components with these characteristics are to be dried, a secondary drying process is often required with the most widely used process being vacuum drying. In this process, a warm, partially dried component is placed in a heated vacuum chamber which is pumped down to 4 to 10 torr to flash off the residual water. This process is very efficient in the removal of small films of water, but it will not successfully remove large volumes or puddles of water. With hot air followed by vacuum drying, most components can be completely dried spot-free.

Several other new non-CFC drying techniques are available for use in precision cleaning. If components with large flat surfaces such as glass plates are to be dried, capillary drying should be used. Capillary drying involves the slow removal of components from hot DI water. The surface tension of the water causes water to be pulled off the surface and the component left dry. If large volumes of parts are to be dried utilizing hot air, a tunnel dryer may be applicable. A tunnel dryer is a large recirculating hot air dryer that racks on a conveyor.

REFERENCE 1

Comparison of Cleaning Data
CFC Versus Aqueous Cleaning System

Test	**Units**	**Before Cleaned**	**CFC Cleaned**	**Aqueous Cleaned**
Ion Chromatography Sulfate	UG/IN^2	0.50	0.400	0.300
Ion Chromatography Nitrate	UG/IN^2	0.20	0.150	0.100
Ion Chromatography Chloride	UG/IN^2	0.80	0.750	0.500
Ion Chromatography Fluoride	UG/IN^2	0.60	0.200	0.030
Non-Volatile Residue (NVR)	UG/IN^2	0.05	0.040	0.020
Densitometer (Particulate)	-----	0.03	0.010	0.005
Dryness Test (Moisture)	UG/IN^2	-----	0.030	0.030
Haze Test (Corrosion)	-----	-----	-----	Better

CONCLUSION

There are a number of features that must be considered when evaluating a precision cleaning system, all of which will affect the system's environmental impact, ease of operation and degree of cleanliness. But I believe that I have shown that there is an environmentally sound and user friendly precision aqueous cleaning technology available that will produce parts with a higher level of cleanliness than those achieved in a CFC cleaning system.

Evaluation of Pressurized Water Cleaning Systems For Hardware Refurbishment

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Abstract

Historically, refurbishment processes for RSRM motor cases and components have employed environmentally harmful materials. Specifically, vapor degreasing processes consume and emit large amounts of ozone depleting compounds. This program evaluates the use of pressurized water cleaning systems as a replacement for the vapor degreasing process. Tests have been conducted to determine if high pressure water washing, without any form of additive cleaner, is a viable candidate for replacing vapor degreasing processes. This paper discusses the findings thus far of Engineering Test Plan - 1168 (ETP-1168), "Evaluation of Pressurized Water Cleaning Systems for Hardware Refurbishment."

Introduction

Thiokol Corporation is one of the largest users of 1-1-1 Trichloroethane (TCA) in Utah. TCA is an EPA targeted Ozone Depleting Compound that is scheduled to be banned from production in 1995. Thiokol currently uses approximately 400,000 pounds of this material per year in its vapor degreasing operations for RSRM hardware refurbishment. Therefore, Thiokol and NASA/MSFC personnel recognized the immediacy of a necessary change in the refurbishment process. A joint Thiokol and NASA/MSFC ODC Elimination team was formed to investigate alternative cleaning methods for RSRM hardware. The team's approach for the elimination of TCA from all RSRM processing is divided into two phases. Phase I is scheduled to eliminate 90% of TCA usage by January 1, 1996. It is accomplished through two main steps. This paper discusses the Phase I Step I effort. The Phase I Step I task is the replacement of the Refurbishment Center's vapor degreasing system with a high pressure water wash system in conjunction with the implementation of greaseless storage and shipment of RSRM hardware.

Body

Thiokol is investigating several approaches to eliminate the use of TCA in the RSRM hardware refurbishment process. This paper focuses on one of these approaches, pressurized water cleaning systems. The investigation of pressurized water cleaning systems is broken into two phases as outlined in ETP - 1168.

Phase One of the test plan was established as a feasibility phase and completed in July of 1993. Phase One testing demonstrated that all non-bonded contaminates such as grease, proof test oil, and magnetic particle inspection residue could be removed at operating pressures not exceeding 15,000 psi. This portion of the testing was so promising that a quick study of paint removal at 15,000 psi was incorporated into Phase One testing. Although the testing proved that paint could be removed at these pressures, it removed the paint too slowly to fit into Thiokol's scheduling requirements. Phase one testing was completed on 8" x 10" witness panels. Further, preliminary erosion testing was accomplished on 2" x 2" steel or aluminum coupons. On the basis of this early testing, more in-depth investigations of bonded contaminates were undertaken in Phase Two testing.

Phase Two of the testing investigates the critical parameters of the high pressure water wash system, the erosion caused by the high pressure water on both D6AC steel and aluminum substrates, the feasibility of cleaning full scale components, and all bond lines that are affected by the change in processing. To accomplish these tasks, Phase II efforts are divided into seven tables investigating five contaminates on 2 different substrates. The contaminates are grease, proof test oil, magnetic particle testing residue, epoxy paint/primer, epoxy based adhesives and insulator residue. The two substrates are D6AC steel and 7075 aluminum. Of the seven tables, the first three have been completed. A description of the tables follows.

The first table is a design of experiments devised to determine the critical process parameters of the high pressure wash system. The parameters investigated were pressure, flow, nozzle rotational speed, nozzle angle, nozzle standoff, and sweep rate across the part. The contaminates and substrates chosen for this testing were grease on steel and aluminum, epoxy paint/primer on steel, and EA913 adhesive on aluminum. The measures for the tests were level of cleanliness and erosion. Thus, the critical parameters yielded by this test were those that had the most impact on level of cleanliness and the amount of erosion. The results are shown in Table 1 below.

Table 1
Engineering Test Plan – 1168
Statistical Evaluation

Parameter	Test Range	Significant Effect Erosion (D6AC)	Significant Effect Rating (D6AC)	Significant Effect Erosion (AL)	Significant Effect Rating (AL)
Pressure	18 - 36 ksi	No	Yes	Yes	Yes
Flow	6 - 12 gpm	No	No	No	No
Nozzle Speed	400 - 800 rpm	No	No	No	No
Nozzle Angle	60 - 80 deg	No	No	No	No
Standoff	3 - 10 in	Yes	Yes	Yes	No
Sweep Rate	1 - 10 in/sec	No	Yes	Yes	Yes

It should be noted that significant effect in this case represents statistical significance. When the erosion rates of the pressurized water cleaning are compared to the current grit balst process, the erosion due to pressurized water cleaning is an order of magnitude lower than the current grit blast process.

The second table of the test plan establishes maximum removal rates for all contaminate/substrate combinations that are present on RSRM hardware. It sets the critical parameters from the first table to their optimum settings and increases/decreases the sweep rate across the part until a 100% clean surface is achieved. The maximum removal rates established are given in Table 2.

Table 2
Engineering Test Plan - 1168
Established Maximum Removal Rates

Contaminate	Substrate	Maximum Removal Rate, sqin/min/nozzle
EA913NA	D6AC Steel	205
EA946	D6AC Steel	499
Chemlok® 205/233	D6AC Steel	281
Chemlok® 205/236A	D6AC Steel	378
Chemlok® 205/220/Tycement®	D6AC Steel	228
Rust-Oleum® Paint/Primer	D6AC Steel	343
Conoco HD-2 Grease	D6AC Steel	723
Shell Diala Oil	D6AC Steel	1250
Magnetic Particle Rinse Solution	D6AC Steel	1250
EA913NA	7075 Aluminum	185
EA946	7075 Aluminum	449
Alodine, Bostic Finch Paint/Primer	7075 Aluminum	228
Conoco HD-2 Grease	7075 Aluminum	723

The third table addresses the feasibility of cleaning full scale components. To this point in the test plan all testing has focused on 8" x 10" witness panels and 2" x 2" erosion coupons. To ensure that similar removal characteristics could be obtained on full scale RSRM hardware, six components were tested that represent all contaminate/substrate combinations. The six components are RSRM Throat Housing, Nose Inlet Housing, Cowl Housing, Fixed Housing, Forward Dome and Forward End Ring. In all cases the maximum removal rates established in table two were met or exceeded on the full scale hardware.

Tables four through seven investigate the bondline sensitivity of RSRM case and nozzle components when the refurbishment process is changed from vapor degreasing to high pressure water washing. These tables process one set of witness panels and surface analysis coupons through the current process in parallel with another set processed through the proposed process. Each step of each process is included in the test plan. For this testing the bond strength is the measure. After completion, the bond strengths associated with each process will be compared to see if there is any significant difference between the two processes. Further, the bond strengths will be compared to historical RSRM data. This testing will be conducted over the next three months.

Conclusions

Testing to date indicates that pressurized water cleaning systems are a viable alternative to vapor degreasing operations. Thiokol has demonstrated that more than just grease removal can be obtained with the high pressure water systems. In fact, a high pressurized water wash system would most likely not be justified if the only contaminate being removed was grease. However, the pressurized water wash systems are extremely versatile and can be adapted to replace many technologies. In this RSRM application the high pressure water wash system will replace vapor degreasing, some manual grit blasting, some manual glass bead, and some manual low pressure (10,000 to 15000 psi) water blasting operations. Further, Thiokol was able to gain added benefits in the form of a more consistent process yielding higher quality components, removal of operators from injury prone environments, less possibility of damaging RSRM hardware, and greatly reduced processing times.

Acknowledgments

The authors wish to thank some of the people that have made the accomplishments thus far possible. Thanks to Ken Schulte, Thiokol Utah, for writing shop planning and preparing samples to be tested. Thanks to Ken Bradford and Phil Thompson, Thiokol Huntsville Space, for their diligent efforts completing testing thus far.

Ultrasonic Cleaning
Fundamental Theory
and
Application

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Abstract -

A presentation describing the theory of ultrasonics, cavitation and implosion. The importance and application of ultrasonics in precision cleaning. Explanations of ultrasonic cleaning equipment options and their application. Process parameters for ultrasonic cleaning. Proper operation of ultrasonic cleaning equipment to achieve maximum results.

Introduction -

Solvent degreasing using chlorinated and fluorinated hydrocarbon solvents, a process used for cleaning by the finishing industry since its very inception, is on its way out, a victim of increased regulation, the Montreal Protocol and the "Green" movement in general. It is understandable why this method achieved its prominent position in metal fininshing - - it is reasonably effective at cleaning and was formerly the most expedient and least expensive cleaning means available. The equipment required is simple and inexpensive, and until recently the chemistry was considered environmentally safe.

Industry is currently in a struggle to replace solvent degreasing with alternative "environmentally friendly" means of cleaning. Although substitute water-based, semi-aqueous and petroleum based chemistries are available, they are often somewhat less effective as cleaners than the solvents and may not perform adequately in some applications unless a mechanical energy boost is added to assure the required levels of cleanliness. Ultrasonic energy is now used extensively in critical cleaning applications to both speed and enhance the cleaning effect of the alternative chemistries. This paper is intended to familiarize the reader with the basic theory of ultrasonics and how ultrasonic energy can be most effectively applied to enhance a variety of cleaning processes.

What is "Ultrasonics?" -

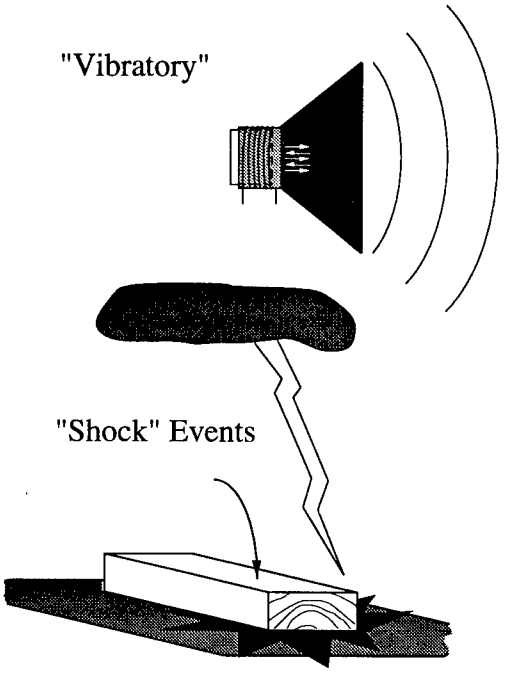
Ultrasonics is the science of sound waves above the limits of human audibility. The frequency of a sound wave determines its tone or pitch. Low frequencies produce low or bass tones. High frequencies produce high or treble tones. Ultrasound is a sound with a pitch so high that it can not be heard by the human ear. Frequencies above 18 Kilohertz are usually considered to be ultrasonic. The frequencies used for ultrasonic cleaning range from 20,000 cycles per second or kilohertz (KHz) to over 100,000 KHz. The most commonly used frequencies for industrial cleaning are those between 20 KHz and 50KHz. Frequencies above 50KHz are more commonly used in small tabletop ultrasonic cleaners such as those found in jewelry stores and dental offices.

The Theory of Sound Waves -

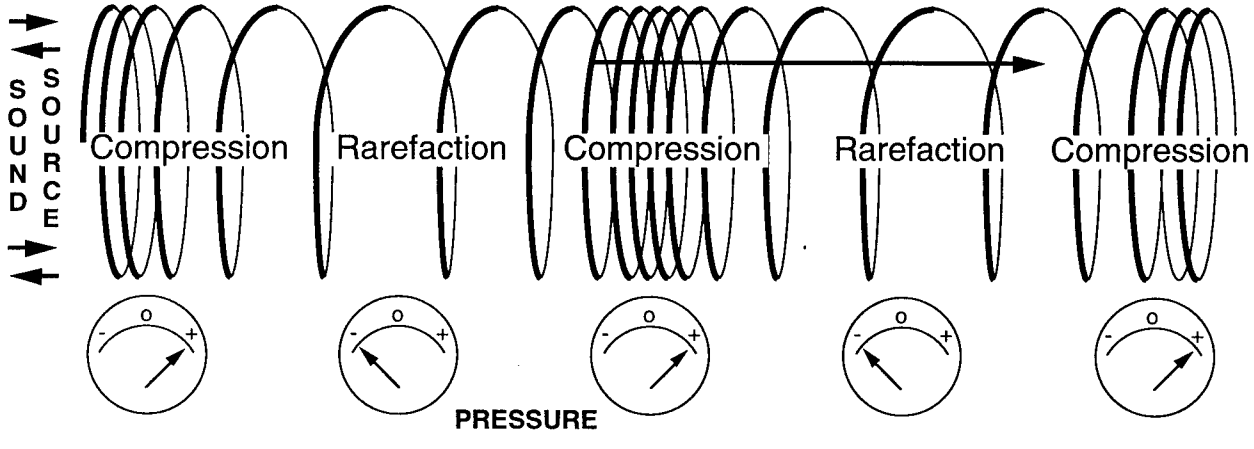
In order to understand the mechanics of ultrasonics, it is necessary to first have a basic unde.stand-ing of sound waves, how they are generated and how they travel through a conducting medium.

Sound Wave Generation -

A sound wave is produced when a solitary or repeating displacement is generated in a sound conducting medium, such as by a "shock" event or "oscillatory" movement. The displacement of air by the cone of a radio speaker is a good example of "oscillatory" sound waves generated by mechanical movement. As the speaker cone moves back and forth, the air in front of the cone is alternately compressed and rarefied to produce sound waves, which travel through the air until they are finally dissipated. We are probably most familiar with sound waves generated by alternating mechanical motion. There are also sound waves which are created by a single "shock" event. An example is thunder which is generated as air instantaneously changes volume as a result of an electrical discharge (lightning). Another example of a shock event might be the sound created as a wooden board falls with its face against a cement floor. Shock events are sources of a single compression wave which radiates from the source.



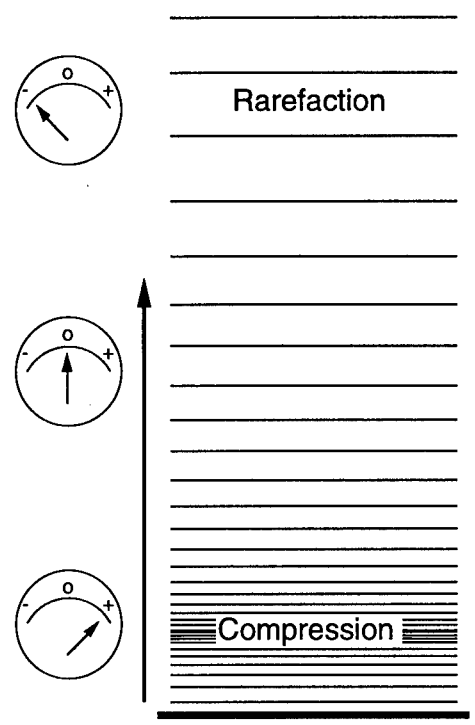
The Nature of Sound Waves -

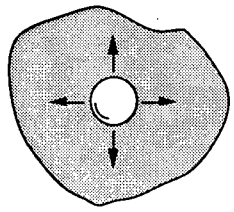


The diagram above uses the coils of a spring similar to a Slinky® toy to represent individual molecules of a sound conducting medium. The molecules in the medium are influenced by adjacent molecules in much the same way that the coils of the spring influence one another. The source of the sound in the model is at the left. The compression generated by the sound source as it moves propagates down the length of the spring as each adjacent coil of the spring pushes against its neighbor. It is important to note that, although the wave travels from one end of the spring to the other, the individual coils remain in their same relative positions, being displaced first one way and then the other as the sound wave passes. As a result, each coil is first part of a compression as it is pushed toward the next coil and then part of a rarefaction as it recedes from the adjacent coil. In much the same way, any point in a sound conducting medium is alternately subjected to compression and then rarefaction. At a point in the area of a compression, the pressure in the medium is positive. At a point in the area of a rarefaction, the pressure in the medium is negative.

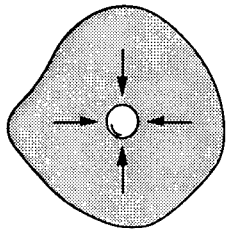
Cavitation -

In elastic media such as air and most solids, there is a continuous transition as a sound wave is transmitted. In non-elastic media such as water and most liquids, there is continuous transition as long as the amplitude or "loudness" of the sound is relatively low. As amplitude is increased, however, the magnitude of the negative pressure in the areas of rarefaction eventually becomes sufficient to cause the liquid to fracture because of the negative pressure, causing a phenomenon known as cavitation.

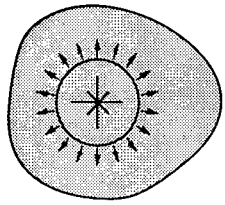




Cavitation "bubbles" are created at sites of rarefaction as the liquid fractures or tears because of the negative pressure of the sound wave in the liquid.



As the wave fronts pass, the cavitation "bubbles" oscillate under the influence of positive pressure, eventually growing to an unstable size.



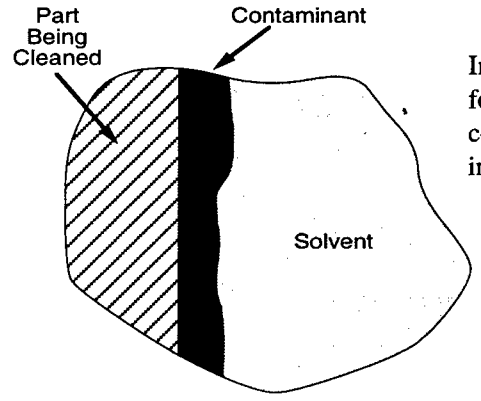
Finally, the violent collapse of the cavitation "bubbles" results in implosions, which cause shock waves to be radiated from the sites of the collapse.

The collapse and implosion of myriad cavitation "bubbles" throughout an ultrasonically activated liquid result in the effect commonly associated with ultrasonics. It has been calculated that temperatures in excess of 10,000°F and pressures in excess of 10,000 PSI are generated at the implosion sites of cavitation bubbles.

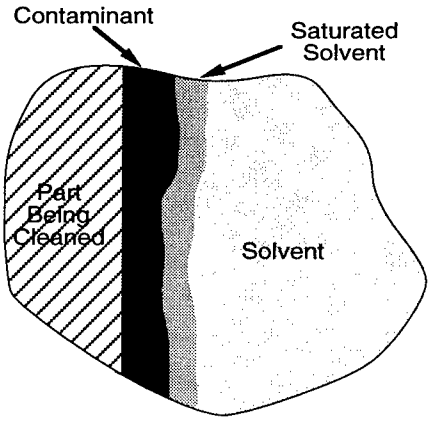
Benefits of Ultrasonics in the Cleaning and Rinsing Processes -

Cleaning in most instances requires that a contaminant be dissolved (as in the case of a soluble soil), displaced (as in the case of a non-soluble soil) or both dissolved and displaced (as in the case of insoluble particles being held by a soluble binder such as oil or grease). The mechanical effect of ultrasonic energy can be helpful in both speeding dissolution and displacing particles. Just as it is beneficial in cleaning, ultrasonics is also beneficial in the rinsing process. Residual cleaning chemicals are removed quickly and completely by ultrasonic rinsing.

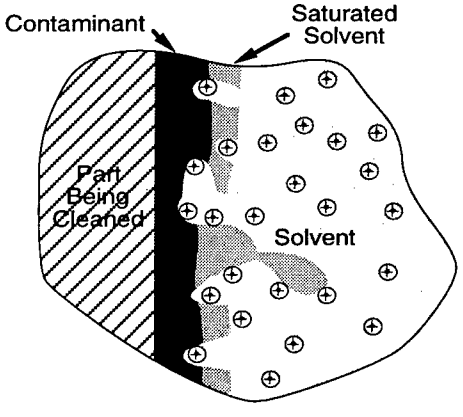
Ultrasonics Speeds Cleaning by Dissolution -



In removing a contaminant by dissolution, it is necessary for the solvent to come into contact with and dissolve the contaminant. The cleaning activity takes place only at the interface between the solvent and the contaminant.

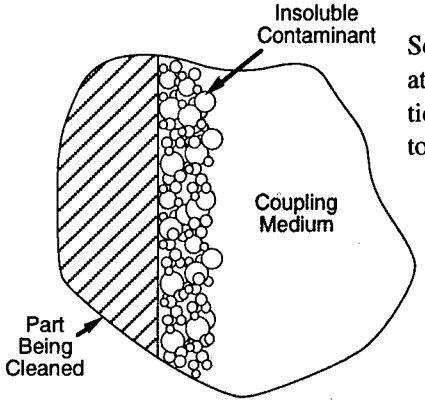


As the solvent dissolves the contaminant, a saturated solvent layer develops at the interface between the solvent and the contaminant. Once this has happened, cleaning action stops as the saturated solvent can no longer attack the contaminant. Fresh solvent cannot reach the contaminant.

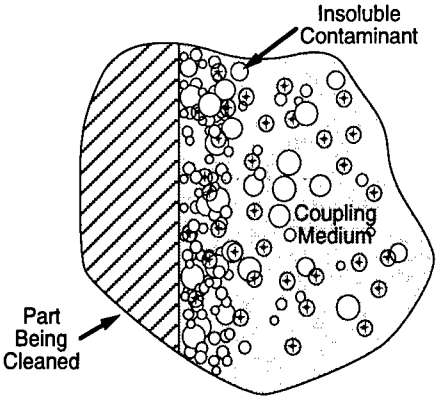


Ultrasonic cavitation and implosion effectively displace the saturated solvent layer to allow fresh solvent to come into contact with the contaminant remaining to be removed. This is especially beneficial when irregular surfaces or internal passageways are to be cleaned.

Ultrasonic Activity Displaces Particles -



Some contaminants are comprised of insoluble particles loosly attached and held in place by ionic or cohesive forces. These particles need only be displaced sufficiently to break the attractive forces to be removed.



Cavitation and implosion as a result of ultrasonic activity displace and remove loosely held contaminants such as dust from surfaces. For this to be effective, it is necessary that the coupling medium be capable of wetting the particles to be removed.

Complex Contaminants -

Contaminations can also, of course, be more complex in nature, consisting of combination soils made up of both soluble and insoluble components. The effect of ultrasonics is substantially the same in these cases, as the mechanical micro-agitation helps speed both the dissolution of soluble contaminants and the displacement of insoluble particles.

Ultrasonic activity has also been demonstrated to speed or enhance the effect of many chemical reactions. This is probably caused mostly by the high energy levels created as high pressures and temperatures are created at the implosion sites. It is likely that the superior results achieved in many ultrasonic cleaning operations may be at least partially attributed to the sonochemistry effect.

A Superior Process -

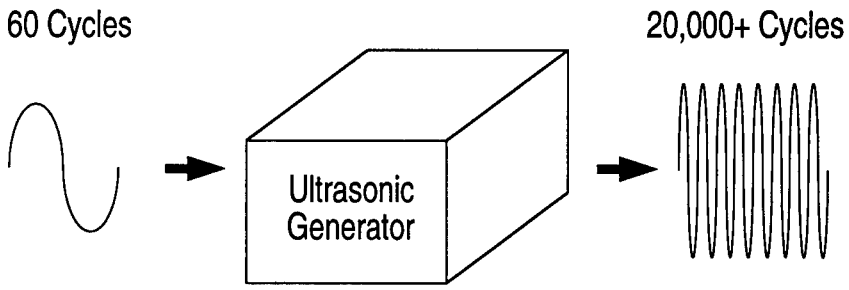
Ultrasonic energy has been proven to be more effective at enhancing cleaning than other alternatives, including spray washing, brushing, turbulation, air agitation, and electro-cleaning in many applications. The ability of ultrasonic activity to penetrate and assist the cleaning of interior surfaces of complex parts is especially noteworthy.

<u>Ultrasonic Equipment</u> -

To introduce ultrasonic energy into a cleaning system requires an ultrasonic transducer and an ultrasonic power supply or "generator." The generator supplies electrical energy at the desired ultrasonic frequency. The ultrasonic transducer converts the electrical energy from the ultrasonic generator into mechanical vibrations.

Ultrasonic Generator -

The ultrasonic generator converts electrical energy from the line which is typically alternating current at 50 or 60Hz to electrical energy at the ultrasonic frequency. This is accomplished in a number of ways by various equipment manufacturers. Current ultrasonic generators nearly all use solid state technology.



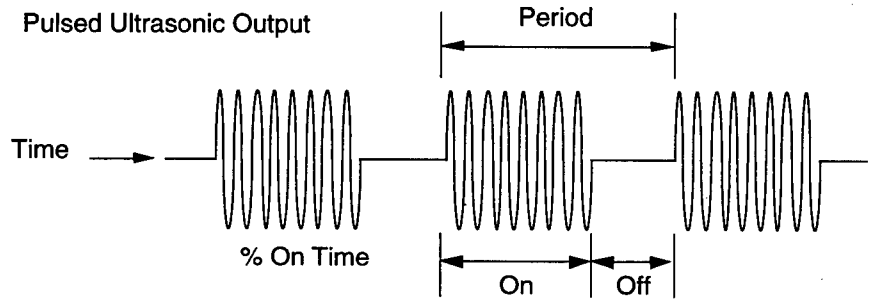
There have been several relatively recent innovations in ultrasonic generator technology which may enhance the effectiveness of ultrasonic cleaning equipment. These include square wave outputs, slowly or rapidly pulsing the ultrasonic energy on and off and modulating or "sweeping" the frequency of the generator output around the central operating frequency. The most advanced ultrasonic generators have provisions for adjusting a variety of output parameters to customize the ultrasonic energy output for the

Square Wave Output -

Applying a square wave signal to an ultrasonic transducer results in an acoustic output rich in harmonics. The result is a multi-frequency cleaning system which vibrates simultaneously at several frequencies which are harmonics of the fundamental frequency. Multi-frequency operation offers the benefits of all frequencies combined in a single ultrasonic cleaning tank.

Pulse -

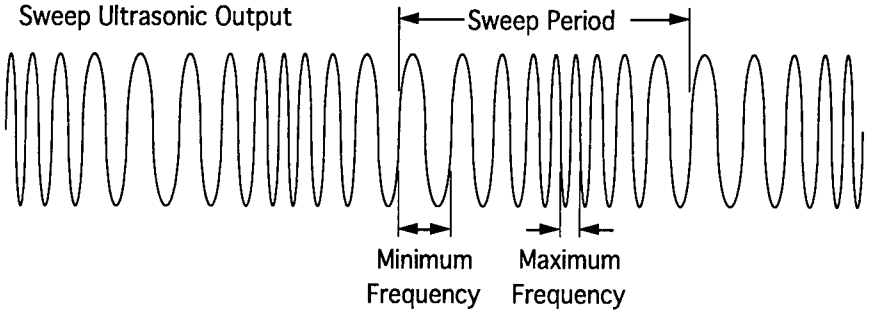
In pulse operation, the ultrasonic energy is turned on and off at a rate which may vary from once every several seconds to several hundred times per second.



The percentage of time that the ultrasonic energy is on may also be changed to produce varied results. At slower pulse rates, more rapid degassing of liquids occurs as coalescing bubbles of air are given an opportunity to rise to the surface of the liquid during the time the ultrasonic energy is off. At more rapid pulse rates the cleaning process may be enhanced as repeated high energy "bursts" of ultrasonic energy occur each time the energy source is turned on.

Sweep -

In sweep operation, the frequency of the output of the ultrasonic generator is modulated around a central frequency which may itself be adjustable.



Various effects are produced by changing the speed and magnitude of the frequency modulation. The frequency may be modulated from once every several seconds to several hundred times per second with the magnitude of variation ranging from several hertz to several kilohertz. Sweep may be used to prevent damage to extremely delicate parts or to reduce the effects of standing waves in cleaning tanks. Sweep operation may also be found especially useful in facilitating the cavitation of terpenes and petroleum based chemistries. Pulse and sweep operation may be especially useful in facilitating the cavitation of terpenes and petroleum based chemistries.

Ultrasonic Transducers -

There are two general types of ultrasonic transducers in use today: Magnetostrictive and piezoelectric. Both accomplish the same task of converting alternating electrical energy to vibratory mechanical energy but do it through the use of different means.

IPA DRYER

Alcohol can be used effectively as a drying agent by immersing parts into an alcohol bath. The alcohol bath essentially captures residual water. This water-capturing process is accomplished by the cracks and crevices inherent in the alcohol's molecular structure that function as absorbents.

The drying techniques described are just some of the new non-CFC precision drying techniques available. With correct implementation, any components can be dried with a non-CFC drying technique.

TYPICAL SYSTEM

The configuration of an aqueous cleaner can vary widely depending upon the wide variety of parts to be cleaned, the level of cleanliness required and the throughput requirements. In its simplest form, the system can be a single wash, rinse and dry tank in a small console. For more complete cleaning it may take multi-stages of each technique as I have described here. One such system that has been used extensively by the disk drive industry is shown in Figure 4.

This design reduces the system footprint by 25 percent without sacrificing the effectiveness of the cleaning. The trade-off is that the reduced system will require more careful maintenance of the cleaning solution and will increase the use of rinse water.

The other area where compromises in design are often required is in rinse water recycling. The operating costs of present systems are sometimes difficult to determine. However, a closed-loop system can be a cost-effective alternative. Considerable research is being performed in this area to identify cost-effective recycling systems as well as cleaning agents that are easier to recycle.

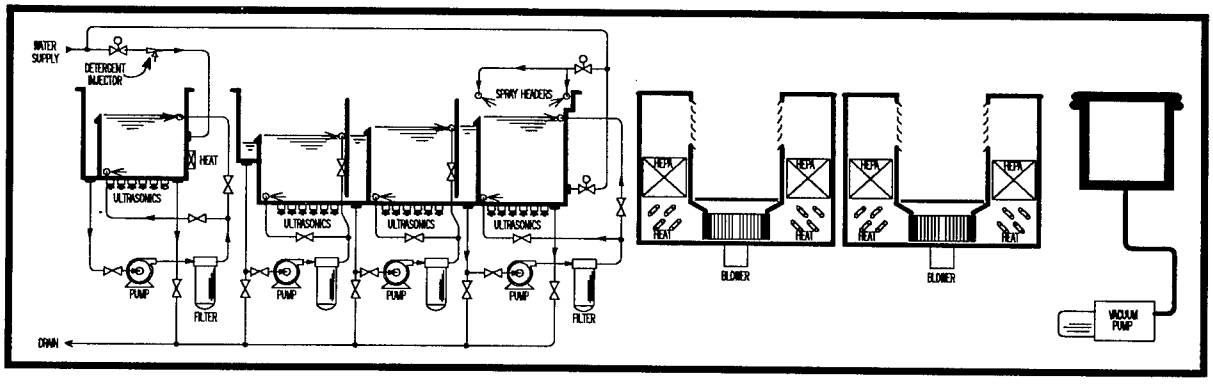
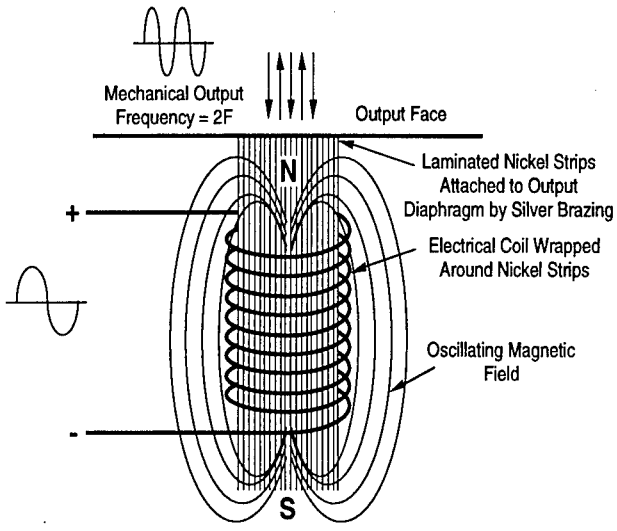


Figure 4: Typical System.

This system uses one wash, three rinses and two recirculating hot air dryers followed by a vacuum dryer. When automated, this system can deliver a basket of parts every 6 minutes to 7 minutes with a single-headed transport system. If an additional head is added, the throughput goes to 3.5 minutes to 4.5 minutes. The following chart shows typical cleaning results obtained with a similar system and compares them to parts cleaned in an ultrasonic CFC degreasing system.

Magnetostrictive -

Magnetostrictive transducers utilize the principle of magnetostriction in which certain materials expand and contract when placed in an alternating magnetic field. Alternating electrical energy from the ultrasonic generator is first converted into an alternating magnetic field through the use of a coil of wire. The alternating magnetic field is then used to induce mechanical vibrations at the ultrasonic frequency in strips of nickel or other magnetostrictive material which are attached to the surface to be vibrated. Because magnetostrictive materials behave identically to a magnetic field of either polarity, the frequency of the electrical energy applied to the transducer is 1/2 of the desired output frequency. Magnetostrictive transducers were first to supply a robust source of ultrasonic vibrations for high power applications such as ultrasonic cleaning.



Because of inherent mechanical constraints on the physical size of the hardware as well as electrical and magnetic complications, high power magnetostrictive transducers seldom operate at frequencies much above 20 kilohertz. Piezoelectric transducers, on the other hand, can easily operate well into the megahertz range.

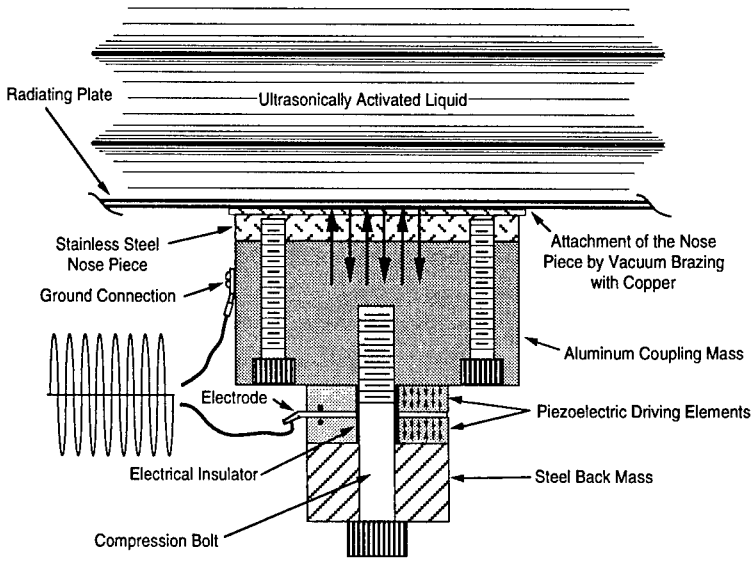
Magnetostrictive transducers are generally less efficient than their piezoelectric counterparts. This is due primarily to the fact that the magnetostrictive transducer requires a dual energy conversion from electrical to magnetic and then from magnetic to mechanical. Some efficiency is lost in each conversion. Hysteresis effects also detract from the efficiency of the magnetostrictive transducer.

Piezoelectric -

Piezoelectric transducers convert alternating electrical energy directly to mechanical energy through use of the piezoelectric effect in which certain materials change dimension when an electrical charge is applied to them.

Electrical energy at the ultrasonic frequency is supplied to the transducer by the ultrasonic generator. This electrical energy is applied to piezoelectric element(s) in the transducer which vibrate. These vibrations are amplified by the resonant masses of the transducer and directed into the liquid through the radiating plate.

Early piezoelectric transducers utilized such piezoelectric materials as naturally occuring quartz crystals and barium titanate which were fragile and unstable. Early piezoelectric transducers were, therefore, unreliable.



Today's incorporate stronger, more efficient and highly stable ceramic piezoelectric materials which were a result of the efforts of the US Navy and its research to develop advanced sonar transponders in the 1940's. The vast majority of transducers used today for ultrasonic cleaning utilize the piezoelectric effect. and its research to develop advanced sonar transponders in the 1940's. The vast majority of transducers used today for ultrasonic cleaning utilize the piezoelectric effect.

Ultrasonic Cleaning Equipment -

Ultrasonic cleaning equipment ranges from the small tabletop units often found in dental offices or jewelry stores to huge systems with capacities of several thousand gallons used in a variety of industrial applications. Selection or design of the proper equipment is paramount in the success of any ultrasonic cleaning application.

The simplest application may require only a simple heated tank cleaner with rinsing to be done in a sink or in a separate container. More sophisticated cleaning systems include one or more rinses, added process tanks and hot air dryers. Automation is often added to reduce labor and guarantee process consistency.

The largest installations utilize immersible ultrasonic transducers which can be mounted on the sides or bottom of cleaning tanks of nearly any size. Immersible ultrasonic transducers offer maximum flexibility and ease of installation and service.

Maximizing the Ultrasonic Cleaning Process -

Process Parameters -

Effective application of the ultrasonic cleaning process requires consideration of a number of parameters. While time, temperature and chemical remain important in ultrasonic cleaning as they are in other cleaning technologies, there are other factors which must be considered to maximize the effectiveness of the process. Especially important are those variables which affect the intensity of ultrasonic cavitation in the liquid.

Maximizing Cavitation

Maximizing cavitation of the cleaning liquid is obviously very important to the success of the ultrasonic cleaning process. Several variables affect cavitation intensity.

Temperature is the most important single parameter to be considered in maximizing cavitation intensity. This is because so many liquid properties affecting cavitation intensity are related to temperature. Changes in temperature result in changes in viscosity, the solubility of gas in the liquid, the diffusion rate of dissolved gasses in the liquid, and vapor pressure, all of which affect cavitation intensity. In pure water, the cavitation effect is maximized at approximately 160°F.

The viscosity of a liquid must be minimized for maximum cavitation effect. Viscous liquids are sluggish and cannot respond quickly enough to form cavitation bubbles. The viscosity of most liquids is reduced as temperature is increased.

For most effective cavitation, the cleaning liquid must contain as little dissolved gas as possible. Gas dissolved in the liquid is released during the bubble growth phase of cavitation and prevents its violent implosion which is required for the desired ultrasonic effect. The amount of dissolved gas in a liquid is reduced as the liquid temperature is increased.

The diffusion rate of dissolved gasses in a liquid is increased at higher temperatures. This means that liquids at higher temperatures give up dissolved gasses more readily than those at lower temperatures, which aids in minimizing the amount of dissolved gas in the liquid.

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A CENTRIFUGE CO_2 PELLET CLEANING SYSTEM

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ABSTRACT

An advanced turbine/CO_2 pellet accelerator is being evaluated as a depaint technology at Oak Ridge National Laboratory (ORNL). The program, sponsored by Warner Robins Air Logistics Center (ALC), Robins Air Force Base, Georgia, has developed a robot-compatible apparatus that efficiently accelerates pellets of dry ice with a high-speed rotating wheel. In comparison to the more conventional compressed air 'sandblast' pellet accelerators, the turbine system can achieve higher pellet speeds, has precise speed control, and is more than ten times as efficient. A preliminary study of the apparatus as a depaint technology has been undertaken. Depaint rates of military epoxy/urethane paint systems on 2024 and 7075 aluminum panels as a function of pellet speed and throughput have been measured. In addition, methods of enhancing the strip rate by combining infra-red heat lamps with pellet blasting and by combining the use of environmentally benign solvents with the pellet blasting have also been studied. The design and operation of the apparatus will be discussed along with data obtained from the depaint studies.

INTRODUCTION

The centrifuge $C0_2$ cleaning system is a method of cleaning surfaces. Use of $C0_2$ is environmentally sound because it is readily available as a by-product stream from many industrial processes. The cleaning action takes place when the high-speed pellet of frozen CO_2 impacts the surface and knocks loose any contamination. Depending on the speed of the pellets, the cleaning action can be adjusted from a low impact pressure regime up to an aggressive impact during which relatively hard surfaces can be removed or etched. The cleaning applications of the centrifuge-based pellet accelerator are similar to those of commercially available $C0_2$ pellet cryoblasting systems that use compressed air to accelerate the pellets. The distinguishing feature of the centrifuge system is that it can achieve much higher pellet speeds at increased efficiency, which allows the centrifuge system to perform more aggressive cleaning and etching tasks. For example, removing epoxy-based paints from aircraft, a task that previously used large quantities of methylene chloride solvents, may be economically feasible with high-speed $C0_2$ pellets. Another application is the cleaning of surfaces contaminated with toxic, hazardous, or radioactive substances. In these applications the lack of a secondary contaminated waste stream is of great benefit.

THEORY OF OPERATION

The centrifuge accelerates cryogenic pellets with virtually no contact forces between the pellet and the accelerator. The acceleration process utilizes the commonly known property that frozen $C0_2$ (dry ice) 'floats' on a self-generated gas bearing when placed on a smooth surface. Pellets injected into a high-speed rotating track are thus accelerated with negligible friction loss, Fig. 1. Figure 2 shows the typical geometry of a track in a centrifuge wheel. Pellets exiting the wheel have a speed v_p determined by the peripheral speed of the wheel v_W and the exit angle θ between the track and the tangent of the wheel, Fig. 2.

$$v_p = 2v_W \cos(\theta/2) \qquad (1)$$

The track geometry for our present wheel has an exit peripheral angle of 45 degrees giving a pellet speed of 1.75 times the wheel tip velocity. Speeds of up to 350 m/s (1150 ft/s) and acceleration efficiencies of 80% (65% overall efficiency) have been achieved. All pellets accelerated by the wheel have essentially the same velocity which means that the entire stream can be delivered to the surface at the optimal velocity for the particular application. This is in contrast to compressed air systems which deliver pellets with a range of velocities.

The interaction of the high-speed pellet with a surface can be modeled using the same physics as the impact of a high speed fluid droplet on a surface, Fig. 3. In this case the impact pressure created on the surface is given by the 'water hammer' equation. This equation relates the impact stress s to the pellet velocity v_p, pellet density ρ_1 and compressive sound speed U_1:

$$s = \rho_1 U_1 v_p \qquad (2)$$

for impact with rigid surfaces and

$$s = v_p \rho_1 U_1 \rho_2 U_2 / (\rho_1 U_1 + \rho_2 U_2) \qquad (3)$$

or impact with semirigid surfaces. The compressive sound speed is one measure of the pellet's hardness. Even though dry ice is relatively soft, at high speeds the pressures developed during impact can be made larger than the yield strength of most materials. Depending on the surface being impacted, there is a characteristic threshold velocity above which erosion takes place. It is interesting to note that this physics model corresponds to any abrasive media which is significantly softer than the surface being impacted. Therefore, all of the soft abrasive and liquid impact cleaning technologies are basically the same. That is, one would expect to achieve comparable results with high pressure water, $C0_2$, or plastic media abrasives for comparable surface impact pressures as given by Equations 2 and 3.

The differentiating features of the soft abrasive technologies depend on the speed and efficiency of the acceleration technology, the cost of the

equipment, the cost of the abrasive material, and the cost of the recovery or cost of disposal of the abrasive material. The principle advantage of the centrifuge $C0_2$ system is that it can achieve pellet speeds high enough to perform aggressive etching. Furthermore, it is efficient and the waste processing is done with a simple high efficiency air filtering system. Another distinguishing feature of the $C0_2$ system is that during impact the $C0_2$ is converted from a solid to a high-pressure supercritical fluid which undergoes a rapid decompression and expansion which can be quite effective in dissolving hydrocarbons and in sweeping away surface deposits. These effects are especially important in cleaning porous surfaces.

EXPERIMENT

The experiment involved design, fabrication, and testing of a robot compatible device, similar to Fig. 1. The hardware used to accelerate the $C0_2$ pellets consists of a high-speed electric motor and a specially designed aluminum accelerator disk. This unit uses a lightweight 11-kW (15-HP) brushless DC motor with a 0.35-m (14-in) wheel. The weight of the accelerator is kept low for compatibility with the robot. This unit will accelerate $C0_2$ pellets delivering up to 454 kg/h (1000 lbs/h) at velocities of 350 m/s (1150 ft/s) and clean a swath about 13-cm (5-in) wide as it is scanned across a surface. A commercial $C0_2$ micropellet fabrication machine was used to feed the centrifuge. The unit was mounted on a GMFanuc S-420F robot, which was programmed to move the device across sheets of painted aluminum panels at various rates in order to obtain depainting rates.

Painted panel samples which measured 0.51 m by 1.02 m (2 ft by 4 ft) were mounted on a horizontal support matrix which was designed to simulate the rib structure of the aircraft. This was mounted on a table top and surrounded by an exhaust shroud to collect the carbon dioxide gas and paint chips. A 57-m^3/min (2000 CFM) HEPA filter system collected this gas and directed the exhaust outside the building. The pelletizer was started about 45 minutes prior to the run to collect a supply of pellets for the run. The robot was programmed to sweep the device in a linear scan at programmable rates for designated distances across the panel. Parameters such as offset distance and starting position were also programmable. The robot scan was generally tested prior to operating the device. If preheating lamps were used during the run, they would be turned on first. The motor speed would then be set and the motor turned on. Pellet feed would then be initiated and the robot scan would be initiated.

Four different aluminum substrates used in this work: 2024-T3 and 7075-T6 aluminum each with a thickness of 0.081 mm (0.032 in) and 1.57 mm (0.062 in). The panels were cut, marked, and sent to Warner Robins ALC for painting. They received a coat of MIL-P-23377 epoxy-polyamide primer on both sides and a finish coat of gray gloss MIL-C-83286 urethane-aliphatic isocyanate paint on the side to be tested. The samples were then artificially aged and returned to ORNL. There were a total of twenty test panels prepared. Samples were run at room temperature with various pellet feed rates and scan rates, at elevated temperatures, and with solvent augmentation. Cleaned areas

were measured using the 'paper dolly' method in which the cleaned area was traced on paper, cut out, and weighed. Weights were then compared to weights of known areas to determined the area cleaned. The results of these tests are presented below.

RESULTS AND DISCUSSION

PELLET VELOCITY MEASUREMENTS

Double pulse strobe lighting with 200 μs between pulses was used to determine pellet velocities. Distances between double-exposure video images of the same pellet were used to calculate distance traveled during this time period. Results of analysis of about 200 individual pellet trajectories from 24 video frames are shown in Fig. 4. The theoretical speed at the point of release on the wheel at this velocity (12,000 rpm) is 390 m/s (1280 ft/s). Theoretical calculation of velocity reduction due to air drag for several sizes of spherical pellets are presented as the lines in the figure. Pellets are fed into the wheel as 1-mm diameter cylinders and it is plausible that they may undergo breakage in the feed line and during acceleration. Video images of the pellets were not of good enough quality to measure actual pellet diameter. Pellets strike the surface being cleaned in the range of 18 to 25 mm (7 to 10 in) from the wheel. In this range, pellets are traveling at a speed of about 350 m/s (1150 ft/s).

STRAIGHT BLASTING RESULTS

During a typical scan, the robot was programmed to clean ten 120-mm (4.72-in) long segments at rates of 64, 32, 28, 16, 12, 8, 6, 4, and 3 mm/s (12.6, 6.3, 5.5, 3.1, 2.4, 1.6, 1.2, 0.8, and 0.6 ft/min). Figure 5 shows the fraction of the surface cleaned as a function of the quantity of pellets striking the surface for three different pellet velocities. The curves have a sigmoid shape showing an incubation period where little or no erosion occurs, followed by period of rapidly increasing erosion rate and finally leveling off as 100% cleaning is approached. The device cleans a 13.3-cm (5.25-in) swath with the cleaning efficiency being the highest at the center. At optimal strip rates, the center of the swath is fully cleaned with the edges left partially stripped. A 2.5-cm (1-in) overlay on the next pass completes the stripping of the edge region. Figure 6 shows the effect of pellet feed rate on cleaning rate at the highest pellet speed (1150 ft/s). This curve again shows behavior typical of most erosion processes in that there is some incubation period below which cleaning does not occur, followed by a segment of rapidly increasing cleaning rates. At higher rates the data is showing signs of leveling off. It appears that at 12,000 rpm at least 79 kg/h (175 lbs/h) is the incubation rate and that about 227 kg/h (500 lbs/h) may be the optimal operating point where depaint rates of about 6.7 m^2/h (1.2 ft^2/min) are achieved.

Figure 7 shows results of Almen strip test runs. Almen test strips were cut from 0.81-mm (0.32-in) thick 2024T3 painted panels and run under typical cleaning conditions. The curves show incubation periods similar to those for cleaning curves shown in Fig. 5. Almen deflection and fractional cleaning also appear to be related, and it appears that the Almen deflection associated with a specific level of cleaning may be independent of the pellet speed. Two

important effects must be considered in evaluation the potential surface hardening, which would result from multiple depaint cycles. First, the Almen deflection curves tend to saturate with additional dosing so that each subsequent cleaning would produce less additional Almen deflection than the previous cycle. Second, the paint actually protects the surface, especially through the incubation period, so that curves for Almen deflection for the accumulated dose for unpainted material will be higher than those for painted specimens.

HEAT AUGMENTED DEPAINTING

In an earlier phase of this program, it was found that mild heating of the surface made dramatic increases in depainting rate; therefore, further tests in this area were performed with this new accelerator. Three heating methods were explored: a 5-kW hot-air gun blowing on the surface just ahead of the blast area in the scan direction, two 1.2-kW Research, Inc., infrared lamps mounted on the unit in the scan direction, and portable Wal-Mart heat lamps used to warm the surface prior to scanning. The temperature of the surface was read just ahead of the blast zone with an Exergen infrared thermometer and recorded. Results show that the important factor in determining depaint rate is the surface temperature and not the method used to produce the temperature increase.

Figure 8 shows the results of experiments to augment the strip rate by heating the paint surface. The quartz infra-red heat lamps, mounted on the turbine wheel housing, preheat the surface to a temperature around the boiling point of water (212° F) for a few seconds preceding the blasting. The heating softens the paint and thereby increases the depaint rate by a factor of 3-to-4 times the unheated strip rate.

SOLVENT AUGMENTED DEPAINIING

Another option available to enhance strip rate is the use of environmentally benign solvents to presoften the paint. There are many such solvents available, but only two were used to test the concept: methyl-ethyl-ketone (MEK) and 3M Safest Strip. MEK is very volatile and would evaporate too rapidly to have any effect if just painted on the surface. This problem was circumvented by laying a towel on the surface, soaking it with MEK, and covering with plastic to prevent evaporation. Safest Strip contains agents that retard evaporation; however, the surface was also covered after application to prevent hardening. With these mild solvents the surface must be soaked for some time to cause an effect. In these tests the solvents were left on the panel over the weekend, or about three days. These samples were run at only one scan rate (9.5 ft/min), and the results are shown in Fig. 9 with results from heating and straight blasting for comparison. As can be seen in the figure, solvent augmented cleaning rates are on the order of four times the unaugmented rates.

ADDITIONAL TESTING

In addition to the paint stripping program, a limited amount of testing with the centrifuge/CO_2 blaster was also performed to characterize its cleaning capabilities on a variety of surfaces. Several objects typical of those found in a decontamination project were cleaned. These included: a painted concrete block, greasy gear assembly, a concrete floor sample, enamel coated steel siding, some limestone rocks, a wooden pallet, and a rusty angle iron. Also, through a DOE-sponsored program designed to assist U.S. industry, a number of private companies ran short tests with their own samples to determine the potential of implementing CO_2 blasting in their specific industrial process.

CONCLUSIONS AND RECOMMENDATIONS

This program has produced a robot compatible centrifugal dry ice pellet depainting device for Warner Robins ALC This device is about ten times the efficiency of conventional dry ice blasting equipment, which utilizes pneumatic acceleration. The device has been shown to be capable of delivering 454 kg/h (1000 lbs/h) at velocities of 350 m/s (1150 ft/s). The device is powered by a specially developed light-weight brushless DC motor which develops over 15 kW (20 HP) at 12,000 rpm. While the device has not been qualified for operation at higher velocities, the motor has been run at 16,000 rpm; the entire device has been tested to 14,000 rpm without pellets. Modest increases in velocity may be desirable to increase cleaning rates. The device was mounted on a robot at ORNL, which scanned it across sample surfaces. It was shown to clean a swath about 13.3-cm (5.25-in) wide with a 3.8-cm (1.5-in) standoff distance. Depainting rates in excess of 5.6 m^2/h (1-ft^2/min) were measured with a pellet feed rate of 227 kg/h (500 lbs/h). Rates in excess of 22 m^2/h (4 ft^2/min) were measured when the paint was preheated to temperatures on the order of 100 C (212 F) or when the paint was presoftened with several environmentally benign paint stripping agents.

Research sponsored by the U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and under Interagency Agreement DOE No. 1974-E122-A1 with Warner Robins Air Logistic Center.

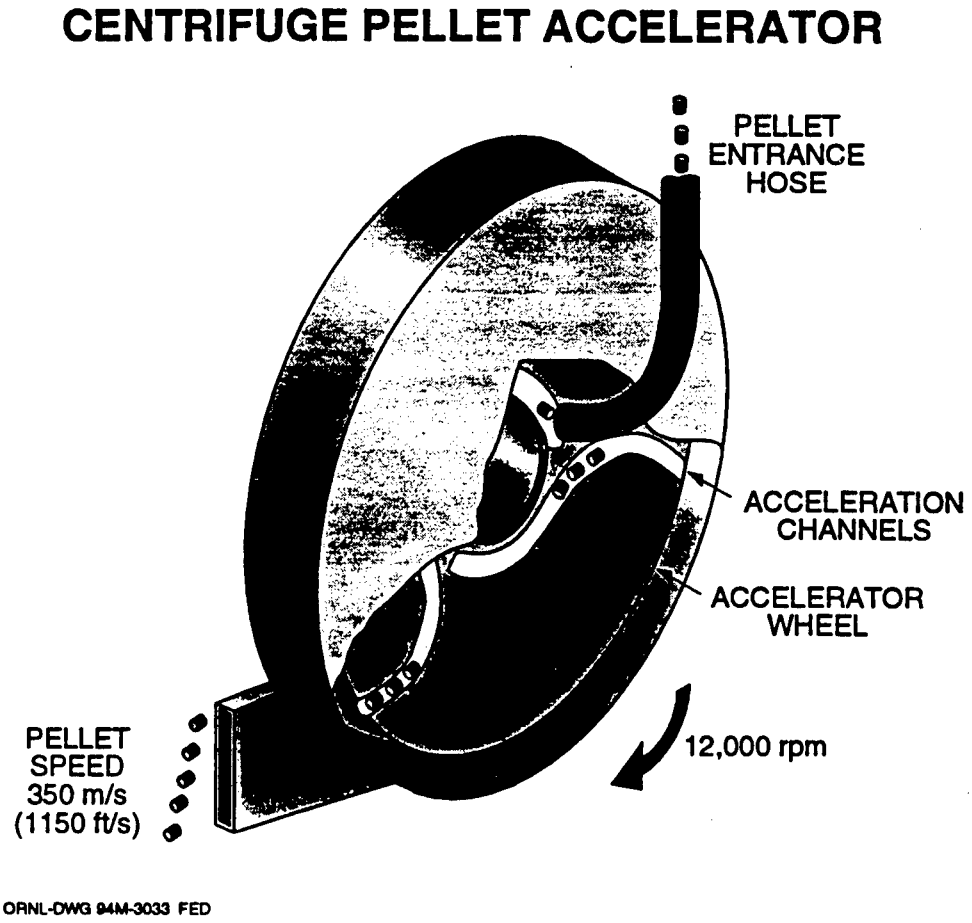

Fig 1. Turbine cryoblaster concept. Pellets are fed into grooves near the center of the wheel and accelerated to 1150 ft/s as they exit the device.

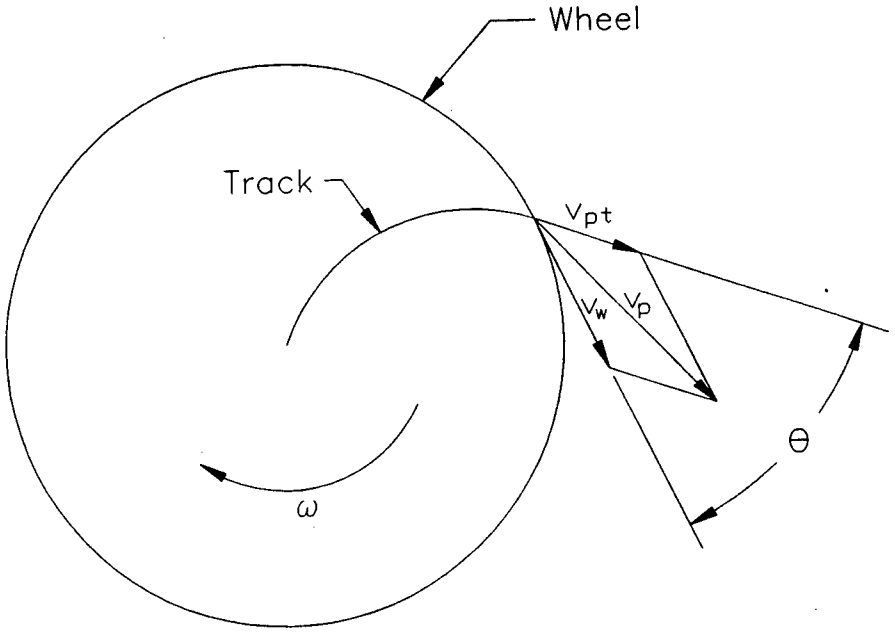

Fig 2. Wheel geometry showing vector sum of velocities as pellets exit the grooves.

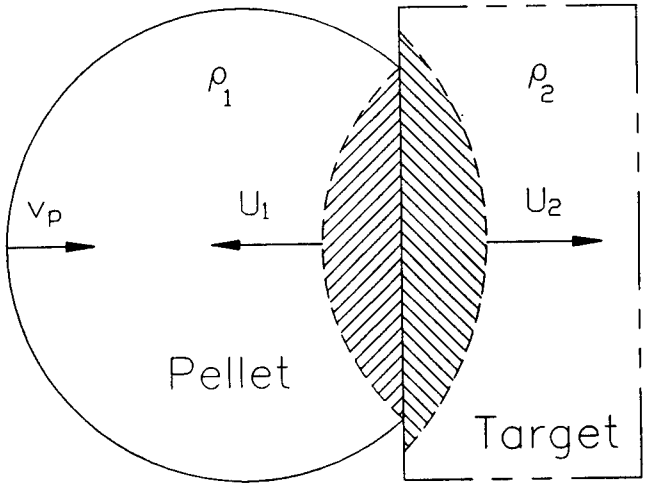

Fig 3. Shock wave propagation in pellet and surface during impact.

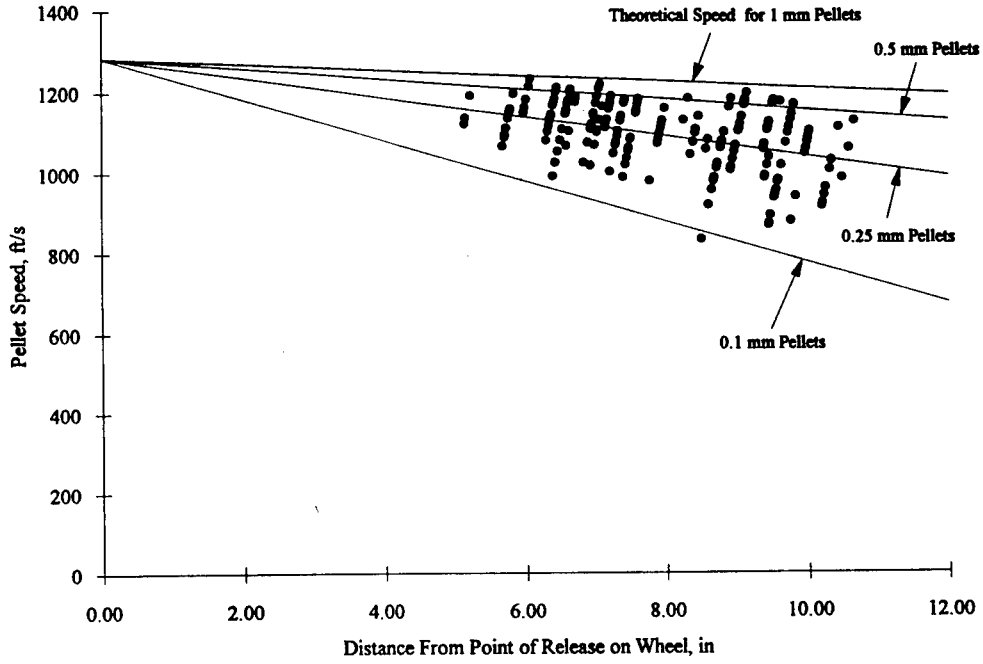

Fig 4. Measured pellet velocities with a rotor speed of 12,000 rpm. Lines show expected velocities for several size pellets undergoing aerodynamic drag.

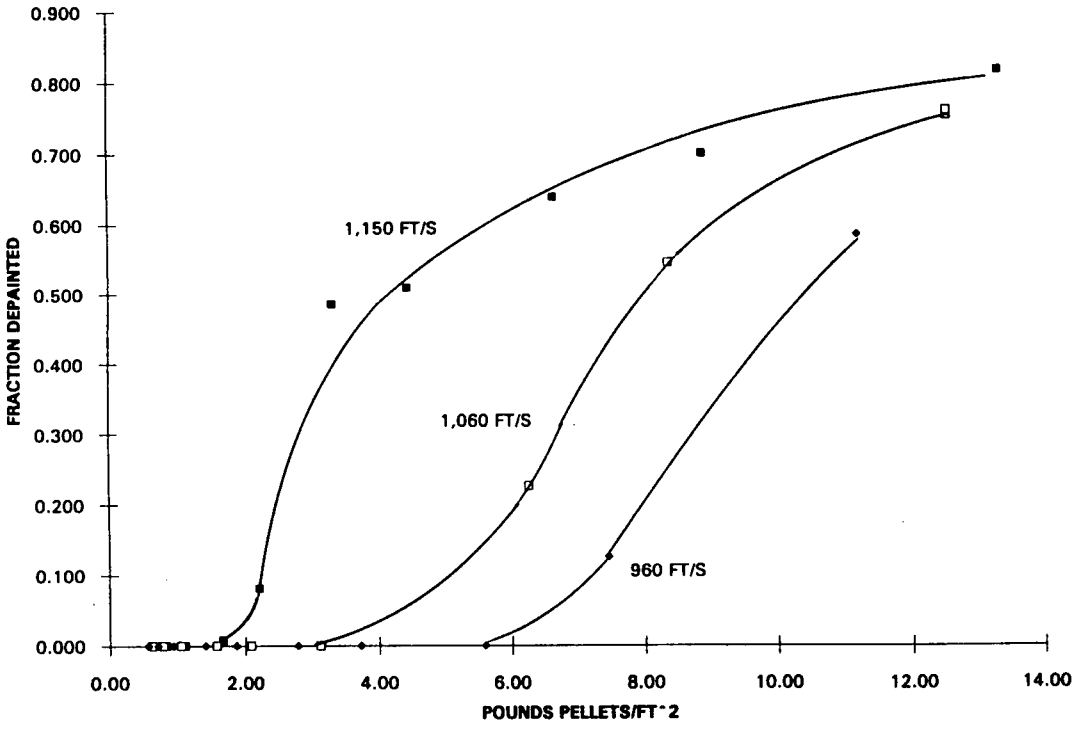

Fig 5. Fraction of surface depainted as a function of the quantity of pellets striking the surface for three different pellet speeds.

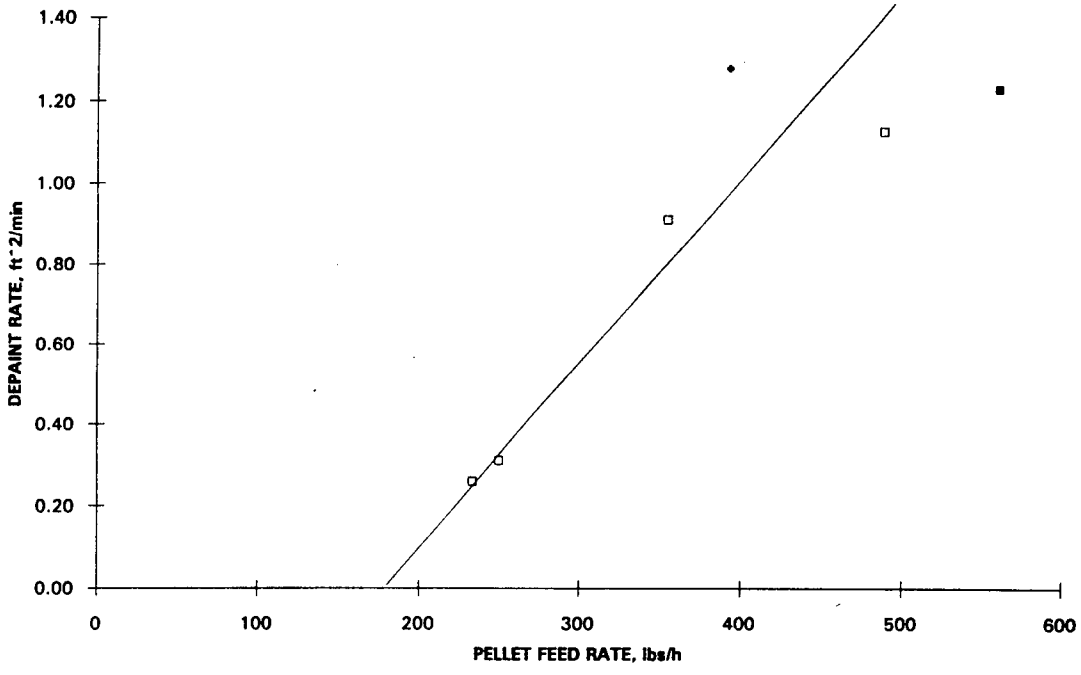

Fig 6. Optimal depaint rates as a function of pellet feed rate at 12,000 rpm (1150 ft/s).

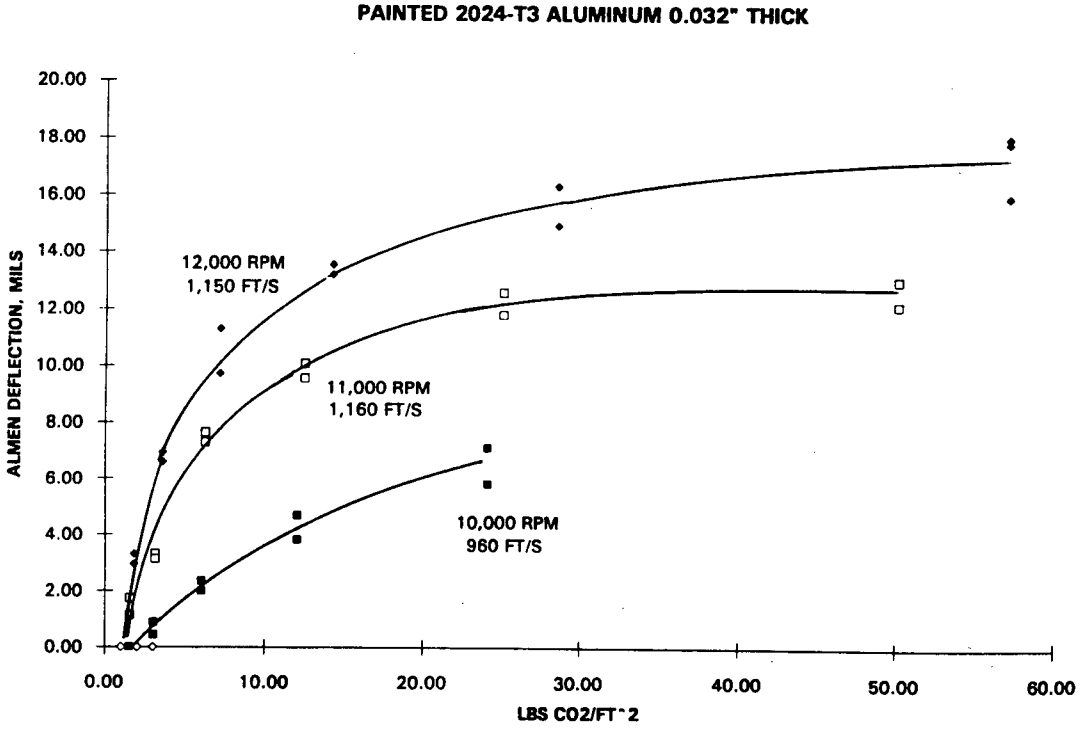

Fig 7. Almen deflection as a function of the quantity of pellets striking the surface for various speed pellets.

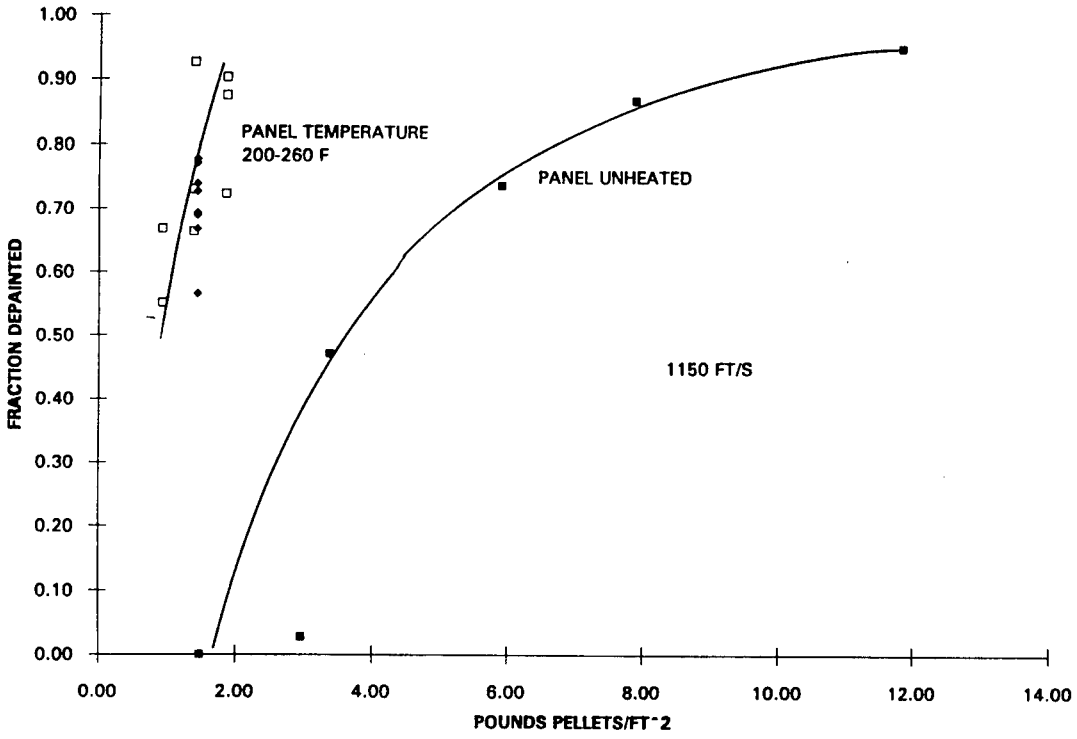

Fig 8. Fraction depainted as a function of the quantity of pellets striking the surface for heated and unheated panels using 1150 ft/s pellets.

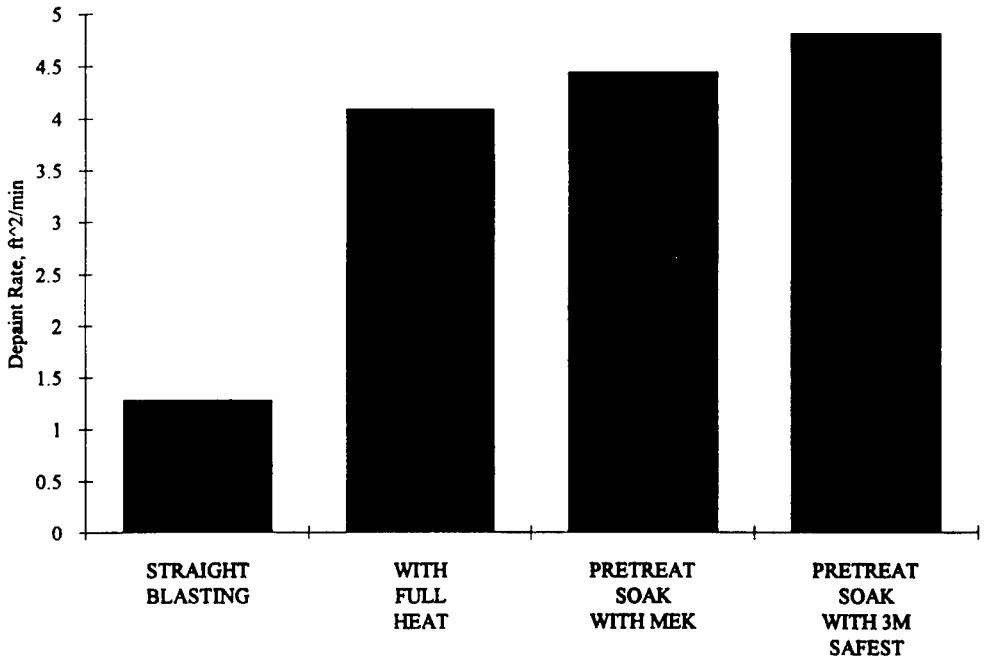

Fig 9. Depaint rates for 500 lbs/h pellets at 1150 ft/s.

CO_2 (DRY ICE) CLEANING SYSTEM

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ABSTRACT

Tomco Equipment Company has participated in the dry ice (solid carbon dioxide, CO_2) cleaning industry for over ten years as a pioneer in the manufacturer of high density, dry ice cleaning pellet production equipment. For over four years Tomco high density pelletizers have been available to the dry ice cleaning industry. Approximately one year ago Tomco introduced the DI-250, a new dry ice blast unit making Tomco a single source supplier for sublimable media, particle blast, cleaning systems. This new blast unit is an all pneumatic, single discharge hose device. It meters the insertion of 1/8 inch diameter (or smaller), high density, dry ice pellets into a high pressure, propellant gas stream. The dry ice and propellant streams are controlled and mixed from the blast cabinet. From there the mixture is transported to the nozzle where the pellets are accelerated to an appropriate blasting velocity. When directed to impact upon a target area, these dry ice pellets have sufficient energy to effectively remove most surface coatings through dry, abrasive contact.

The meta-stable, dry ice pellets used for CO_2 cleaning, while labeled "high density," are less dense than alternate, abrasive, particle blast media. In addition, after contacting the target surface, they return to their equilibrium condition: a superheated gas state. Most currently used grit blasting media are silicon dioxide based, which possess a sharp tetrahedral molecular structure. Silicon dioxide crystal structures will always produce smaller sharp-edged replicas of the original crystal upon fracture. Larger, softer dry ice pellets do not share the same sharp-edged crystalline structures as their non-sublimable counterparts when broken. In fact, upon contact with the target surface, dry ice pellets will plastically deform and break apart. As such, dry ice cleaning is less harmful to sensitive substrates, workers and the environment than chemical or abrasive cleaning systems.

Dry ice cleaning system components include: a dry ice pellet supply, a non-reactive propellant gas source, a pellet and propellant metering device, and a media transport and acceleration hose and nozzle arrangement. Dry ice cleaning system operating parameters include: choice of propellant gas, its pressure and temperature, dry ice mass flow rate, dry ice pellet size and shape, and acceleration nozzle configuration. These parameters may be modified to fit different applications. The growth of the dry ice cleaning industry will depend upon timely data acquisition of the effects that independent changes in these parameters have on cleaning rates, with respect to different surface coating and substrate combinations. With this data, optimization of cleaning rates for particular applications will be possible. The analysis of the applicable range of modulation of these parameters, within system component mechanical constraints, has just begun.

INTRODUCTION

Dry ice cleaning is an environmentally sound and user friendly, dry, abrasive process. It is similar in principle to sandblasting, though much more broad in scope and application. Specially designed equipment is necessary to deal with the differences in mediums while taking full advantage of different applications. Using dry ice cleaning systems in place of grit or water blasting or chemical cleaning systems to remove a surface coating leaves only the waste behind. The carbon dioxide used in this cleaning process has already been generated by industry and thus does not increase the quantity of green house gasses that contribute to global warming. Furthermore, many cleaning applications would suffer from the use, or introduction, of moisture in the cleaning process. Dry ice cleaning may be performed without introducing moisture by careful specification of system components.

The use of sublimable-media, abrasive blasting systems will reduce the space required in landfills and eliminate the costly separation and filtration of potentially hazardous waste products from the blast media at the end of a job. Similarly, the remediation of cleaning or stripping chemicals adds time and cost to the inherent biological hazards associated with chemical cleaning systems. Stringent and costly masking requirements of some aerospace applications may be relaxed because dry ice pellets quickly sublime after impact, which makes dry ice cleaning an attractive alternative. Dry ice within the fuselage of an air- or spacecraft will eventually sublime, and thus the weight of the craft will not be increased.

Carbon dioxide is primarily generated by petrochemical and fertilizer production processes, and secondarily from flue gas purification processes. Thus it is readily available in most industrial locations in the US and abroad. The process of transforming CO_2 into a useable solid phase for dry ice cleaning systems is a technology that was borrowed from the food processing industry, which has also benefited from the advances in pellet production equipment. The replacement of sublimable dry ice pellets for non-sublimating, abrasive blasting media requires special pellet extrusion equipment, capable of producing a smaller, more dense pellet than what is currently being used in food processing. In addition to changes in dry ice pelletizers, blasting equipment modifications necessary to facilitate the use of this near cryogenic media necessitates a different system design than that used for sandblasting.

The dry ice cleaning process is just that: dry. No water is used in the dry ice cleaning process. While the dry ice temperature of -109.33°F will cause rime ice to temporarily freeze onto substrates in uncontrolled environments, this side-effect may be eliminated with proper specification of atmospheric and propellant characteristics. Small cleaning booths supplied with dry, inert, positive pressure atmospheres, used in conjunction with cryogenically produced nitrogen as the propellant gas will limit the introduction of moisture to that which may have been frozen to the surface of the dry ice pellets during production. In addition, by "tenting" the dry ice pellet extruder and insulated receiver container (enclosing the extrusion heads and container within a tent) and again providing a positive-pressure inert atmosphere inside, the introduction of atmospheric moisture to the cleaning process may be all but eliminated.

SYSTEM EQUIPMENT

A typical dry ice cleaning system will consist of the following components:

A supply of dry ice blasting pellets of proper size, shape and density.
A propellant gas source of suitable temperature, pressure and dew point.
A device for containing the media, and modulating the flow of dry ice and propellant to the delivery hose.
A device to transport and accelerate dry ice pellets to high velocities, and direct them to the work surface.

A moderate increase in the temperature of a liquid brings it closer to its vapor pressure, meaning that vaporous cavitation is more easily achieved. Vaporous cavitation, in which the cavitation bubbles are filled with the vapor of the cavitating liquid, is the most effective form of cavitation. As the boiling temperature is approached, however, the cavitation intensity is reduced as the liquid starts to boil at the cavitation sites.

Cavitation intensity is directly related to Ultrasonic Power at the power levels generally used in ultrasonic cleaning systems. As power is increased substantially above the cavitation threshold, cavitation intensity levels off and can only be further increased through the use of focusing techniques.

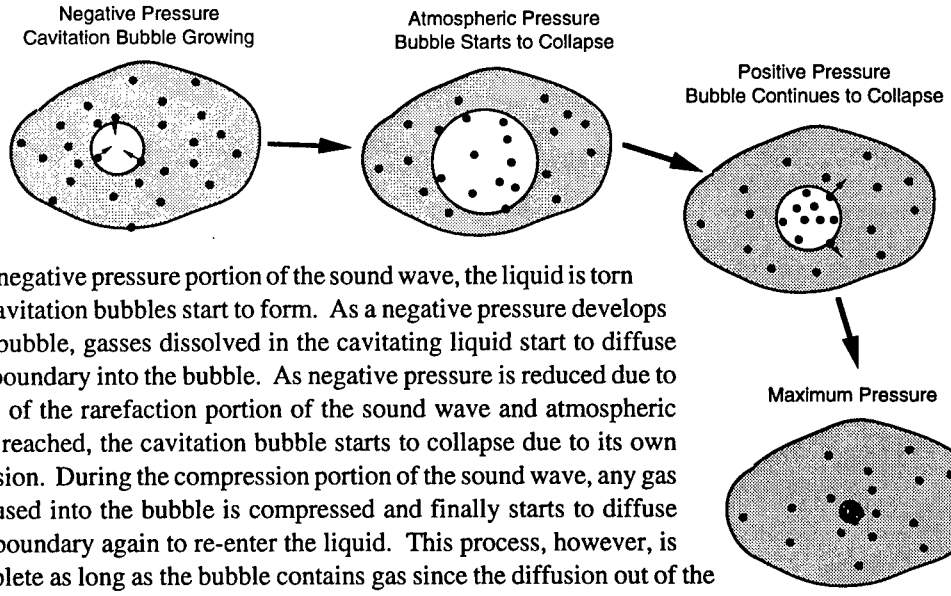
Cavitation intensity is inversely related to Ultrasonic Frequency. As the ultrasonic frequency is increased, cavitation intensity is reduced because of the smaller size of the cavitation bubbles and their resultant less violent implosion. The reduction in cavitation effect at higher freqencies may be overcome by increasing the ultrasonic power.

Maximizing Overall Cleaning Effect

Cleaning Chemical selection is extremely important to the overall success of the ultrasonic cleaning process. The selected chemical must be compatible with the base metal being cleaned and have the capablility to remove the soils which are present. It must also cavitate well. Most cleaning chemicals can be used satisfactorily with ultrasonics. Some are formulated especially for use with ultrasonics. However, avoid the non-foaming formulations normally used in spray washing applications. Highly wetted formulations are preferred. Many of the new petroleum cleaners, as well as petroleum and terpene based semi-aqueous cleaners, are compatible with ultrasonics. Use of these formulations may require some special equipment considerations, including increased ultrasonic power, to be effective.

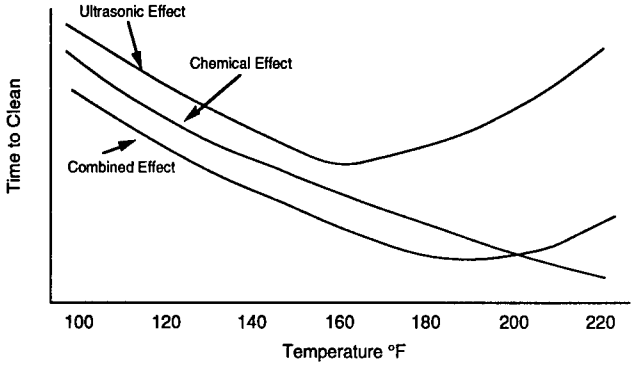
Temperature was mentioned earlier as being important to achieving maximum cavitation. The effectiveness of the cleaning chemical is also related to temperature. Although the cavitation effect is maximized in pure water at a temperature of approximately 160°F, optimum cleaning is often seen at higher or

Importance of Minimizing Dissolved Gas



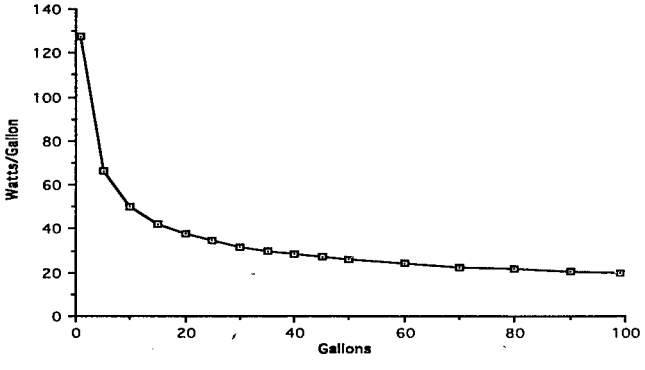
During the negative pressure portion of the sound wave, the liquid is torn apart and cavitation bubbles start to form. As a negative pressure develops within the bubble, gasses dissolved in the cavitating liquid start to diffuse across the boundary into the bubble. As negative pressure is reduced due to the passing of the rarefaction portion of the sound wave and atmospheric pressure is reached, the cavitation bubble starts to collapse due to its own surface tension. During the compression portion of the sound wave, any gas which diffused into the bubble is compressed and finally starts to diffuse across the boundary again to re-enter the liquid. This process, however, is never complete as long as the bubble contains gas since the diffusion out of the bubble does not start until the bubble is compressed. And once the bubble is compressed, the boundary surface available for diffusion is reduced. As a result, cavitation bubbles formed in liquids containing gas do not collapse all the way to implosion but rather result in a small pocket of compressed gas in the liquid. This phenomenon can be useful in degassing liquids. The small gas bubbles group together until they finally become sufficiently buoyant to come to the surface of the liquid.

lower temperatures because of the effect that temperature has on the cleaning chemical. As a general rule, each chemical will perform best at its recommended process temperature regardless of the temperature effect on the ultrasonics. For example, although the maximum ultrasonic effect is achieved at 160°F, most highly caustic cleaners are used at a temperatures of 180°F to 190°F because the chemical effect is greatly enhanced by the added temperature. Other cleaners may be found to break down and lose their effectiveness if used at temperatures in excess of as low as 140°F. The best practice is to use a chemical at its maximum recommended temperature not exceeding 190°F.



Degassing of cleaning solutions is extremely important in achieving satisfactory cleaning results. Fresh solutions or solutions which have cooled must be degassed before proceeding with cleaning. Degassing is done after the chemical is added and is accomplished by operating the ultrasonic energy and raising the solution temperature. The time required for degassing varies considerably, based on tank capacity and solution temperature, and may range from several minutes for a small tank to an hour or more for a large tank. An unheated tank may require several hours to degas. Degassing is complete when small bubbles of gas cannot be seen rising to the surface of the liquid and a pattern of ripples can be seen.

The Ultrasonic Power delivered to the cleaning tank must be adequate to cavitate the entire volume of liquid with the workload in place. Watts per gallon is a unit of measure often used to measure the level of ultrasonic power in a cleaning tank. As tank volume is increased, the number of watts per gallon required to achieve the required performance is reduced. Cleaning parts that are very massive or that have a high ratio of surface to mass may require additional ultrasonic power. Excessive power may cause cavitation erosion or "burning" on soft metal parts. If a wide variety of parts is to be cleaned in a single cleaning system, an ultrasonic power control is recommended to allow the power to be adjusted as required for various cleaning needs.



Part Exposure to both the cleaning chemical and ultrasonic energy is important for effective cleaning. Care must be taken to ensure that all areas of the parts being cleaned are flooded with the cleaning liquid. Parts baskets and fixtures must be designed to allow penetration of ultrasonic energy and to position the parts to assure that they are exposed to the ultrasonic energy. It is often necessary to individually rack parts in a specific orientation or rotate them during the cleaning process to thoroughly clean internal passages and blind holes.

Conclusion -

Properly utilized, ultrasonic energy can contribute significantly to the speed and effectiveness of many immersion cleaning and rinsing processes. It is especially beneficial in increasing the effectiveness of today's preferred aqueous cleaning chemistries and, in fact, is necessary in many applications to achieve the desired level of cleanliness. With ultrasonics, aqueous chemistries can often give results surpassing those previously achieved using solvents. Ultrasonics is not a technology of the future -- it is very much a technology of today.

BLASTING MEDIA

Dry ice cleaning pellets are larger, and less dense than alternative grit blasting mediums. In addition, they are ductile and do not share the same molecular structure as their predecessors. Unlike their counterparts, the qualities of dry ice may be modified during production to better mate the cleaning pellet to the application. This ability to alter the physical characteristics of dry ice during the ice production or cleaning step enables the abrasive CO_2 cleaning process to compete in applications that were previously the sole domain of chemical solvent cleaning systems. Due to the meta-stable nature of dry ice, the problem of transportation of cleaning pellets to the work site is a primary concern of CO_2 cleaning equipment manufacturers.

The size of dry ice pellets best suited for use in CO_2 cleaning systems are 0.125 inch diameter, or less. However, unless special sizing equipment is incorporated within the pellet production equipment, the length of the extruded pellet will be proportional to its density. Currently, this length may range from 3/16 of an inch, to well over 6 inches. The suggested pellet length used in dry ice blasting equipment (to assure a reliable, steady, uninterrupted flow of pellets from the storage hopper to the insertion mechanism) is approximately 1/2 inch or less. Here smaller is definitely better. The minimum size should depend upon the application, with regard to the potential for substrate damage, and the nature of the coating being removed. Normal pellet production, storage, and handling will reduce the pellet length to this value. Furthermore, mechanical insertion into the propellant stream, the subsequent transport, (and accompanying sublimation) and acceleration processes will reduce the pellet length to a maximum of 0.125 inch at the target surface.

Tomco Equipment Company's High Density Pelletizers (HP equipment designation) extrude dry ice pellets in density ranges from 42 Lbm/F^3 to approximately 55 Lbm/F^3 for use in CO_2 cleaning systems. For comparison, the density range of dry sand is 90 - 105 Lbm/F^3. This lower density of dry ice cleaning pellets is significant in that dry ice cleaning systems will exhibit less overall cleaning energy density at the work surface for the same particle and propellant velocities than those using smaller, sharper, grit-blasting media. Also different are the fracture mechanics of dry ice. Most currently used grit blasting media are silicon dioxide based, which possess a sharp tetrahedral molecular structure. These tiny, extremely hard substances ($E=45 \times 10^6$ PSI) will always break into smaller sharp-edged replicas of the original grain. The softer dry ice pellets do not produce the same sharp-edged crystalline structures as their non-sublimable counterparts when broken. Upon contact with the target surface, the dry ice pellets will plastically deform and break apart. Any particle remnants left over from this collision will be repelled from the work surface by the gaseous forces from the propellant and the sublimating dry ice. Thus dry ice cleaning does not share the same potential for subsurface erosion (substrate etching) as alternative, grit-blasting systems. This enables CO_2 cleaning to be used in sensitive substrate applications.

Tomco Equipment Company is preparing to research the effects of dry ice cleaning pellet size, shape, density and mass flow rate on cleaning rate and efficiency. To make this data relevant (and widen the application base for this cleaning technology) these rates must be referenced to surface coatings and substrates. This requires the assistance of industries interested in gaining from advances in CO_2 cleaning technology. It is reasonable to expect that blasting times in certain applications may be shortened with the use of smaller, more dense pellets dispersed over a given nozzle exit area. This is due to a smaller pellet's superior ability to penetrate coating grain boundaries. Smaller, irregularly shaped pellets should also possess sharper crystalline points than their larger counterparts, further enhancing cleaning rates.

Transportation of dry ice cleaning pellets over long distances tends to settle and compact the pellets into a large block. Any block or clumping of pellets must be broken up into free flowing pellets prior to use, and this separation process creates "fines". (Fines are 1-2mm sized dry ice particles.) These miniature particles will completely sublime within the delivery hose. Consequently, their mass can not be counted on for cleaning. Smaller pellets suffer more deterioration from settling and separation. For this

reason, Tomco believes that it is more desirable to include a device within the blast apparatus for reducing pellet size to that required in a specific cleaning application if the size required is less than 0.125 inch diameter. Currently, several low cost, prototype pellet sizing designs are being tested.

PROPELLANT SYSTEMS

A CO_2 cleaning system utilizes a pressurized gas stream, under controlled expansion to the local surrounding environmental pressure, to accelerate the sublimable media pellets to cleaning velocities. The two propellants primarily used in dry ice blasters are compressed air and nitrogen. (Standard compressed air and nitrogen propellant supply systems are illustrated in Appendix B, Figures 1 & 2 at the end of this report. The equipment comprising either propellant system is largely contingent upon the application, its location and level of aggressiveness necessary to perform in that application.) Typically, the pressurized gas stream must exceed local surrounding pressure by a minimum of 100 PSIG. The volume of propellant used by any CO_2 cleaning system will be a function of the nozzle configuration (See Acceleration Nozzles), the molecular weight and the density of the carrier gas at the nozzle restriction.

Naturally, the pellet exit velocity (and thus cleaning capacity) is a function of the available propellant energy as well as the particle ballistics including: size, specific weight and any translation or tri-axial rotation. Using a ballistic chronograph, the dry ice pellet velocity from the DI-250 blaster operating on compressed air at 175 PSIG, 75°F and 40° pressure dew point has been measured. Due to the combined effects of non-uniform pellet size, 3-dimensional translation and tri-axial rotation of the pellets within the delivery hose and nozzle, the pellet velocities range from 350 to 550 feet per second. Clay target impregnation testing corroborated the wide dry ice particle energy range suggested by the 200 foot per second fluctuation in measured velocity.

The densities of compressed air and nitrogen throughout the operating pressure range of most currently available CO_2 cleaning systems differs by approximately 3.5%. Therefore, as has been confirmed by testing, a similar difference in volumetric flow rates between the two gasses will be encountered, given the same temperature, pressure and nozzle orifice diameter. The propellant properties having the greatest effect on cleaning pellet velocity are its pressure and the temperature. Tomco Equipment Company has produced a Nitrogen versus Air Propellant Report. In this report, the effects of variations in these properties on propellant consumption are investigated (as they relate to dry ice cleaning with the Tomco, DI-250 blast unit) in addition to providing readers with alternative system component configurations, specifications and general CO_2 cleaning information.

In most dry ice cleaning systems there is a temperature differential between the dry ice, which is usually manufactured and transported at atmospheric pressure, and the propellant gas. The dry ice temperature will be -109.33°F, and the propellant gas will usually be close to ambient temperature. The effects of propellant pressure and temperature on dry ice pellet sublimation rates within single hose blasting equipment has been investigated. As expected, higher propellant gas temperatures and longer delivery hoses will increase the mass of dry ice lost to sublimation within the hose. Losses of 100% are possible in some circumstances. As long as the propellant temperature is greater than -109.33°F, a quantity of dry ice will sublime in the delivery hose.

Testing results on the DI-250 (See Appendix A) show that the propellant and dry ice mixture temperature, as measured at the acceleration nozzle, got colder as the pressure was decreased. This indicated an increase in pellet sublimation within the delivery hose as the pressure decreased. Because the transport hose diameter was unchanged, this increase was attributed to the longer time the pellets were in the delivery hose at the lower pressures.

FIGURE 1: LIQUID NITROGEN PROPELLANT DELIVERY SYSTEM

LOCATIONS:

① LIN STORAGE - DAY TANK
② LIN DOWNSTREAM OF REGULATOR
③ GN2 OUT OF VAPORIZER
④ GN2 DOWNSTREAM OF OPTIONAL TEMPERATURE CONTROL POINT

☐ ☐ =NOT REQUIRED FOR SYSTEM OPERATION

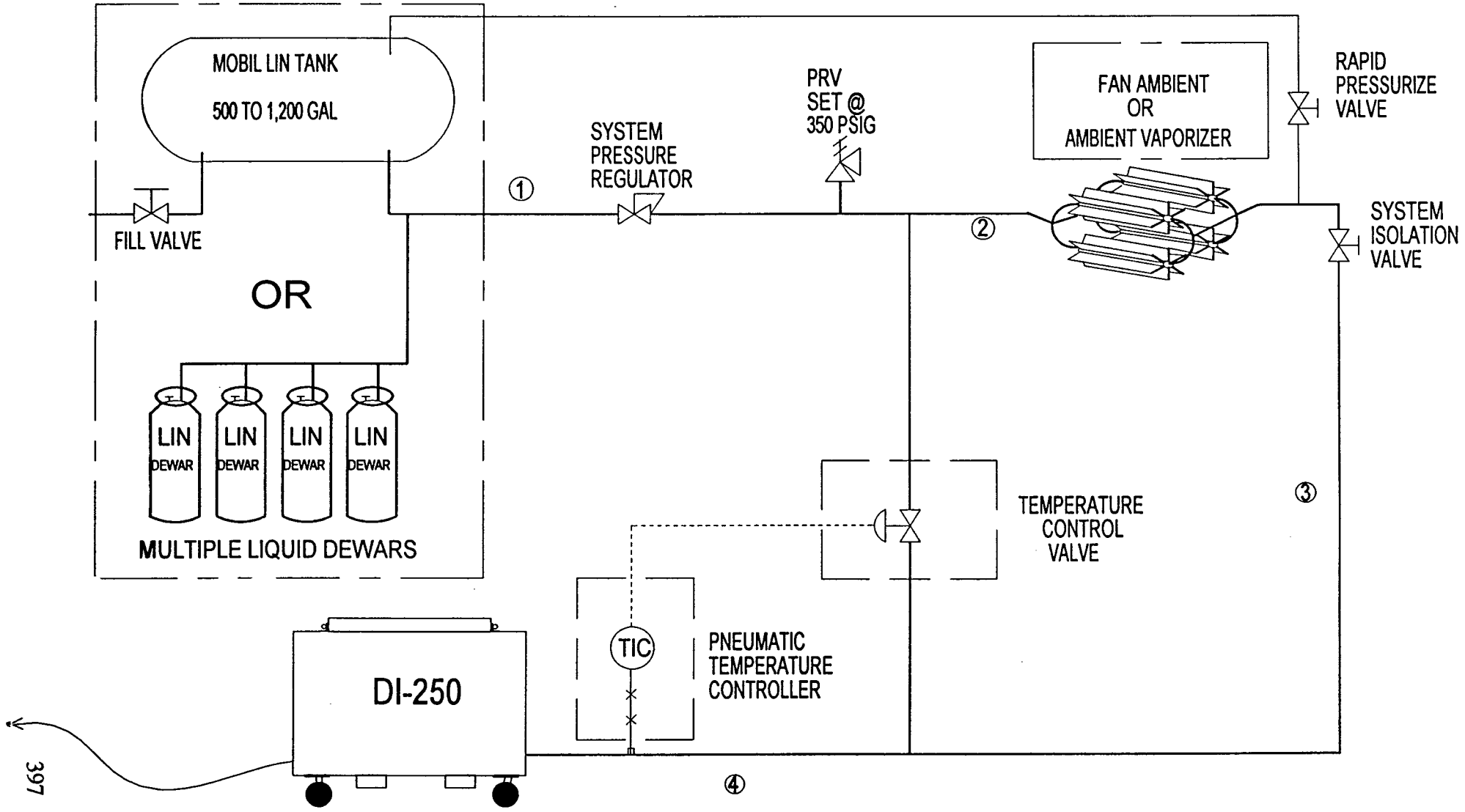
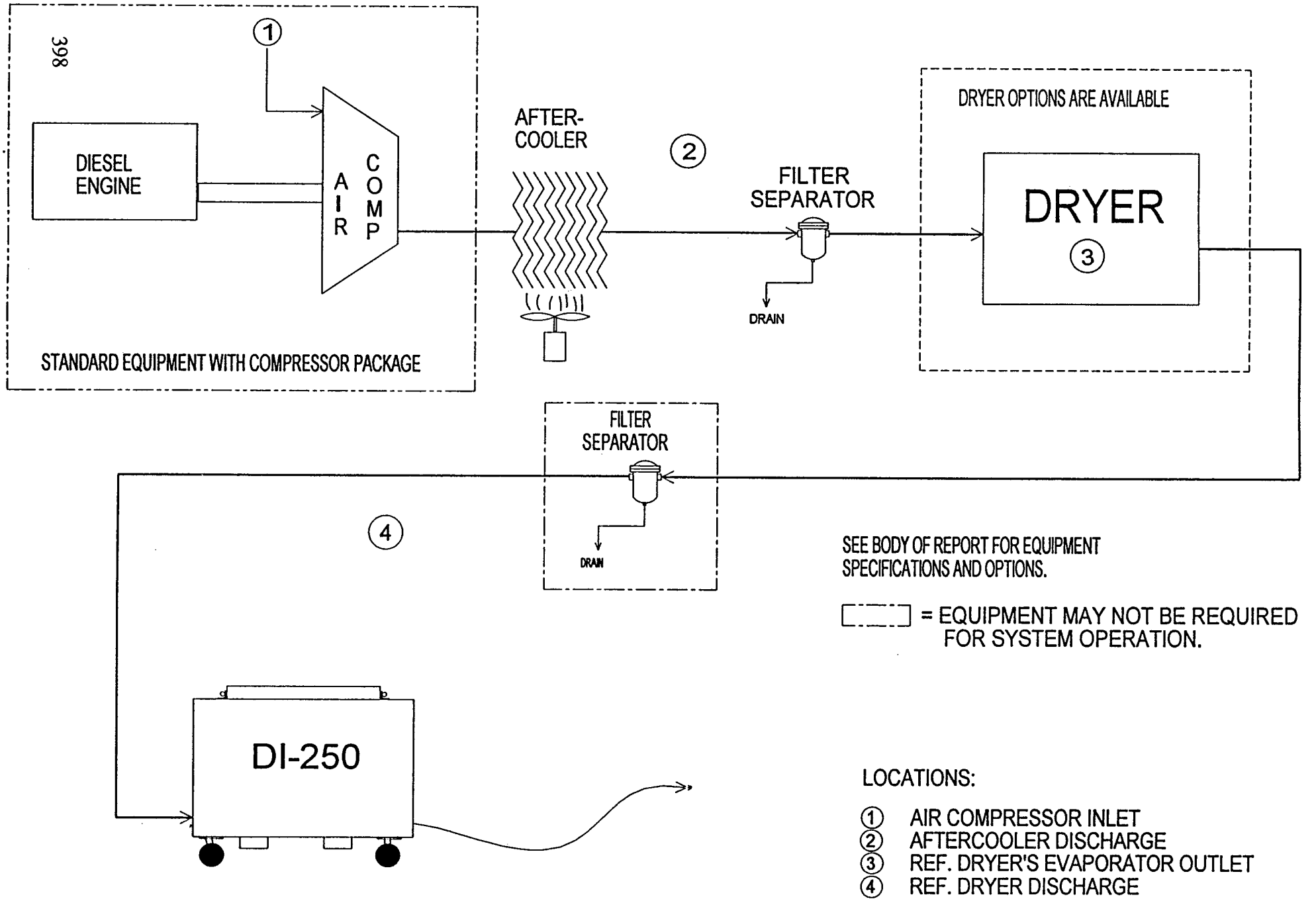


FIGURE 2: COMPRESSED AIR DELIVERY SYSTEM



A MICROWAVE PLASMA CLEANING APPARATUS

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Abstract

In a microwave electron cyclotron resonance plasma source, reactive plasmas of oxygen and its mixtures of argon have been used for evaluating plasma cleaning technologies. Small aluminum samples (0.95 × 1.9 cm) were coated with thin films (≤ 20 μm in thickness) of Shell Vitrea oil and cleaned with reactive plasmas. The discharge parameters, such as gas pressure, magnetic field, substrate biasing, and microwave power, were varied to change cleaning conditions. A mass spectroscopy (or residual gas analyzer) was used to monitor the status of plasma cleaning. Mass loss of the samples after plasma cleaning was measured to estimate cleaning rates. Measured cleaning rates of low-pressure (0.5-mtorr) argon/oxygen plasmas were as high as 2.7 μm/min. X-ray photoelectron spectroscopy was used to determine cleanliness of the sample surfaces. In this paper, significant results of the plasma cleaning are reported and discussed.

I. INTRODUCTION

Plasma surface cleaning has been widely used to clean surfaces in fusion energy research, in high-energy accelerators, and in materials processing (Refs. **1-4**). This cleaning method utilizes radical species generated in reactive gas discharges to remove surface contaminants. The energetic species in these discharges consist of photons, electrons, ions, and reactive neutral species. Physically, these energetic particles attack surfaces to cause sputtering, thermal evaporation, or photodecomposition. Chemically, these energetic particles dissipate their energy to raise surface temperatures and greatly enhance chemical reactions. These impinging particles are generally very hot; for example, 1 eV of energy equivalent to a temperature of ~ 11,600 K. Thus, the hot plasma particles have higher rates of surface cleaning than those of thermal reactive gas particles.

It is well known that reactive oxygen plasmas are very effective for removing organic contaminants from surfaces. Recently, we developed a microwave electron cyclotron resonance (ECR) plasma source to generate reactive species of oxygen for plasma etching on silicon wafers (**5**). The plasma density and its distribution could be varied by the source parameters including source magnetic fields, sample bias potentials, and gas pressures. Typical low-pressure (≤ 1-mtorr) discharges can produce uniform plasmas having electron densities of ~1×10^{11} cm^{-3} and electron temperatures of 2 to 5 eV. Using this source, we have prepared a microwave plasma cleaning apparatus for removing organic contaminants (**6**). By controlling gas pressure, applied power, and other discharge parameters of this apparatus, we have evaluated plasma cleaning technologies for performing damage-free cleaning on oil film contaminated surfaces of finished workpieces. Such plasma cleaning technologies are being developed for replacing conventional solvent cleaning. In this paper, we describe the plasma cleaning apparatus, and preliminary results of plasma cleaning on small samples coated with a thin oil film. The significant results using reactive plasmas of oxygen and argon/oxygen mixture are then further discussed.

II. PLASMA CLEANING APPARATUS

Figure 1 shows main components of the microwave plasma cleaning apparatus being used for evaluating advanced cleaning technologies. These components are the microwave plasma source, a vacuum chamber, and a turbomolecular pump. The vacuum chamber is mounted under a supporting frame. The microwave plasma source is mounted on the top of the vacuum chamber. The turbomolecular pump is installed beside the vacuum chamber and has a pumping speed of ~ 400 L/s for air. Installed in the vacuum chamber is an rf feedthrough on which a sample holder is fastened. The sample holder is at the down stream end of the plasma source. The source pressure is measured by a capacitance manometer (MKS Baratron Type 170M-6C) on the top flange of the source, and the pressure in the vacuum chamber is measured by an ionization gauge on the side port. Achievable base pressures are often below 1×10^{-6} torr. A throughput control valve on the turbomolecular pump regulates the pumping speed. The working gas is fed continuously into the plasma source, and the gas flow rate is measured by a flowmeter. Both the pumping speed and the flow rate are used to adjust the source pressure.

Other supporting equipment (not shown in Fig. 1) are electrical supplies, electronics equipment, and a water-cooling system. The outputs of these supplies are adjustable. The 1500-W microwave (2.45-GHz) supply is used for creating plasmas. The 200-W radio frequency (rf, 13.56-MHz) supply is used to provide a negative bias potential to the sample holder. Sometimes, the 400-V dc supply is used for providing a negative bias potential. Two low-voltage supplies (respectively rated at 500 and 40 A) are used to provide exciting currents to a source coil (or magnet) and an enhancing magnet for controlling plasma properties and cleaning conditions.

Both the bias potential of the sample holder and the enhancing magnetic field can provide a flexibility in controlling plasma density distributions (**5, 6**). The plasma density adjacent to the sample holder tends to be higher for the case with the negative bias potential and lower for the positive bias holder. However, when the source coil and the enhancing magnet have the opposite polarity, the magnetic cusp fields so formed can improve confinement of plasma particles. Thus, the plasma density and uniformity do not vary significantly with the bias potential of the sample holder. With the flexibility of varying plasma density and ion energy, this plasma cleaning apparatus is suitable for evaluating plasma cleaning technologies.

III. PLASMA CLEANING

III.1 Sample Preparation

Plasma cleaning technologies have been evaluated by using reactive plasmas of pure oxygen and/or mixtures with argon to remove oil films on small test samples (0.95×1.91 cm) made of aluminum 6061. Each test sample was prepared by cleaning the top surfaces with alcohol spray, drying with an air jet, and then coating with a thin film of Shell Vitrea oil. Some bare samples were polished to achieve a mirror surface (~ 0.5-μm flatness) and then ultrasonically cleaned. The mass of the oil film on each test sample was measured by weighing the sample before and after oil coating. With a density of 865 mg/cm^3, the typical thickness of a 1-mg oil film is ~ 6 μm. The test sample with oil film was then placed on the center of the sample holder for plasma cleaning.

III.2 Operating Conditions

The plasma cleanings were conducted by using pulsed microwave plasmas while the working gas was fed continuously. The pulsed microwave plasmas were usually created by applying both a pulsed exciting current to the source coil and a pulsed microwave power to the plasma source simultaneously. The nominal pulse width was set to be 1 s at a duty factor of 10%. The pulsed rf power was adjusted to provide a desired negative bias potential to the sample. During plasma cleaning, the current density of the plasma was measured by using a Langmuir probe. Other operating parameters—such as gas pressure, gas flow rate,

microwave power, magnet current, sample-bias potential, and operating time (or accumulated plasma exposure time)—were also recorded. Signal amplitude changes of carbon monoxide (CO) of a mass spectrometer, a UTI Model 100C residual gas analyzer (RGA), were recorded for each sample being plasma cleaned. After plasma cleaning, the mass loss of each sample was measured. Subsequently, test sample surfaces were studied for cleanliness by using X-ray photoelectron spectroscopy (XPS) analysis.

III.3 Preliminary Results

We have conducted a plasma cleaning study on 56 small samples (6). Preliminary results reveal that the microwave plasma cleaning works well for samples coated with oil films with thickness approaching 20 μm. The reactive plasmas of oxygen or oxygen/argon were created in low-pressure (ranging from 0.3- to 5-mtorr) microwave discharges. During plasma cleaning, the samples were biased negatively either by using the rf or the dc supply. Table 1 lists some cleaning parameters for 11 plasma-cleaned samples, part of the 56 samples. The column "oil mass" is the mass of oil film coated on sample surfaces, and the column "mass loss" is the mass removed by the plasma cleaning. The estimated film removed during the operating (plasma-on) time is used to calculate the average cleaning rate. Significant results of these 11 samples are summarized below.

1. The first six samples with a negative dc bias potential ranging from 0 to 100 V were cleaned by oxygen plasmas at a source pressure of ~ 0.5 mtorr. The surfaces of sample 92-51 with –100-V biasing were cleaned but damaged with etched spots.

2. The last five samples were cleaned by oxygen plasmas at a source pressure of 5 mtorr. Samples 92-73 and -74 (with negative dc bias) were not completely cleaned. Instead, the residue of oil films became plastic materials. However, oil films of the last three samples with negative rf bias were cleaned up. No visual residue on the sample surfaces was observed.

These features imply that energy and flux of plasma ions can play a dominant role in the plasma cleaning. The reactive oxygen plasmas created in low-pressure (0.5-mtorr) discharges were found to be very effective in cleaning samples coated thin oil films, as described in item 1 above. With a negatively biasing (dc or rf) potential to the sample, plasma ions can be accelerated to high energies. Such energetic ion bombardment on sample surfaces enhances chemical reactions between hydrocarbon molecules and plasma particles, leading to decomposition and vaporization of the oil film in the form of a volatile gas effluent. Plasma cleaning rate increases with the current density and the energy of impinging ions, which increases proportional with the negative bias potential. Thus, the average cleaning rate increases with the rf bias potential as shown in Fig. 2.

However, the different effects of dc and rf biasing as mentioned in item 2 above may be influenced by insulated particles produced in plasmas. Oxygen plasmas at 5 mtorr may produce some insulated particles and deposit them on the sample surfaces. In this case, owing to the dielectric property of these particles, the applied dc voltage cannot establish an electric field in the plasma sheath to accelerate ions. This will lower kinetic energy of ions and slow down plasma cleaning rates. Consequently, the oxygen plasmas cannot clean up oil films on Samples 92-73 and -74 that were dc biased. But, the insulated particles cannot prevent the applied rf voltage from establishing an electric field in the plasma sheath to accelerate plasma ions. Thus, the plasma ions impinge on the rf biased samples at an energy equivalent to the bias potential. Consequently, in Table 1, the last three samples with rf biasing were cleaned up at higher rates. Following the above discussions, we conclude that energetic ions in oxygen plasmas are the dominant reactive particles for cleaning surfaces with oil film contaminants.

III.4 RGA Signal

With oxygen plasma cleaning, the dominant species of the gaseous effluent measured by the mass spectrometer (or RGA) are H_2, O, OH, H_2O, CO, O_2, and CO_2. These volatile gas molecules are produced by chemical reactions of bombarding oxygen plasma particles and hydrocarbon molecules in the oil film on sample surfaces. One of the dominant effluent gas signals, carbon monoxide (CO), changes greatly during

each pulsed discharge. Figure 3 shows the amplitude changes of mass 28 peak of CO for a sample that has been cleaned under a sequence of pulsed discharges. At the beginning of the sequence, the amplitude of the mass 28 increased rapidly to a maximum, then decreased slowly. At the end of the sequence, the amplitude of the mass 28 decreased slightly during the pulsed discharge. For this type of plasma cleaning, the waveform of mass 28 (or CO) signal closely correlates to the cleanliness of the sample surfaces. Thus, the waveform of CO signal was used for recording the history of plasma cleaning and for indicating the end point of the cleaning (6).

III.5 XPS Analysis

To verify surface cleanliness of plasma cleaned samples, X-ray photoelectron spectroscopy (XPS) has been used. The XPS survey analyzes the surface composition of the top 40-Å surface layer. With a sample size of 9.5 × 19.1 mm, the 0.8-mm spot survey on a representative surface area to perform quantitative analysis of surface composition. The ratio of carbon-to-aluminum concentration measured by the XPS analysis is denoted by C/Al. In Table 1, the sample is considered clean if its value of C/Al ratio is below the average value of 1.15 that is measured for bare control samples. (Refer to the row "Control mean" in Table 2 .) Similarly, the oxide layer is thinned down by plasmas, if the value of O/Al ratio is below 3.34 of the bare control samples. In Table 1 the surfaces of unsuccessfully cleaned samples 92-73 and -74 have C/Al ratios to be 10's to 100's times higher than 1.15.

Table 2 shows the surface composition measured by the XPS analysis of three bare samples and their plasma-cleaned samples. The alloy composition of the bare samples is 98% Al, 0.8 to 1.2% Mg, 0.4 to 0.8% Si, 0.2% Cr, and 0.3% Cu. This table also lists the composition of analyzed bare samples as Control in the rows 92-50-CON, -72-CON, and -100-CON and their mean in the row "Control mean." The average composition of these control samples is 17.2% Al, 57.5% O, 19.8% C, 0% Mg, 0.7% Ca, 0.9% Si, 0% Cu, 0% Ag, 3.2% P, and 0% Cr. The average surface composition of plasma cleaned samples 92-50, -72, and -100 (or "Sample mean) listed is 22.1% Al, 48.6% O, 25.7% C, 1.9% Mg, 0.1% Ca, 0.4% Si, 0.6% Cu, 0.1% Ag, 0% P, and 0% Cr. Comparing the values in the rows "Sample mean," "Control mean," and "Bulk alloy," we highlight the following significant points.

1. The surface of these control samples was covered with a thin oxide layer with impurities of carbon and others. In fact, the XPS survey did not detect the elements Mg, Cu, and Cr of the bulk alloy.

2. The surfaces of plasma cleaned samples received fewer impurities than those of the control bare samples. For example, compared to its own control bare sample, the plasma cleaned samples 92 50, -72, and -100 had higher Al atomic concentration, lower O/Al ratio, and lower C/Al ratio (except Sample 92-100).

3. The great decrease of impurities Ca, Si, and P on plasma cleaned samples indicated that the impurities on the bare-sample surfaces were removed by oxygen plasmas. The presence of magnesium on the plasma cleaned samples indicated that the surface layer was partially removed.

VI. CONCLUSIONS

Preliminary results reveal that reactive plasma cleaning using a microwave ECR source works well for test samples coated with Shell Vitrea oil films with thicknesses approaching 20 μm. In low-pressure (ranging from 0.3- to 5-mtorr) discharges, reactive plasmas have been created and powered by microwave energies. The fifty-six small, flat aluminum samples have been plasma cleaned, and their surface cleanliness has been confirmed by the XPS. Significant results are summarized below (6).

1. The dominant cleaning particles in oxygen and argon/oxygen plasmas are energetic ions.

2. Argon/oxygen plasmas have cleaning rates 2 to 3 times higher than those of oxygen plasmas.

3. The cleaning rates of oxygen/30%-argon plasmas can be as high as 2.7 μm/min.

4. For thick oil films (~ 20 μm), only samples with rf biasing can be effectively cleaned in high-pressure (~ 5-mtorr oxygen) plasmas, but samples with dc biasing cannot.

5. Samples with –200-V rf biasing can be cleaned without etch damage, but samples with –75-V dc biasing tend to have etch damage on sample surfaces.

6. The XPS analysis for measuring relative concentration of aluminum, carbon, and oxygen on sample surfaces confirmed that the surfaces of plasma cleaned samples can be cleaner than the surfaces of control bare samples.

VII. ACKNOWLEDGMENTS

The authors would like to thank their colleagues who helped with this project, particularly V. B. Campbell, H. H. Haselton, and W. L. Stirling for their valuable discussion; B. E. Argo and G. C. Barber for their technical support on keeping electrical and electronic equipment functional at the facility; and J. E. Simpkins for his advice on the use of a residual gas analyzer.

VIII. REFERENCES

1. Asmussen, J., "Electron cyclotron resonance microwave discharges for etching and thin film deposition," in *Handbook of Plasma Processing Technology*, edited by S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood (Noyes Publication, 1990), Chap. 11.

2. Coburn, J. W., "Surface processing with partially ionized plasmas," IEEE Trans. on Plasma Science **19** (6), 1048–1062 (1991).

3. Dylla, H. F., "Glow discharge techniques for conditioning high-vacuum systems," J. Vac. Sci. Technol. A **6** (3), 1276–1287 (1988).

4. Shmayda, W. and Antoniazzi, A., "Tritium decontamination—plasma driven decontamination technique," Canadian Fusion Fuels Technology Project Journal **8** (3), ISSN 0847–9437, May 1992.

5. Tsai, C. C. et al., "Potential applications of an electron cyclotron resonance multicusp plasma source," J. Vac. Sci. Technol. A **8** (3), 2900–2903 (1990); and Tsai, C. C. "Potential applications of a new microwave electron cyclotron resonance multicusp plasma source," Nucl. Instr. and Methods in Physics Research B **56/57**, 1166–1170 (1991).

6. Tsai, C. C. et al., Plasma Surface Cleaning in a Microwave Plasma Source, ORNL/TM-12495, March 1994.

Table 1. Oxygen plasma cleaning on aluminum samples coated with thin oil films

Sample	Oil mass	Mass loss	Bias potential	Surface feature	Remarks	C/Al	O/Al
	mo (mg)	m' (mg)	Vsh (V)			1.15	3.34
#92-50	0.8	0.8	-50	Clean	DC	0.75	2.34
#92-51	1.0	1.2	-100	Clean / Etched	DC	0.85	2.62
#92-57	0.9	0.9	0	Clean / Gold	DC	0.71	2.47
#92-96	0.9	0.7	-50	Clean	DC	0.74	2.76
#92-70	1.1	1.1	-75	Clean	DC	0.99	2.35
#92-72	0.9	0.8	-25	Clean with spots	DC	1.10	2.18
#92-73	1.0	0.6	-50	Etched, not clean	DC	340.33	21.33
#92-74	1.0	0.4	-25	Plastic drops	DC	109.72	8.44
#92-82	1.1	0.9	-25	Clean	RF	0.99	1.81
#92-84	1.1	1.0	-50	Clean, etched trees	RF	1.26	2.11
#92-100	1.3	1.3	-40	Clean	RF	1.91	2.04

Table 2. Surface composition of test samples in percentage											
					Elements						
Sample	Al	O	C	Mg	Ca	Si	Cu	Ag	P	Cr	N
92-50-CON	18.05	58.27	18.98	0.00	0.40	0.79	0.00	0.00	3.50	0.00	0.00
92-50	23.55	55.18	17.56	3.53	0.00	0.00	0.00	0.00	0.00	0.00	0.18
92-72-CON	16.23	55.35	21.61	0.00	1.17	0.68	0.00	0.00	3.11	0.00	1.84
92-72	22.72	49.57	24.97	0.91	0.29	0.67	0.00	0.00	0.00	0.00	0.87
92-100-CON	17.39	58.92	18.70	0.00	0.53	1.08	0.00	0.00	3.06	0.00	0.31
92-100	20.06	40.98	34.71	1.27	0.00	0.37	1.75	0.30	0.00	0.00	0.55
Sample mean	22.11	48.58	25.75	1.90	0.10	0.35	0.58	0.10	0.00	0.00	0.53
Control mean	17.22	57.51	19.76	0.00	0.70	0.85	0.00	0.00	3.22	0.00	0.72
Bulk alloy	97.90	0.00	0.00	1.00	0.00	0.60	0.28	0.00	0.00	0.25	0.00

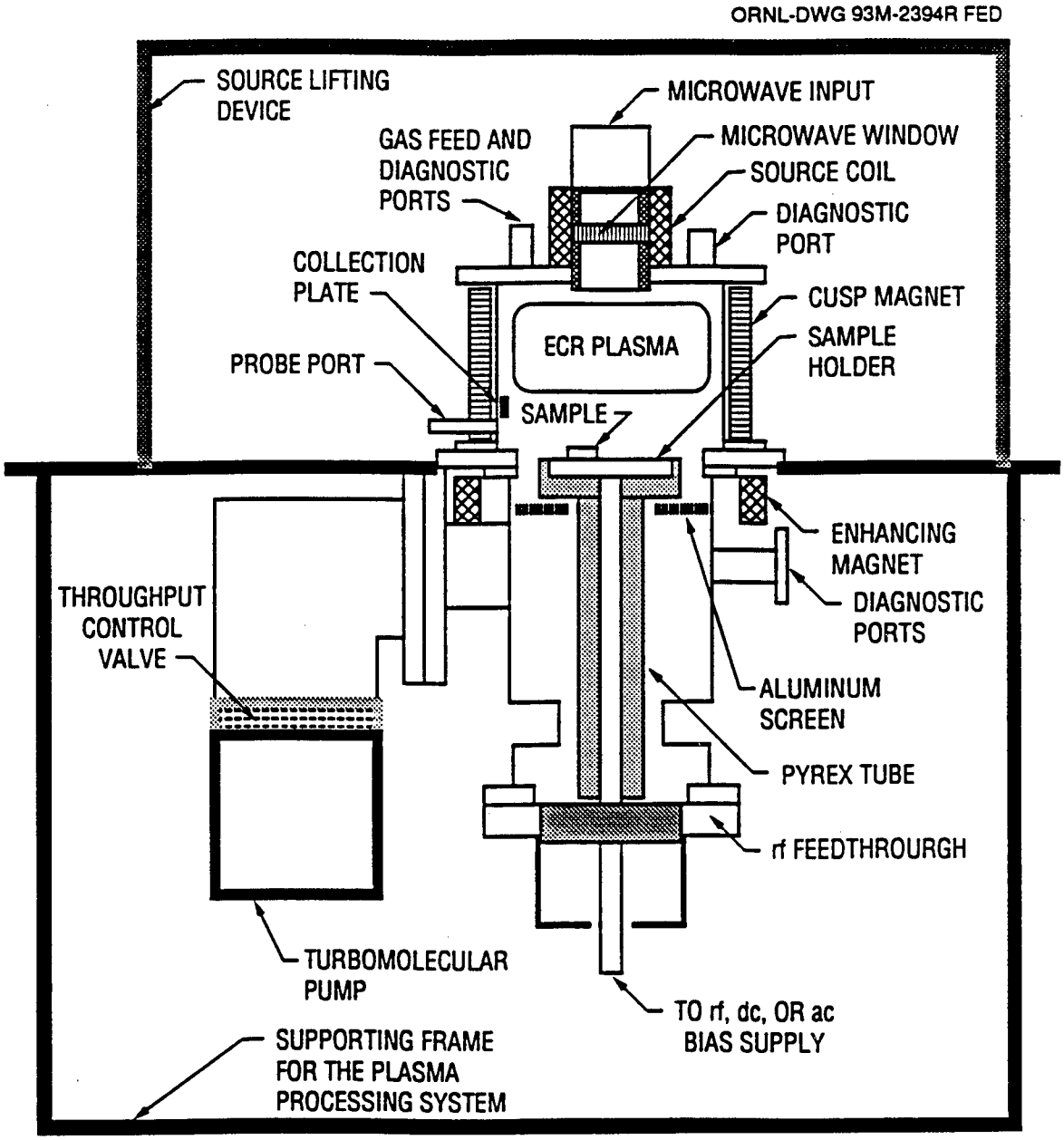

Fig. 1. A plasma cleaning apparatus including a plasma source, sample holder, vacuum chamber, and vacuum system.

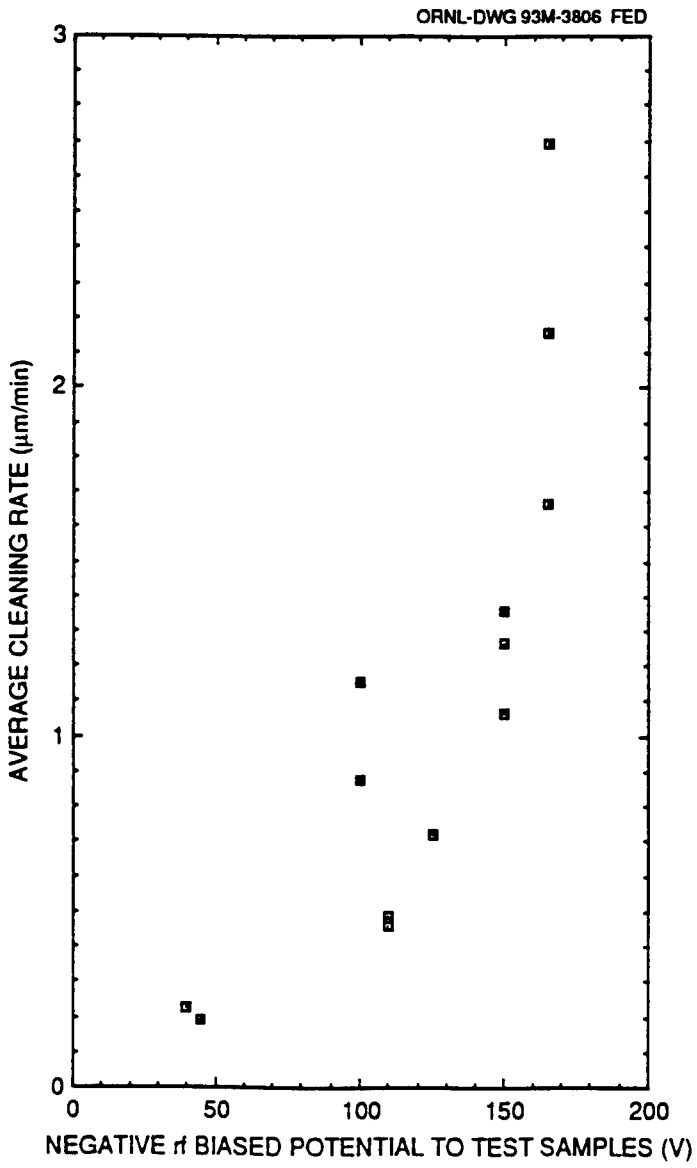

Fig. 2. The change of average cleaning rate as a function of rf bias potential to the sample holder.

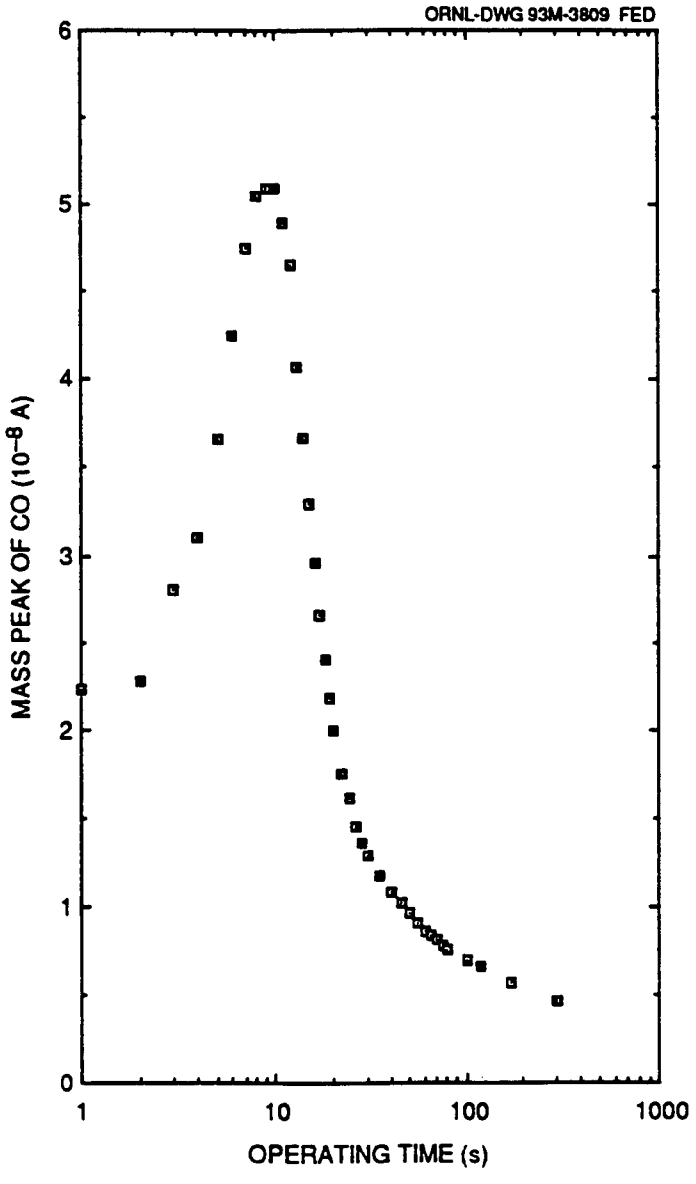

Fig. 3. Signal changes of mass peak of CO (28 amu) during oxygen plasma cleaning with a test sample.

NON-CFC CLEANING SOLVENTS, PROCESSES AND PARAMETERS 1

AQUEOUS CLEANING AND VERIFICATION PROCESSES FOR PRECISION CLEANING OF SMALL PARTS

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ABSTRACT

The National Aeronautics and Space Administration (NASA), Kennedy Space Center (KSC) Materials Science Laboratory (MSL) has developed a totally aqueous process for precision cleaning and verification of small components. In 1990 the Precision Cleaning Facility at KSC used approximately 228,000 kg (500,000 lbs) of chlorofluorocarbon (CFC) 113 in the cleaning operations. It is estimated that current CFC 113 usage has been reduced by 75% and it is projected that a 90% reduction will be achieved by the end of calendar year 1994.

The cleaning process developed utilizes aqueous degreasers, aqueous surfactants, and ultrasonics in the cleaning operation and an aqueous surfactant, ultrasonics, and Total Organic Carbon Analyzer (TOCA) in the nonvolatile residue (NVR) and particulate analysis for verification of cleanliness. The cleaning and verification process will be presented in its entirety, with comparison to the CFC 113 cleaning and verification process, including economic and labor costs/savings.

INTRODUCTION

In 1991, NASA set forth a mandate to begin the reduction and eventual phase-out of all use of CFCs at their centers by the year 1995. Precision cleaning and surface wipe down accounts for approximately 80% of CFC use at KSC, Florida and is considered an integral player in the processing of shuttle hardware and ground support equipment.

The Component Refurbishment and Chemical Analysis Laboratory (CRCA) located at KSC supplies decontamination, cleaning, and refurbishment services to most all the direct NASA contractors at the center. The CRCA is a high volume precision cleaning facility which receives approximately 120 work tasks per day. These work tasks represent configurations ranging from the smallest nut or screw to the largest 18" pneumatically controlled butterfly valve. The components, as they process through the facility, are reduced to their smallest piece part and represent over 11,000 individual pieces per day or approximately 250,000 piece parts a month.

The NASA Materials Science Laboratory and Wiltech of Florida Corp., Inc., the contractor which operates the KSC CRCA facility, have been working together to implement a total aqueous process for precision cleaning and verification of small parts as an alternative to the current CFC 113 precision cleaning process used to clean aerospace hardware. It is believed that aqueous cleaning, if controlled and managed correctly, is the most desirable process to use. It is non-toxic, non-flammable, recyclable, and inexpensive.

ROUGH CLEANING

Components or hardware to be precision cleaned are brought to the CRCA by the many contractor customers at KSC in support of an array of aerospace support and launch activities. The components, when received from the customer, are routed to the rough clean and disassembly areas. They are reduced to the smallest piece part possible and readied for surface degreasing. Degreasing is the first step of the cleaning process. It is considered by many to be the most important use of CFC 113 in the precision cleaning process at CRCA. All fluorocarbon and hydrocarbon greases and oil films must be removed prior to chemical conditioning. Any oil or grease contamination could block the chemical surface conditioning and ultimately be suspect as the source of failure during the NVR analysis, (Kennedy, 1994).

The degreasing step of the CRCA rough cleaning process is shown in the flow process diagram of Figure 1. The degreasing process lowers parts into a typical vapor degreaser using CFC 113 as the degreasing medium as shown in Figure 2.

Figure 1
Rough Cleaning Flow Process

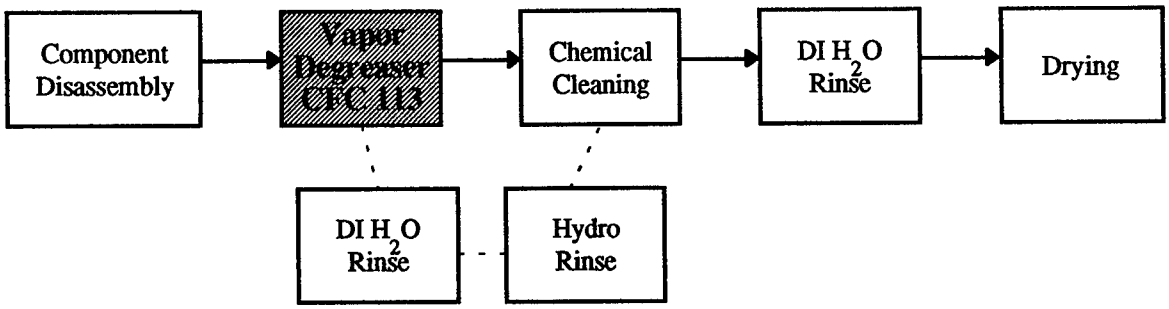
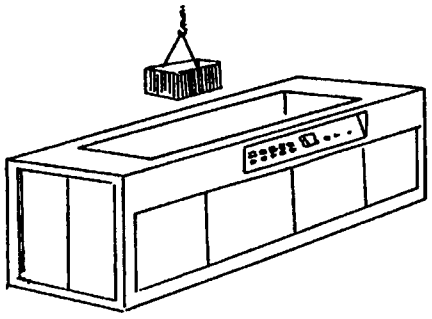


Figure 2
Equipment and Solvent Specifications are:



Tank Size:	132" x 6"
Solvent Volume:	210 Gallons
Solvent:	CFC 113
Work Area:	125" x 30"
Temperature of Solvent:	110 ± 5 °F
Condensing Coil Medium:	Chilled Water

The parts remain in the solvent vapor until their surface temperature stabilizes at 110 ± 5 °F, or approximately ten minutes. Any stubborn contaminants are removed by dispersing the solvent through a pumping system and directing it to the part.

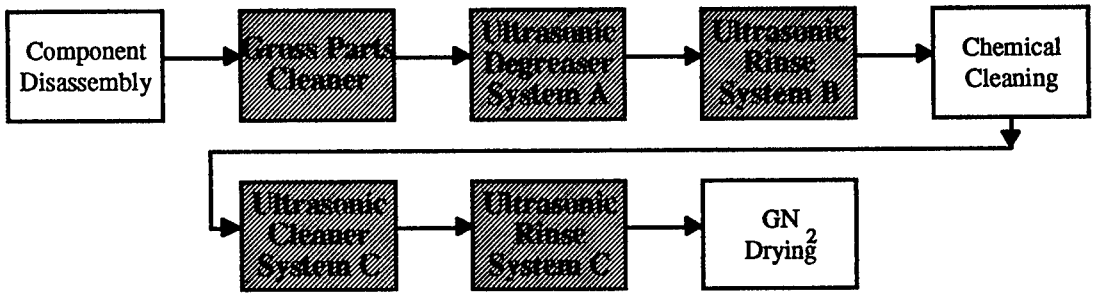
Often, after the parts where removed from the vapor degreaser, inspection revealed that fluorocarbon grease contamination remained. To remove this contamination, the parts are either brushed using a soft bristle brush with a surfactant and water or washed using a hand held pressurized hydro-wash

wand. The removal of all visual contaminants on the parts prior to entry into the chemical cleaning process generally warrants a smooth flow through the remaining cleaning process.

To eliminate vapor degreasing and CFC 113 during the rough cleaning process, a system of equipment and nonionic aqueous surfactants has been developed and is currently being phased into daily production. This system employs several pieces of equipment using ultrasonics, high pressure, high volume aqueous agitation, GN_2 agitation and hand wand spraying, (Kennedy, 1994).

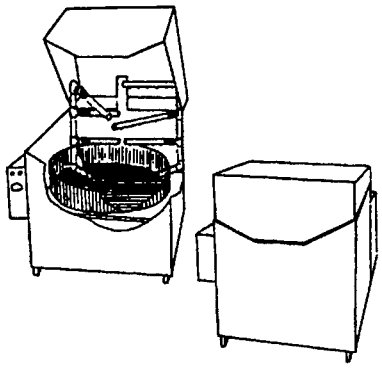
The aqueous degreasing steps of the rough cleaning process are shown in the flow process diagram of Figure 3.

Figure 3
Rough Cleaning Flow Process



Aqueous degreasing begins with gross cleaning parts washing shown in Figure 4. This parts washer is required to remove gross contamination prior to entering the primary process degreaser, System A. This equipment is top loading to provide the most efficient access possible for the various size parts and production personnel. An overhead hoist provides the lifting capability for parts weighing up to 200 lbs. Three tiers of spray manifolds are available for the many different sized parts. These various levels of spray manifolds are adjustable to accommodate the many different heights. In addition, a rotating turntable rotates the parts during the wash and rinse cycles at a rate of three revelations per minute resulting in approximately 95-100% contaminate removal efficiency.

Figure 4
Equipment and Solution Specifications

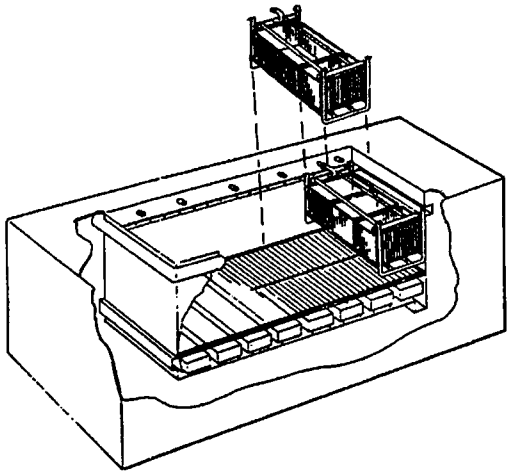


Equipment Foot Print:	4' x 4' x 6'
Work Access:	Top Loading
Tank Capacity:	30 Gallons
Surfactant:	Brulin 1990 GD @ 3%
Operating Temperature:	150 ± 10 °F
Functions:	Timer
Cycles:	Wash and Rinse
Operating Pressure:	400 ± 50 PSIG
Working Area:	3' x 3' x 3'

If inspection of the parts reveals a visual absence of contaminants, the parts are placed in the primary process degreaser, System A, shown in Figure 5. This degreaser is the main workhorse in removing contaminants that play a negative part in achieving precision clean hardware. It is a single tank

cabinetized ultrasonic cleaning system. The primary functions of the unit include: ultrasonic cleaning, agitation of parts, filtration of chemical solution, heating of cleaning solution, hand spraying of parts and GN_2 filter element processing. Ultrasonics, parts agitation and the nitrogen processing can be operated in an automated mode as well as manually. Parts processing for this unit is accomplished by the use of removable cradle fixtures which are supported inside the tank. The degreaser unit also contains a remote generator station for the ultrasonics.

Figure 5
Equipment and Solvent Specifications



Equipment Foot Print:	113" x 54" x 54"	Electrical:	480 VAC, 30, 60 Hz, 90 AMPS
Work Area:	65" x 36"		
Work Access:	Top Loading	Filtration:	• 5 Micron Absolute
Tank Capacity:	260 Gallons		• Cotton String
Surfactant:	Brulin 815 GD @		• Porous Bag
Operating Temperature:	150 ± 10 °F	Ultrasonic Power:	9600 Watts @ 27 KHz
Functions:	• Agitation		
	• Recirculation	Average Ultrasonic	
	• GN_2 Injection	Process Time:	10 Minutes
	• Ultrasonics		

In this equipment, the parts are placed into special agitation racks. These racks are support fixtures that position the parts approximately eight to ten inches from the ultrasonic devices. They provide upper and lower agitation spray manifolds to assist the removal of remaining contaminants. Once the contaminants are removed and into solution, they are circulated through the filtration system where they are removed to help maintain clean solutions. The control panel consists of four separate timed systems: 1) the agitation system, 2) the ultrasonic system, 3) the GN_2 injection system, and 4) the recirculation system.

At the end of the primary degreasing effort, the parts are immediately removed and placed into the primary process rinse, System B, shown in Figure 6. The primary process rinse is a two tank cabinetized ultrasonic rinse system. The first tank is a manually operated rinse spray water deluge tank. The second tank is a status rinse tank with the following functions: ultrasonic rinsing, agitation of parts, filtration of rinse water and hand spraying of parts. The ultrasonics as well as the agitation can be

verification process. KSC has concentrated on developing an aqueous NVR procedure that can be used for small component verification. The two major issues to resolve if water were to be used in a verification process was the method of removal of any remaining NVR and particulate from the components the technique to use to measure the NVR and particulate removed.

Ultrasonics has been well documented as a successful method for the removal of surface contamination, (Kuttruff, 1991). Extensive evaluations were conducted to determine its applicability to NVR removal. These included the effectiveness of removal of low level surface contamination by selected materials, optimum frequencies and temperatures to be used, and the potential effects of ultrasonic cavitation on metallic and nonmetallic surfaces, (Mehta, 1992). Extensive experimentation concluded that 25 kilohertz frequencies and 52 degree Celcius water temperature were the best combination for maximum NVR removal, (Bryan and Gebert-Thompson, 1992).

Several analytical techniques were evaluated and the Total Organic Carbon Analyzer (TOCA) was selected as the technique of choice for detection of NVR. Through experimentation it was determined that the Total Organic Carbon Analyzer (TOCA) was the easiest and most repeatable and reliable of all analytical methods evaluated.

The cleaned components are rinsed with deionized water and ultrasonicated at 25 kilohertz for five minutes in 52 degree Celsius deionized water. Two hundred microliters of the water are injected into a high temperature (880° C) combustion chamber and any carbon is converted to carbon dioxide using high purity oxygen. Carbon dioxide is then measured using an infrared detector, (Allen, 1994).

A relationship between milligrams of NVR per 0.09 m^2 of surface area to total carbon was formulated using:

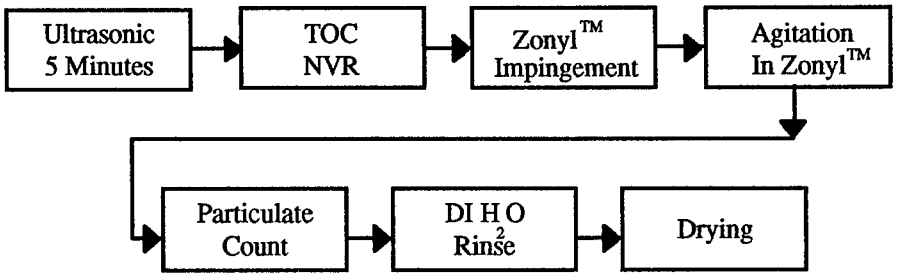
$$\frac{\text{mg NVR}}{0.09\ m^2} = \frac{(TC_s - TC_b)(\text{ml of water used})}{(m^2 \text{ in tank})(500\ \text{ml})(0.64\text{ppm/mg})}$$

where:
TC_s = Total carbon of sample
TC_b = Total carbon in water blank
500 ml = normalized value for TOCA sensitivity factor
0.64 ppm/mg = weighted average TOCA response to materials evaluated

The components are then analyzed for particulate using a 25 ppm mixture of Zonyl™ FSN and deionized water, (Clausen, 1994). Zonyl™ FSN is a nonionizing surfactant manufactured by Dupont. It is liquid oxygen (LOX) compatible and simply reduces the surface tension of water from 71 dynes per centimeter to approximately 34 dynes per centimeter. This allows complete wetting of the component surfaces and results in particulate analyses using the Zonyl™/water mixture which correlate well with the CFC 113 particulate analysis. The final step in the aqueous method of measuring particulate is similar to the CFC 113 method since the samples are agitated in the Zonyl™ water mixture and the mixture is then filtered through a gridded filter where the particulate retained on the filter pad is counted microscopically.

This aqueous system is in use at Kennedy Space Center and is working well. It has been noted that handling of the components through out the new process is much more critical than the CFC 113 process. The components must be completely clean prior to entering the clean room for verification and handled very carefully to avoid recontamination. In the prior process there was a final cleaning step after the components had been moved into the clean room. Figure 8 shows the sequence of the aqueous verification process.

Figure 8
Aqueous Verification Process



It has been estimated that the process time will be lengthened by about 35 percent to 45 percent. This is not contact time since most of the process time is in ultrasonics which does not have to be attended. It is felt that some of the ultrasonic times may be decreased as the process is further evaluated and improved. The process itself is extremely economical. Table 1 summarizes the costs involving the use CFC 113 as a cleaning and verification solvent and Table 2 shows the costs associated with the solvents utilized new aqueous process.

Table 1. CFC 113 Economic Analysis

Year	Cost per Pound	Usage (pounds)	Annual Costs
1984	$ 1.82	500,000	$ 910,000
1994	$ 8.75	500,000	$ 4,375,000
Current Consumption		50,000	$ 437,500

Table 2. Aqueous Process Economic Analysis

Product	Unit Cost	Annual Usage	Cost
Brulin	$ 12.00/gal	600 gal	$ 7,200
Zonyl ™ FSN	$ 25.00/lb	16 lb	$ 400
Breathing Air	$ 11.25/1000 SCF	300,000 SCF	$ 3,375
Water	$ 0.08/gal	2,000,000 gal	$ 160,000

CONCLUSION

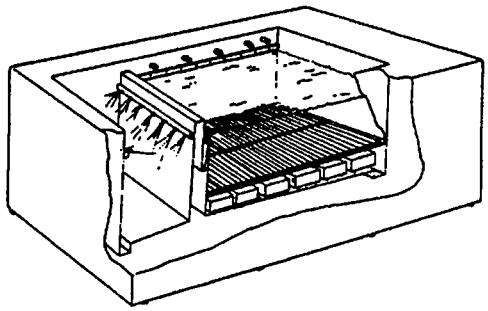
The NASA, Kennedy Space Center and Wiltech Corporation have developed a totally aqueous based process for the cleaning and verification of small components. These components can be either metallic or nonmetallic but are limited in size to and mass to 0.09^2 meters or approximately 1500 grams respectively. The new aqueous method does extend the overall process time but is very economical from a cost of materials standpoint. The verification technology is currently under evaluation for large components utilizing impingement via an air/water supersonic nozzle as the mechanical means for NVR removal.

ACKNOWLEDGEMENTS

The authors wish to recognize the Kennedy Integrated Team (KIT), I-NET Incorporated, Wiltech Corporation, the University of Central Florida, and the Kennedy Space Center Materials Science

operated manually or automatically. Parts processing for this unit is accomplished by the use of removable cradles fixtures which are supported inside the tank. The rinse unit also contains a remote generator station for the ultrasonics.

Figure 6
Equipment and Solution Specifications



Equipment Foot Print:	126" x 54" x 54"	Electrical:	480 VAC, 30, 60 Hz, 45 Amps
Work Area:	54" x 36" x 20"		
Work Access:	Top Loading	Filtration:	• 5 Micron Absolute
Tank Capacity:	205 Gallons		• Cotton String
Solution:	DI Water	Ultrasonic Power:	7200 Watts @ 40 KHz
Operating Temperature:	140 ± 10 °F		
Functions:	• Agitation	Average Ultrasonic Processing Time:	5 Minutes
	• Recirculation		
	• Ultrasonics		

As the parts are removed from the primary process degreaser, System A, they are immediately placed in a multi-manifold DI water spray rinse for approximately 30 seconds to remove any surfactant solutions from basket and parts. This is done to prevent any fast drying of contaminants when parts are removed from the previous 150 °F degreaser bath.

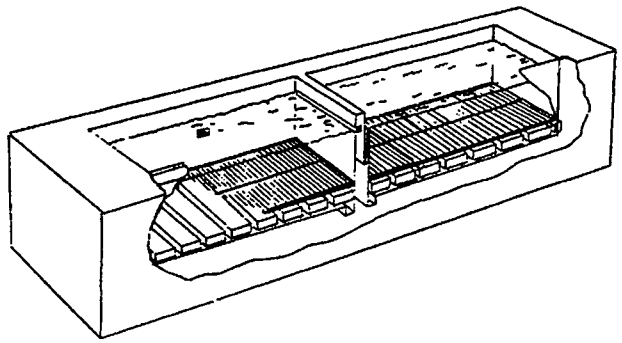
The parts are then placed in agitation racks like those installed in the primary process degreaser, System A. The parts are rinsed under agitation and ultrasonic conditions for five minutes.

Unlike the primary degreaser, fresh hot water enters the main tank through a five micron filter system and exits the tank over an open weir to drain.

The control panel is much like the primary process degreaser, System A, in that it consists of three separate timed systems: 1) the agitation system, 2) the ultrasonic system, and 3) the recirculation system.

The parts are removed from the primary process rinse, System B, and placed into one of the various chemical baths required for the various materials and their surface conditioning for removal of oxides and surface passivation. They are then rinsed with copious amounts of hot deionized water until a neutral pH between 6.0 - 8.0 is reached. Before the parts are allowed to dry, they are placed into the secondary process degreaser, System C, shown in Figure 7. This removes any contaminants received during the chemical cleaning baths.

Figure 7
Equipment and Solution Specifications



Equipment Foot Print:	138" x 44" x 48"	Electrical:	• 480 VAC, 30, 60 Hz, 70 Amps
Working Area:			
• Wash Tank:	78" x 28"	Filtration:	5 Micron Absolute
• Rinse Tank:	60" x 28"		• Cotton String
Work Access:	Top Loading		• Porous Bag
Tank Capacity:		Ultrasonic Power:	
• Wash Tank	160 Gallons	• Wash Tank:	4800 Watts @ 40 KHz
• Rinse Tank	120 Gallons	• Rinse Tank:	3600 Watts @ 40 KHz
Operating Temperature:	140 ± 10 °F	Average Ultrasonic	
Functions:	• Recirculation	Process Time:	
	• Ultrasonics	• Wash Tank:	5 Minutes
Surfactant:	Dupont Zonyl FSN	• Rinse Tank:	5 Minutes

The secondary process degreaser is a two tank cabinetized ultrasonic clean and rinse system. The cleaning tank functions include: ultrasonic cleaning, heating of solution, filtration of wash solution and hand spraying of parts. The rinse tank functions include: ultrasonic rinsing and an overflow rinse to drain. Ultrasonics in the wash rinse tanks can be operated in a timed cycle or in a manual mode.

In this final degreasing process, the parts are placed into a surfactant and deionized water bath. They are ultrasonicated for a period of five minutes and then placed immediately into the rinse tank and ultrasonically processed for five minutes. After the final rinse, the parts are removed and prepared for cleanroom entry for particulate validation and NVR verification.

VERIFICATION

The current methods for verifying cleanliness are a gravimetric procedure using CFC 113 to measure nonvolatile residue and microscopic particulate measurement using a gridded filter. Alternatives include other organic solvents such as HCFCs, spectroscopic surface examination, and water. Water was chosen as the desirable verification solvent. The major drawback to water has been the lack of an established procedure for NVR and the issue of drying components after completion of the cleaning and

The problem of pellet sublimation may be all but eliminated by lowering the propellant gas temperature to the dry ice temperature to eliminate the transfer of heat from the propellant gas to the cleaning pellets. This may be done by injecting cryogenic, gaseous nitrogen into the propellant supply line prior to the insertion of the cleaning pellets. However, operation at this low temperature will cost more, because a greater quantity of gas will be required to maintain both gas and pellet velocities. In addition, the Tomco machine uses a silicone rubber, pellet transport hose that would have to be replaced with a (less) flexible stainless hose due to the lower temperature.

BLASTING EQUIPMENT

The blasting equipment itself must be capable of storing a quantity of dry ice pellets that will allow operation over a period of time without excessive handling of the dry ice media. The duration of blasting between pellet refills will be dictated by the location, ambient conditions and by the cleaning operation itself. This is where Tomco and some of its competitors diverge in theory of operation. Tomco believes that it will benefit the cleaning industry in the long run to separate pellet production and blasting equipment. This separation keeps initial capital costs low by allowing small or occasional users to purchase blasting units only, without incorporating heavy, cumbersome, pellet extruding devices that require high voltage electrical inputs that make them very unwieldy. Occasional users may then purchase the cleaning pellets on an as needed basis from manufacturers near the cleaning location.

Beyond the pellet storage capacity, blasting equipment must include an apparatus for metering and delivering the flow of dry ice to the work surface. CO_2 Cleaning machines usually incorporate a means for operator control of the inlet propellant pressure, or the dry ice pellet flow, or both. The capacity to modulate dry ice flow and propellant pressure allows economical cleaning through a wide range of applications from sensitive substrates and light contaminants to extremely tough powdered paint coatings with the same piece of equipment.

TRANSPORT AND ACCELERATION DEVICES

TRANSPORT METHODS

Typically, the delivery of pellets to the work surface is accomplished with either a single- or a dual-hose system. Currently, it is believed that the single-delivery hose is the configuration of choice for more aggressive application requirements, such as paint and hard coating removal processes. Through the adaptation of interchangeable components and/or equipment modifications, the single-hose apparatus will be capable of performing in the more highly sensitive substrate applications. Most single-hosed blasting equipment pellet insertion and modulation apparatus are patented and/or proprietary. The single-delivery hose method inserts dry ice cleaning pellets into the high pressure propellant stream within the blasting cabinet. This must be done downstream of the propellant throttling valve to eliminate erosion of the throttling valve. In addition, the single hose apparatus presents the ideal platform for the addition of sublimation reduction components.

The dual-hose system, on the other hand, dedicates one hose for propellant gas delivery to the acceleration nozzle, while the second hose delivers dry ice pellets to the same nozzle. At the nozzle, the pellets are drawn into a lower pressure area created behind the expanding propellant stream. The second, or pellet delivery, hose may transport the pellets to the nozzle via positive pressure or vacuum induction. The vacuum method of two-hose pellet transport necessarily introduces atmospheric moisture to the blasting process, which is unwelcome in some applications.

Beyond the single hose equipment being more aggressive, it also facilitates the option of nearly eliminating the sublimation of cleaning pellets within the delivery hose on the path to the acceleration nozzle. As cited in the PROPELLANT SYSTEMS section, the sublimation losses will depend on the

length of the delivery hose, the velocity of the propellant gas, and the temperature difference between the dry ice and the gas. Any ancillary sublimation reduction components or systems will require the replacement of the standard, highly flexible silicone delivery hose for a less flexible, stainless steel hose. While unfortunate for operator ergonomics, it is necessary for safety reasons.

ACCELERATION NOZZLES

Once a controllable and reliable means of delivering dry ice pellets and high pressure gas to the actual work surface is accomplished, the last item necessary is a means of delivering this solid-gas mixture to the work surface over a wide enough area and with sufficient energy to remove contaminants or coatings. This requires an acceleration nozzle of sufficient length to allow the velocity of the cleaning media to approach the velocity of the expanding carrier gas. Most of these nozzles are interchangeable enabling the operator to tailor the pellet's kinetic energy to the specific application. Often, these nozzles incorporate bends that ergonomically enhance operator and cleaning system performance.

Nozzle design is highly proprietary. Frequently, different applications require compromises in pellet velocity to provide a convenient, ergonomic nozzle exit angle, length, or width. A nozzle designed to work optimally over one range of pressures, temperatures or dry ice flow conditions may be barely adequate in others. Therefore, as the range of applications for CO_2 cleaning expands, nozzle design will be one of the most important areas of growth and development.

An important area of nozzle research is the adaptation of sound attenuating technology to the blasting process. Currently, operating sound levels are in excess of 112 dBA at distances less than 6 feet. OSHA regulations require an ongoing hearing analysis program for workers continually exposed to this noise level, in addition to all workers within 200 feet wearing hearing protection. (This assumes 6-hours of continuous blasting in an 8-hour day.)

CONCLUSION

The current range of applications for dry ice cleaning systems is growing rapidly. Paint removal, including epoxies, enamels, acrylics, and lead rich paints, is an area in which CO_2 cleaning is becoming highly cost competitive. The electronic industry is beginning to look toward dry ice blasting as a means of removing flux from electronic circuit boards. The automotive (and supporting) industries are using dry ice cleaning in applications ranging from the degreasing of engine blocks to the removal of rubber from hot tire molds, to general plant maintenance clean-ups. The nuclear industry is using CO_2 cleaning for the decontamination of tools and equipment. Most of these applications produce what the EPA considers hazardous waste. With state and federal waste disposal laws becoming more stringent, a reliable economical replacement for those cleaning systems that produce more waste than they remove will be necessary.

Current areas of research and development include: the development of acceleration nozzles to cover a wide range of applications; research on the effects of dry ice pellet shape, size and density on cleaning efficiency; the development of noise attenuation devices; and research on the effects of propellant temperature on sublimation rates and cleaning efficiency. The range of applications of CO_2 cleaning are expected to grow substantially, with strategic alliances forming between Tomco, its potential customers and engineering research firms.

The Tomco dry ice cleaning system is highly flexible. With interchangeable nozzle capability, (which may be specifically designed for certain coatings, substrates and propellant flow ranges and pressures) adjustable media density and flow rates, and a present operating pressure range from 100 to 350 PSIG, the Tomco system is the ideal replacement for older, and more hazardous chemical and abrasive cleaning systems.

Laboratory for the hours of work put into this project and to congratulate them on a successful, environmentally safe process.

REFERENCES

[1]Allen, G. "An Aqueous Nonvolatile Residue Method for Cleanliness Verification" Precision Cleaning Vol II, No. 4, April, 1994, pp. 43-45.

[2]Bryan, C. and Gebert-Thompson, K. "Alternatives to Chlorofluorocarbons", ASTM, STP 1181, 1992.

[3]Clausen, C. "Annual Report on NASA CFC 113 NVR Project", NASA Grant No. NAG10-0094, July, 1994.

[4]Kennedy Space Center "Chemical Cleaning and Testing Manual" No. 4-0-385, App. 8.9.23, 8.35.10 and 8.35.13 - 8.35.15, 1994.

[5]Kuttruff, H. Ultrasonic Fundamentals and Applications, Elsevier Applied Sciences, London, New York, 1991.

[6]Mehta, N. H. "Evaluation of Ultrasonic Cavitation of Metallic and Nonmetallic Surfaces", NASA/ASEE Summer Faculty Fellowship Program, NASA CR-191004, September, 1992, pp. 258 - 315.

ULTRASONIC FREQUENCY SELECTION FOR AQUEOUS FINE CLEANING

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Abstract

A study was conducted to evaluate ultrasonic cleaning systems for precision cleaning effectiveness for oxygen service hardware. This evaluation was specific for Rocketdyne Div. of Rockwell Aerospace alloys and machining soils. Machining lubricants and hydraulic fluid were applied as soils to standardized complex test specimens designed to simulate typical hardware. The study consisted of tests which included 20, 25, 30, 40, 50, and 65 kHz ultrasonic cleaning systems. Two size categories of cleaning systems were evaluated, 3- to 10-gal laboratory size tanks and 35- to 320-gal industrial size tanks. The system properties of cavitation; frequency vs. cleaning effectiveness; the two types of transducers; and the power level of the system vs. size of the cleaning tank were investigated. The data obtained from this study was used to select the ultrasonic tanks for the aqueous fine clean facility installed at Rocketdyne.

INTRODUCTION

The technique to preclean and fine clean Rocketdyne hardware includes the use of 1,1,1-trichloroethane (TCA), an ozone depleting chemical that will be banned as of 12/31/95. Rocketdyne is committed to using aqueous cleaning techniques to replace the majority of the cleaning processes in order to minimize environmental impact.

The use of TCA provides a very effective cleaning which is achieved mainly through chemical action and relies very little on mechanical action. To change to aqueous cleaning techniques requires that the majority of the cleaning be achieved through mechanical action as the effectiveness of the chemical action is greatly reduced with aqueous cleaning agents. The mechanical technique selected for the fine cleaning process was ultrasonic cavitation. The selection of ultrasonic cleaning for aqueous fine cleaning was influenced by the work performed by IBM General Products Division, San Jose, CA;**[1,2]** Aerojet, Sacramento, CA; Newark Air Force Base, Ohio;**[3]** and NASA Kennedy Space Center, Florida.**[4]**

A study was conducted to select the most effective ultrasonic cleaning system for the fine cleaning requirements at Rocketdyne. Each manufacturing environment is unique for the hardware alloys and soils generated. From the results of previous studies, it was determined that the ultrasonic fine cleaning process was to include a three-step cleaning process. In addition, this study evaluated the possibility of enhanced cleaning capability by varying the frequency within the steps of the cleaning process. The theory reported by D. H. McQueen suggested that cleaning with low ultrasonic frequencies were more effective in removing large deposits of contamination and higher frequencies were more effective in removing microlayers of hydrocarbons.**[5]**

For the purpose of this study, low ultrasonic frequency is defined as 20, 25, and 30 kHz and high frequency is defined as 40, 50, and 65 kHz. This range of frequencies was limited due to the availability of equipment for industrial size cleaning systems. The equipment manufacturers offer cleaning systems which differ in frequencies, types of transducers and levels of power. The selection of equipment for the Rocketdyne facility was based on comparing the cleaning effectiveness of system combinations that were available at the time of this study.

BACKGROUND

There were several properties associated with ultrasonic cleaning that Rocketdyne found necessary to learn in detail in order to effectively discuss the various aspects of the ultrasonic cleaning

equipment. These properties were the phenomenon of cavitation, the frequencies available, the types of transducers, and the power levels required.

Ultrasonic Cavitation

Cavitation is the mechanism by which ultrasonic tank systems clean. Cavitation is defined as the formation and collapse of vapor bubbles in liquids by means of a mechanical force. In ultrasonic cleaning, the mechanical force is the sound wave. Sound waves are longitudinal mechanical waves that can be transmitted through solids, liquids, or gases. There is a large range of frequencies in which these waves can be generated. The human hearing range is from about 20 cycles/sec to about 20,000 cycles/sec. Ultrasonic waves are sound waves above 16,000 cycles/sec (16 kHz).**[6,7]**

A sound wave is transmitted through a liquid producing a series of compressions and rarefactions. The compression zone in a half-cycle of the sound wave exerts a positive pressure on the molecules of the liquid and pushes them together. The rarefaction zone in the other half-cycle of the sound wave exerts a negative pressure which pulls the molecules away from each other.**[6]** The force in this latter half-cycle will form a cavity when the negative pressure generated is great enough to overcome the surface tension (tensile strength) of the liquid. The ideal cavity is the generation of a vacuum bubble. In the negative pressure zone of the sound wave, a drop in pressure reduces the boiling point of the liquid creating a vapor bubble. This vapor recondenses to liquid as a result of an increase in pressure due to the positive pressure zone created in the other half-cycle of the sound wave creating a vacuum bubble. When the bubble grows large enough, it implodes with great violence producing liquid jets and shock waves, minute areas of extremely high temperature (about 5000K) and very high pressures.**[7,8]**

The size of the cavitation bubble is dependent on the frequency of the sound wave, the higher the frequency, the smaller the size of the bubble. The relationship of the size of the cavitation bubble to frequency under normal atmospheric pressure was roughly given by D. H. McQueen:

$$R_0 = 300/f,$$

where R_0 is the equilibrium bubble radius in cm and f is the frequency in Hz.**[5]** This relationship is a simplified version of the derivation presented by Noltingk and Neppiras for the relationships for cavitation bubble dynamics.**[9]** For an ultrasonic cleaning system that is 20 kHz, the cavitation bubble size is about 150 um; for 40 kHz, the bubble size is about 75 um. The lower frequencies produce larger cavitation bubbles which have a greater implosion energy, as it requires more work to generate the larger bubble.**[10]** Neppiras has reported that not only does the cavitation intensity increase with reduced frequency, but also the cavitation threshold is decreased.**[11]**

The volume concentration of the cavitation bubbles can be increased by increasing the amplitude or intensity of the sound wave until the density of bubbles reaches a self-limiting state. This state is known as unloading. This condition is a result of the fact that sound is transmitted from one medium to another only when the densities of the two media are similar. The density difference between air and water is too great for the transmission of sound from one to the other. Therefore, if a layer of cavitation bubbles becomes too concentrated at the surface of the radiating plate the sound wave is prevented from propagating due to the barrier the cavitation bubbles create. The density between water and metals is close enough that the transmission of sound waves between these two media is effective, which is why this cleaning technique is so useful.**[10]**

Cavitation Damage. As was stated above, the frequency of the sound wave determines the size of the cavitation bubble and the resultant implosion forces. The implosion energy at the lower frequencies is great enough to remove deposits that can include an oxide layer or any other thin passivation layer.**[12]** This can result in mechanical erosion of the surface being cleaned and is, of course, an important factor in the selection of a cleaning system.

Ultrasonic Frequency

Conventional ultrasonic cleaning tanks are available in discrete frequencies of 20, 25, 30, 40, 50, and 65 kHz. Some ultrasonic cleaning equipment is available in frequencies as high as 80 kHz to 1 MHz and more. One manufacturer is providing combinations of frequencies in the same cleaning tank.

Frequency vs. Cleaning Effectiveness. The knowledge that the lower the frequency the greater the implosion energy has been the basis for the selection of ultrasonic frequencies for cleaning systems through the decades. In 1959, Koontz and Amron published their work which showed that as the ultrasonic frequency decreased, the cleaning effectiveness increased. This work was based on particulate contamination using weighing and visual inspection techniques. In 1986, a study was reported by D. H. McQueen that evaluated cleaning effectiveness in terms of the type of contaminant to be removed. McQueen grouped contamination into two classifications: the microscopic or particulate contaminants which included particles from cutting, grinding, or polishing operations; and, the submicroscopic or molecular contaminants which included fats, oils, or proteins deposited as a very thin film such as from fingerprints or deposited from condensation of these soils. McQueen's study agreed with Koontz and Amron for particulate matter, the cleaning efficiency increased as the ultrasonic frequency decreased. However, for what McQueen has termed as molecular or submicroscopic contaminants such as fingerprints, the cleaning efficiency increased as the frequency increased.[5]

McQueen's hypothesis is that there is a different rate limiting mechanism for the two types of contaminants. The microscopic or particulate contamination is held to a surface by several bonds. In order to remove the particle, all the bonds must be broken at the same time; if they are not the few bonds that are broken are repaired by the time the next series of cavitation bubbles develop to break the remaining bonds. Therefore, the lower frequency, higher cavitation energy cleaning system is required to remove particulate contamination. McQueen states that the submicroscopic contamination such as fingerprints are held by a much smaller number of bonding sites. That in actuality the contaminant is removed at the molecular level, molecule by molecule, and is, therefore, dependent on diffusion as the rate limiting step. For this latter mechanism, the ultrasonic activity in the water increases the diffusion process and as the frequency increases the efficiency of the diffusion process increases.[5]

Ultrasonic Transducers

The transducers manufactured for cleaning equipment are available in two different types, magnetostrictive for 20 and 30 kHz and piezoelectric for 25 and 40 kHz and higher. The actual operating frequency of a transducer will vary $\pm$3 kHz from the design frequency.

Magnetostrictive Transducers. The magnetostrictive type of transducer is constructed of thin nickel strips placed together in a stack. A magnetic field is produced around this nickel stack through copper wire windings. The magnetic field causes the nickel atoms to align, taking up less space than the normal random atomic configuration. This phenomenon causes the nickel to contract. By causing the material to contract and relax, a resonant frequency in the nickel strip. The length of the nickel strip determines the frequency of the sound wave in the same manner as the length of an organ pipe, the longer the strip the lower the frequency. The length of the strips that are stacked together must be precision cut so that each individual strip resonates at the same frequency so the stack resonates in unison. This resonating frequency is then transmitted to the radiating plate and into the cleaning solution.[10] Magnetostrictive transducers can be made to produce frequencies greater than 20 or 30 kHz, however, the efficiency drops off dramatically as the frequency increases.[11]

Piezoelectric Transducers. The piezoelectric transducers used today for cleaning applications are made of lead zirconate-titanate ceramic crystals that are sandwiched together with electrodes that provide voltage to the crystals. There are two complementary effects that give rise to the phenomenon that is inherent in the piezoelectric crystal; when pressure (piezo- is taken from the Greek word piezein, to press)

is applied to the crystal, an electrical field is produced on the surface. Conversely, if an electrical field is applied to the surface, a strain is produced that causes the crystal to contract.**[13,14]** It is this latter condition that is utilized in the production of ultrasonic transducers. An alternating electric field is applied to the crystal at the desired frequency and causes it to contract and relax thus transforming the electrical frequency to the mechanical sound wave that is transmitted through the radiating plate and into the cleaning solution.

Transducer Bonding Techniques. Both types of transducers require bonding to a radiating plate, which is either the bottom of the cleaning tank or the face of an immersible transducer. There are two types of bonding techniques, brazing or epoxy bonding. The brazing technique produces a stronger bond and a better ultrasonic coupling medium; but, it requires a thicker radiating plate due to warping that occurs on a thinner plate with the braze heat cycle. Thus, brazing is limited to use with lower, higher energy frequencies, 20, 25, and 30 kHz. The epoxy adhesive bonding technique is used on thinner radiating plates and is typically used for the higher frequencies, 40 kHz and higher.

Power Requirements

The power levels in an ultrasonic tank system are a result of the amount of power the generator applies to the transducers and the number of transducers. The amount of power supplied to the transducers dictates the amplitude of the sound wave. The minimum power at which cavitation is produced, the cavitation threshold, is 0.3 Watts/cm^2 (1.9 Watts/in^2) at the radiating plate.**[12]** The optimum power density for aqueous solutions was reported to be 2-3 Watts/cm^2 (13-19 Watts/in^2) and for solvents at 1.5-2 Watts/cm^2 (10-13 Watts/in^2) by Neppiras in a 1962 report.**[11]**

A power density measure that is more meaningful when discussing ultrasonic cleaning tank systems is the power per gallon of cleaning solution rather than the power per square inch of radiating plate surface. Cleaning systems are manufactured with varying power levels. Laboratory size tanks of up to about 10 gal generally have a power level of 100-200 Watts/gal. Newark Air Force Base uses small cylindrical 5-gal ultrasonic cleaning tanks that were designed to provide 500-600 Watts/gal.**[3]** Ultrasonic manufacturers, industry-wide, provide charts that show a significant decrease in power densities, 10-30 Watts/gal, as the size of the tank increases. However, this practice has not been supported by data that correlates cleanliness levels with the size of tank vs. power level.

The adjustment in power levels between small and large tanks is achieved by the number of transducers that are provided for the individual tank. The number of transducers directly influences the number of sites that will generate cavitation. Increasing the number of transducers improves the cavitation coverage and reduces the amount of "shadowing" to the different facets of a complex piece of hardware.**[10]**

TEST PROCEDURE

The specific details of the ultrasonic cleaning tank systems evaluated for this study are given in Table 1. These tank systems were used in various combinations in the three-step cleaning process. The frequency for cleaning steps 1 and 2 was held constant and the frequency for step 3 was either held the same or varied from steps 1 and 2.

Standard complex test specimens were contaminated and then cleaned as described below. The cleaning agents were Rocketdyne approved cleaners. After cleaning, the test specimens were evaluated for the remaining particulate matter and the nonvolatile residue (NVR).

Standard Complex Test Specimens. The test specimens were made of either 718 nickel base alloy or 304 stainless steel and were designed with through holes, blind passages, and threaded holes to simulate the complexity of the hardware, as shown in Fig. 1.

TABLE 1. Ultrasonic Tank Systems I.D. Code, Power Density, and Size

Tank System Frequency, kHz	I.D. Code	Volume Power Density, Watts/gal	Area Power Density, Watts/in2	Dimensions I.D., inches	Soln. Cap., gal.
Laboratory Size Tank Systems:					
20	20-A	140	6	12x14x12 ht	7
20	20-B	100	10.5	10x19x16 ht	10
30	30-L	167	3.6	15.5xX9x6 ht	3
30	30-I	115	3.5	12x18x10 ht	6.5
40	40-B	210	6.2	9.75x14x10 ht	4
40+/-1	40-1	100	3.6	10x14x10 ht	5
40+/-2	40-2	100	3.6	10x14x10 ht	5
47	47	83	1.5	19.5x11x6 ht	4
Industrial Size Tank Systems:					
20	20-C	52	6.7	50x36x36 ht	230
25	25	25	4.6	48.5x54x31 ht	320
40	40-D	25	5.1	40x36.5x23 ht	145
50	50	25	4.6	48.5x54x31 ht	320
65	65	30	2.7	16x22x20 ht	32

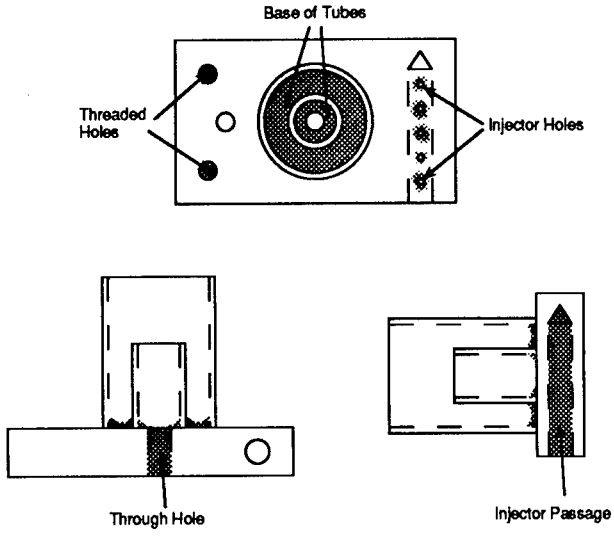

Fig. 1. Standard Complex Test Specimens with Placement of Contaminants.

Contamination of Test Specimens. The test specimens were contaminated, as shown in Fig. 1, with one of the following shop lubricants: 1) Cool Tool, by Monroe Fluid Technology; 2) Microfinish, by PetroChem Corp.; 3) Hydraulic Oil, by Mobil Oil Corp.; and 4) Centerpoint Lube, by Chicago Manufacturing and Distribution Co. Metallic fines were added to the contaminated areas and the specimens were heated in an oven at 200 F for 1 hr to simulate conditions of the machining processes.

Cleaning Procedure. The cleaning procedure was comprised of three steps. Each step consisted of placing the test specimens in the ultrasonic cleaning tank containing a cleaning agent, the ultrasonics were activated for 15 min, the specimens were removed, drained, immersion rinsed in hot deionized water, removed, and thoroughly flushed with ambient temperature deionized water. Each cleaning agent was diluted using deionized water. Cleaning Step 1 used a solution of 20% by volume of the emulsion degreaser Turco™ 3878 NC-LF*; Cleaning Step 2 used a 3.3 percent by weight (%/wt) solution of the mild alkaline cleaner Turco™ 4215 NC-LT plus 0.4%/wt solution of the nonionic surfactant Turco™ 4215 Additive; and Cleaning Step 3 used a 0.04%/wt solution of the nonionic surfactant Turco™ 4215 Additive. This last step was performed in a 100,000 Class cleanroom for the tests using the laboratory size tanks. The tests using industrial size tanks were conducted in the manufacturing shop which was not a controlled environment.

Laboratory Evaluation of Cleanliness. The cleanliness evaluation process was performed in a 30,000 Class cleanroom. Each specimen was evaluated by flushing with 500 ml of TCA. The TCA was filtered to extract the particles for particle count and the filtrate was evaporated to dryness and weighed to determine the nonvolatile residue. Particles greater than 400 microns were counted and recorded. The weight of the nonvolatile residue was divided by the surface area of the test specimen to calculate the amount of residue per surface area which was reported in mg/ft^2.

Comparison to Current Fine Clean Process Using TCA. The test specimens were contaminated and processed through the current manufacturing processes using aqueous solutions for preclean and vapor degreasing for fine clean. These specimens were then evaluated for cleanliness by the laboratory method given above.

RESULTS AND DISCUSSION

The cleaning effectiveness of each ultrasonic cleaning system was evaluated based on the nonvolatile residue and number of particulates remaining on the test specimens after cleaning. The NVR was further evaluated for the signal-to-noise ratio (S/N) which is a measure of the precision of the cleaning effectiveness. The calculation for the S/N was based on the Taguchi methods of analysis for results that aim for smallest-is-best.**[15]** The calculation used the following relationship:

$$S/N = -10 \log(MSD), \text{ and, } MSD = (y_1^{\,2} + y_2^{\,2} + \ldots + y_n^{\,2})/n$$

where MSD is the mean squared deviation, y is the NVR value in mg/ft^2, and n is the total number of data points for that test sequence.

Table 2 provides a list of the cleaning system combinations tested and the results. Fig. 2 provides a graph of the average NVR vs. the S/N, the data plotted also includes the comparison data for vapor degreasing. The best results on a graph for NVR vs. S/N for smallest-is-best are in the farthest lower right corner.

No obvious trend in effectiveness of frequency level or combination appeared on the graph of the overall results. Therefore, the data was grouped by manufacturer in order to compare ultrasonic frequency

*Trademark for Turco Products Division of Atochem North America, Inc., Westminster, California.

TABLE 2. Test Results of Ultrasonic Tank Systems Listed in Order of Best Performance First

Cleaning Systems Steps 1&2/Step 3 by I.D. Codes	Tank Size Type	Avg. NVR, mg/ft2	Signal-to-Noise Ratio(1)	Total Number Particles
20-B/20-B	Lab	1.7	-7.3	0
20-A/47	Lab	2.7	-8.7	0
25-D/40-D	Indust.	3.0	-9.8	0
40-1/40-2	Lab	3.0	-10.5	9
25-D/25-D	Indust.	3.2	-11.3	0
25-D/50-D	Indust.	3.6	-12.3	1
47/47	Lab	3.9	-13.4	0
20-C/20-C	Indust.	4.1	-13.8	0
20-C/65	Indust.	4.8	-13.7	3
30-I/47	Lab	4.9	-14.1	0
40-B/40-B	Lab	5.0	-14.5	0
20-B/40-B(2)	Lab	5.3	-15.0	4
30-I/30-I	Lab	5.6	-15.2	0
20-B/40-B(3)	Lab	5.7	-16.4	0
30-L/30-L	Lab	5.8	-16.5	0
40-1/40-1	Lab	5.8	-17.2	9
40-B/20-B	Lab	6.1	-16.8	5
47/20-A	Lab	10.7	-20.6	0

(1) Signal-to-Noise Ratio = -10 log(Mean Squared Deviation).
(2) Soil remained on these test specimens for 2 days.
(3) Soil remained on these test specimens for 24 days.

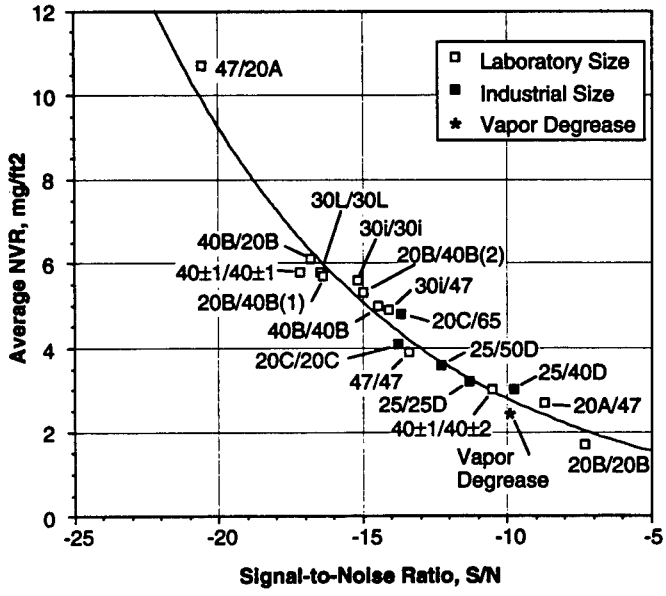

Fig. 2. A plot of the results of the cleaning effectiveness of the ultrasonic systems evaluated.

combinations while holding design differences a constant, Fig. 3a-f.

There were several ultrasonic cleaning systems that provided cleaning effectiveness close to that of vapor degreasing as can be seen in Fig. 2.

The best overall test result was for the cleaning sequence 20B/20B which appears to be a possible anomoly, Fig. 3a. It would be expected that the 20B/40B results would at least be somewhere between 20B/20B and 40B/40B, if frequency combination order were not an influencing factor. Therefore, the test for 20B/40B was repeated, but similar results were obtained. This would indicate that the results for either 20B/20B or 40B/40B were not accurate.

The results of three of the cleaning sequences, Fig. 3b, c, and d, appeared to support the suggestion that a low frequency to remove the greater deposits of soil followed by a high frequency to remove the last microlayer of soil enhances cleaning effectiveness. In Fig. 3b, results are shown that indicate that frequency combination order are an influencing factor. The cleaning sequence results provided in Fig. 3c indicate that cleaning with a higher ± 2 sweep frequency in the last cleaning step improves the cleaning effectiveness over that of using the lower ± 1 sweep frequency in all three cleaning steps. The cleaning sequence results provided in Fig. 3d show that cleaning with 25 kHz followed by 40 kHz in the last cleaning stepp gives improved cleaning effectiveness over using 25 kHz for all three steps. The system using 25 kHz followed by 50 kHz was not very effective. The 50 kHz ultrasonic system did not perform well because this system used 25 kHz transducers that were driven at 50 kHz by adjusting the generator. To drive the ultrasonic transducers at a frequency different from the design frequency does not appear to provide an efficient transfer of energy and as a result its performance is poor. This same type of situation was also evaluated by A. A. Busnaina, etal., and reported to be ineffective.**[16]**

It was visually observed that if a water break free surface was not obtained after Step 2, Step 3 was not very effective. With the 20C/20C and 20C/65 systems, very poor results were being obtained after Step 2 with the 20 kHz system, Step 3 added significantly to these cleaning processes. As can be seen in Fig. 3e, no significant difference in cleaning effectiveness was observed between these two different processes.

The ultrasonic frequencies of the cleaning systems were classified as a low frequency system for 20, 25, and 30 kHz and as a high frequency system for 40, 50, and 65 kHz. Study performed by D. H. McQueen used much higher frequencies for the high frequency evaluation. The 50 and 65 kHz systems tested in this study were still being considered as experimental equipment. Therefore, the high frequencies McQueen used are not currently available in industrial size equipment.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this study, it has been concluded that a cleaning system should be tested to evaluate its effectiveness on the specific subtrate and soil that must be cleaned. The overall performance of the frequency levels, low or high, varied from manufacturer to manufacturer. It appeared that the ultrasonic generator-transducer-radiating plate design differences between manufacturers were more of an overriding factor in cleaning effectiveness than the frequency levels or combinations of frequencies in the cleaning system. However, based on the limited tests performed, it appeared that, when the manufacturing design of the system was held constant, the use of low frequency ultrasonic systems in preliminary cleaning steps to remove gross amounts of soil followed by high frequency to remove the microlayer of soil in the final cleaning step gave enhanced cleaning effectiveness. It was also determined that lower power levels are acceptable for industrial size tanks compared to the smaller laboratory size tanks, but a little higher than that recommended by the manufacturer, at least for the Rocketdyne application.

The system selected by Rocketdyne was 25 kHz for cleaning steps 1 and 2 and 40 kHz for step 3. The power levels requested were 4.2 watts/in^2 at the radiating plate with 43 watts/gal for each tank.

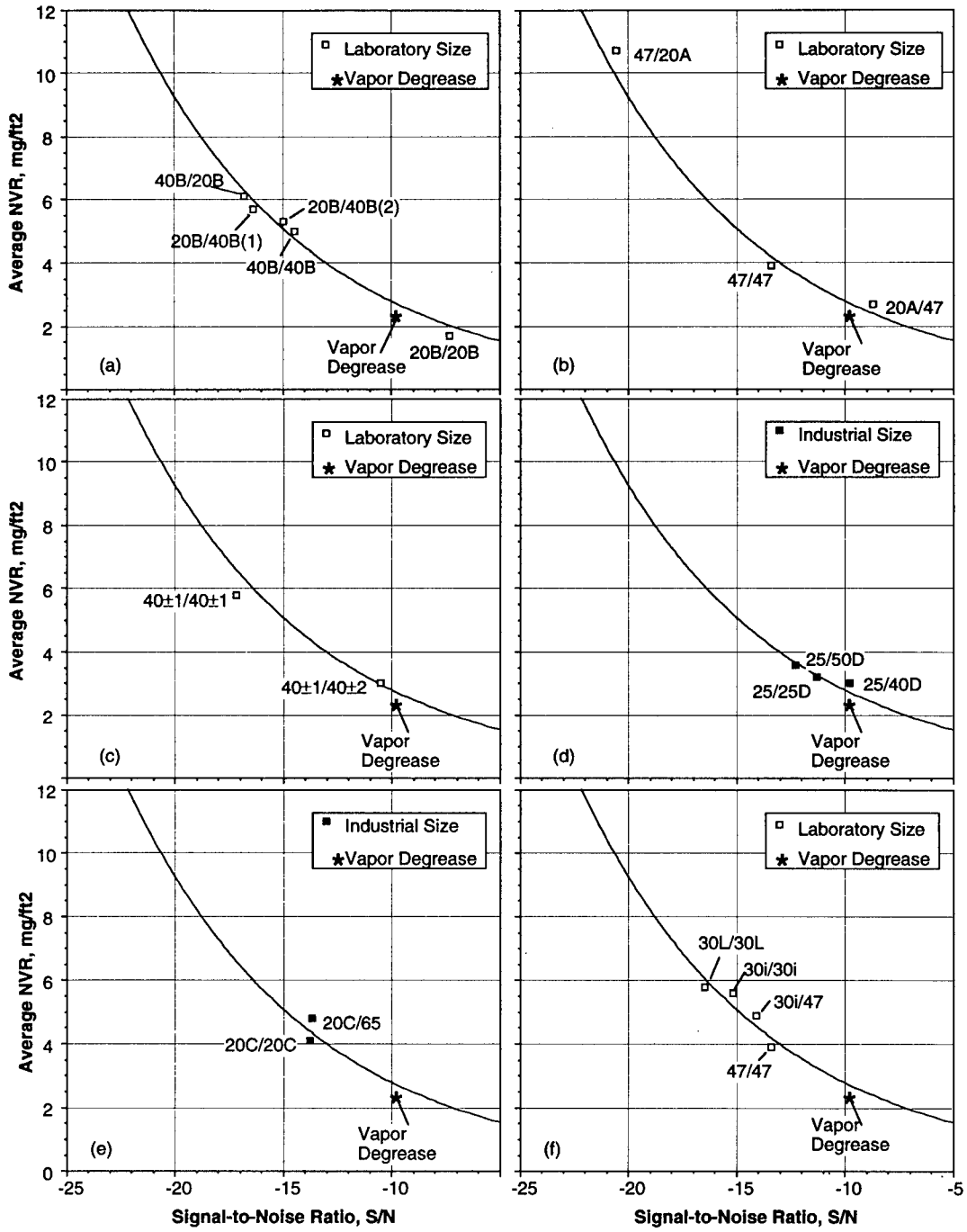

Fig. 3. A plot of the cleaning effectiveness of the ultrasonic systems by manufacturer.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the technical assistance of Sonya Farrow, Susan Lim, Tim Edwards and especially Kelli Kallenborn.

REFERENCES

1. Ko, M., "Comparison of Freon with Water Cleaning Processes for Disk-Drive Parts", Particles on Surfaces II: Detection, Adhesion, Removal, K. L. Mittal, Ed., Plenum Press, New York, 1989, pp 283-291.

2. Ko, M., Shull, D., James, P., Carroll, M., Hignite, C. Development of New Aqueous Cleaning Process for Disk-Drive Parts Swiss Contamination Control (1990) **3 Nr.4a** 451-456.

3. Hunt, D. E., Ott, G. W., Ciupak, T. L., Vargas, R., "Aqueous Cleaning for Precision Bearings and Beryllium," Aerospace Guidance and Metrology Center, Newark Air Force Base, Ohio, Nov. 26, 1991, unpublished.

4. Allen, G. J., Hoppesch, C. W., Johnson, R. S., Buckley, M. D., "Aqueous Nonvolatile Residue Validation of Precisioned Cleaned Hardware," Alternatives to Chlorofluorocarbon Fluids in the Cleaning of Oxygen and Aerospace Systems and Components, ASTM STP 1181, Coleman J. Bryan and Karen Gebert Thompson, Editors, American Society for Testing and Materials, Philadelphia, 1993, pp 37-48.

5. McQueen, D. H. Frequency Dependence of Ultrasonic Cleaning Ultrasonics (1986) **24** 273-280.

6. Halliday, D. and Resnick, R., Fundamentals of Physics, John Wiley & Sons, Inc., New York, c.1970, pp 323-325.

7. Suslick, K. S., "The Chemical Effects of Ultrasound" Scientific American February 1989, pp 80-86.

8. Flint, Edward B. and Suslick, Kenneth S., "The Temperature of Cavitation" Science (1991) **253** 1397-1399.

9. Neppiras, E. A., "Acoustic Cavitation" Phys. Reports (1980) **61** 159-251.

10. Finch, Robert D., Professor, Department of Mechanical Engineering, University of Houston, conversation on 9/10/93, unpublished.

11. Neppiras, E. A., "Problems in the Technology of Ultrasonic Cleaning", Soviet Physics-Acoustics, Vol. 8. No. 1, July-Sept. 1962, pp 4-16.

12. Power Sonic and Ultrasonic Transducers Design, Proceedings of the International Workshop, Held in Lille, France, May 26 and 27, 1987, B. Hamonic and J. N. Decarpigny, Editors, p 187.

13. Beyer, R. T., and Letcher, S. V., Physical Ultrasonics, Academic Press, New York, c.1969, p 38.

14. Heuter, T. F., and Bolt, R. H., Sonics, Techniques for the Use of Sound and Ultrasound in Engineering and Science, John Wiley & Sons, Inc., New York, c.1955, pp 86-88.

15. Phadke, M. S., Quality Eingeering Using Robust Design, Prentice Hall, New Jersey, c.1989 by AT&T Bell Laboratories, pp 109-110.

16. Busniana, A. A., Gale, G. W., Kashkoush, I. I., "Ultrasonic and Megasonic Theory and Experimentation" Precision Cleaning April 1994 **11 No.4** 13-19.

QFD Analysis of RSRM Aqueous Cleaners

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ABSTRACT

This paper presents a Quality Function Deployment (QFD) analysis of the final down-selected aqueous cleaners to be used on the Redesigned Solid Rocket Motor (RSRM) program. The new cleaner will replace solvent vapor degreasing. The RSRM Ozone Depleting Compound Elimination program is discontinuing the methyl chloroform vapor degreasing process and replacing it with a spray-in-air aqueous cleaning process. Previously, 15 cleaners were down-selected to two candidates by passing screening tests involving toxicity, flammability, cleaning efficiency, contaminant solubility, corrosion potential, cost, and bond strength. The two down-selected cleaners were further evaluated with more intensive testing and evaluated using QFD techniques to assess suitability for cleaning RSRM case and nozzle surfaces in preparation for adhesive bonding.

INTRODUCTION

Quality Function Deployment (QFD) is a team method to plan and design new or improved products, processes, or services. The design is based upon customer requirements and the approach is to do it right the first time and document what you are doing and thinking. The concept was first proposed in 1966 by Yoji Akao, vice president of the Japan Society for Quality Control and professor of industrial engineering at Tamagawa University in Tokyo, Japan. The purpose of QFD was spawned from the need to find a way to get production to grasp the notion of quality assurance at the stage of planning before going into production. This notion was later named "concurrent engineering." QFD was introduced in 1972 by Akao at the Kobe shipyards of Mitsubishi Heavy Industries to coordinate the logistics for building complex supertanker cargo ships. The technique developed further sophistication at Toyota and has gained worldwide acceptance as a powerful product planning method in numerous industrial and service sectors.

Rocketdyne[1] used QFD to redesign a fuel turbopump for a heavy-lift launch vehicle, Thiokol uses QFD on the RSRM program to the point that a QFD training course[2] was developed, and NASA Marshall Space Flight Center (MSFC) has prepared a technical paper[3] to encourage NASA wide usage of the technique.

The strategy of QFD is to focus development and improvement activities on the customer. Multidisciplinary teams are used to arrive at decisions by consensus. This approach allows customer requirements to be deployed from features to characteristics to operations to requirements. It provides a framework for concurrent engineering. Documentation is simple and consistent, and results in a optimum design that allows qualitative requirements to be converted in measurable activities.

Thiokol engineering is using the technique to assist in the down-selection of new processes as a result of the Montreal Protocol ban on certain ozone depleting chemicals. The schedule for implementation is short and the task is awesome; perfect reasons to use QFD.

DISCUSSION

The QFD analysis followed a logic flow as illustrated in Figure 1. A brainstorming session was held with members of Materials and Processes Engineering. The process was facilitated by a Total Quality Management (TQM) advisor. Quality characteristics were identified which would answer all major program concerns. Safety, processability, and finished product performance were key elements in arriving at the final characteristics. The number of items was

limited to 12 as recommended by good TQM practice. A binary comparison analysis was conducted using the 12 items. Using a scale of 0.1 to 10, key members of safety, engineering, quality, waste disposal, facilities engineering, and NASA were asked to compare between two criteria at a time, working through all 12 characteristics (Figure 2). The results provided a weight by item for each individual criteria which was then grouped by organization (Figure 3). A QFD form was developed for material selection that listed the quality characteristics, weight factors, ranking of data, total score, and total grand score for each material, and provided space for lab data (Figure 4). The laboratory tests were then conducted on each candidate and the data were entered, weighted, and ranked. A total score for each item as well as a grand total score for each material was obtained.

The first series of tests was designed to down-select 15 cleaners to five by comparing each to the others and to the control, which was methyl chloroform vapor degreasing. Figure 5 shows the total QFD scores with three semi-aqueous and two aqueous cleaners winning out. The organic cleaners were eliminated due to their volatile nature during a spray in air mode.

Since the first series of tests satisfied all of the safety concerns, the second series of tests designed to down-select five cleaners to two could concentrate on processability and product performance factors. Again, a binary comparison analysis was conducted to obtain the weighted value for the next series of tests. The five cleaners were submitted for lab tests and the results were analyzed.

Residue from contaminants and cleaners was determined by surface chemistry analysis. Hydrocarbons were quantified by measuring carbon levels and silicates were measured by ratioing the silica peak to the zirconium peak. A typical ratio of the Si/Zr is 2.0 for a surface cleaned by grit blasting with zirconium silicate media. Any ratio higher than 2.0 indicates the presence of excess silicates which is a constituent in some of the cleaners.

Cleaning efficiency was measured by optical stimulating electron emission (OSEE). The OSEE unit scans the surface with ultraviolet light in the 185 nanometer region and provides surface cleanliness measurements in centivolt units which are correlatable to contaminant levels. The higher the centivolt reading, the cleaner the surface. The technique is sensitive to 1 mg/ft^2 of hydrocarbon contaminant. The acceptance level for bonding ranges from 10 to 25 mg/ft^2 depending upon the bond criticality.

Bond strength was determined using tensile adhesion of an epoxy adhesive (Hysol EA913NA) with D6AC steel and 7075 aluminum buttons. Fracture toughness was measured using tapered double cantilever beams with the same adhesive per a modified American Society for Testing Materials (ASTM) method. Fracture toughness was chosen because of its sensitivity to lower levels of surface contaminants which provides a clearer distinction between cleaner candidates.

Various process options were tested for bond strength including no grit blasting with and without aging prior to bond, grit blasting with no aging, and soil loading with no grit blast or aging. Aging conditions were 135°F and 100 percent RH for four weeks. Soil was added to the cleaner in successive cycles to establish a saturation level that would affect strength. Five mg/l of soil simulated a typical years worth of soils the hardware would see.

Corrosion potential was tested three ways: visual inspection, electrochemical potential per an ASTM method, and corrosion rate in mils lost per year.

The major difference that separated the cleaners was soil loading capability. One semi-aqueous cleaner performed equally with the aqueous cleaners except for the soil loading test, where it was eliminated (Figure 6). The two final candidates were Brulin 815GD and Jettacin. They are both aqueous alkaline cleaners. Jettacin also contains a terpene solvent.

As the number of cleaners were reduced, more tests were performed to establish some statistical confidence. The third series of down-selection, two cleaners to one, introduced design of experiments (DOE) as a tool to gain maximum information with minimum testing.

The DOE (Figure 7) was a seven-variable, two-level design requiring 16 coupons for each alloy. The variables were carefully chosen after lengthy discussions with processing experts. Additionally, two repeat sets were run to establish process and testing variability levels. The 2-sigma bands show in Figure 8 establish these statistical boundaries for this set of experiments. Therefore, only parameters that exceed these levels are considered as significant changes. When reviewing the main effects, the response to each variable could be measured against the 2-sigma window and each cleaner could be scored accordingly (Figure 8). Again, a new QFD matrix was developed to make the 2-to-1 down-selection. This matrix showed that both cleaners were acceptable in the product performance category. However, subscale cleaning tests highlighted potential processability issues, i.e. foaming and cleaner life.

In addition to the standard laboratory tests, processability tests were expanded to further define the transition from subscale to full-scale processing. During this scaleup, some cleaner foaming was encountered. Therefore, further testing will study low foaming cleaners from the same chemical family. Preliminary work with one such cleaner, Brulin 1990, using electron spectroscopy for chemical analysis (ESCA) showed that at the molecular level, the nonfoaming and standard aqueous cleaners produced similar surface chemistry. Preliminary bond testing with Brulin 1990 (tensile and fracture energy) showed equal strengths to the foaming version. Thus Brulin 1990 appears to be a viable cleaner for our application.

CONCLUSIONS

The QFD approach has proven to be an effective way to assimilate the varied concerns and opinions of various organizations early in the design process. The QFD format allows clear and concise reporting of the test data in a nonbiased manner. Many technical factors are used in an engineering decision. By limiting the factors of customer concern, speedy decisions can be made about numerous cleaner systems. However, as the selection of cleaners narrows more engineering judgement from technical data is necessary. A lesson learned is that any issue, even if given minimal weight in the scoring process, can impact the final decision.

ACKNOWLEDGEMENT

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REFERENCES

[1]Butler, K.N., Aerospace America, April 1993, pp. 28-30
[2]Thiokol Corporation, QFD Training Workbook, 1992
[3]Cruit,W.,et.al., Prioritization Methodology for Chemical Replacement, NASA Technical Paper 3421, 1993

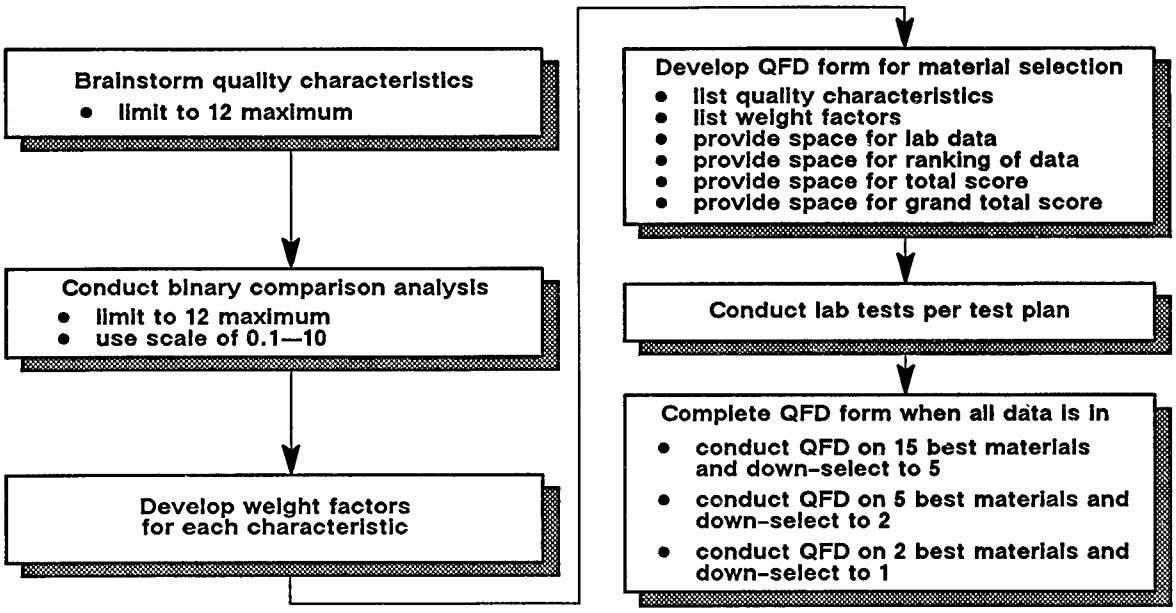
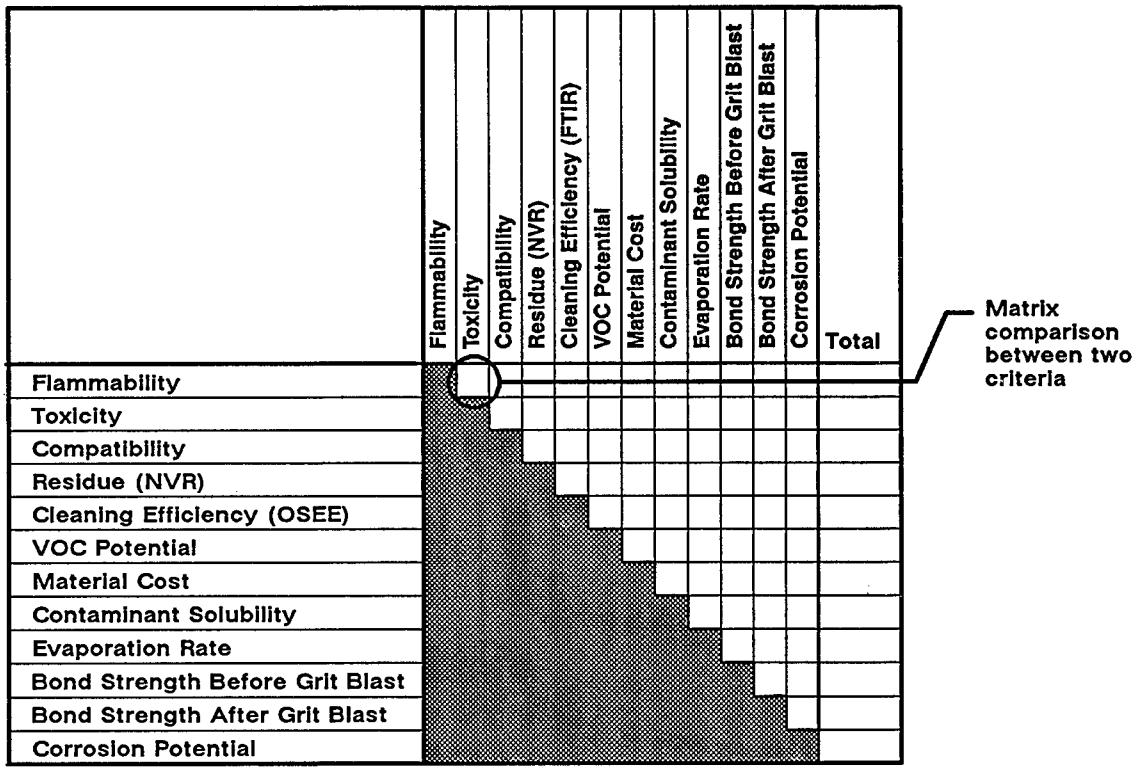


Figure 1. QFD Liquid Flow



- Individual cells contain the comparison between two criteria
- The reviewer should read the comparison from row to column as in the following example:

  Flammability is: (choose one)
  - Exceedingly more important
  - Significantly more important
  - Equally important
  - Significantly less important
  - Exceedingly less important than toxicity
- The reviewer decides which statement is true, then marks the appropriate score in the cell. Calculations will be done on the other cells to determine total weight of each criteria
- Do not calculate totals at this time.

Figure 2. Binary Comparison Analysis

Criteria	Design Engineering	Program Management	Labs	Materials and Processes	Facilities	Customer	Materials and Processes	Project Engineering	Total	Percent
Flammability	10.8	85.0	58.2	51.2	77.0	73.2	34.1	38.4	427.9	13
Toxicity	39.6	38.2	58.2	38.2	77.0	103.2	34.1	38.4	426.9	13
Compatibility	52.4	15.0	9.1	39.0	28.4	76.4	13.3	61.0	294.6	9
Residue (NVR)	13.6	18.8	9.3	7.0	23.6	26.4	7.7	11.0	117.4	3
Cleaning Efficiency (OSEE)	70.0	20.5	33.6	28.9	24.4	65.2	20.5	33.6	296.7	9
VOC Potential	88.0	38.2	35.2	9.2	47.0	75.2	6.9	1.8	301.5	9
Material Cost	22.6	1.7	1.5	12.3	1.7	24.8	6.9	9.3	80.8	2
Contaminant Solubility	41.6	23.9	9.1	19.0	27.0	20.2	7.7	10.2	158.7	5
Evaporation Rate	51.2	13.3	9.1	10.1	32.6	8.8	10.9	9.9	145.9	4
Bond Strength Before Grit Blast	59.2	19.0	39.2	31.9	13.6	10.8	26.1	42.4	242.2	7
Bond Strength After Grit Blast	78.4	67.2	85.0	68.0	17.6	140.0	110.0	61.0	627.2	19
Corrosion Potential	80.4	24.7	32.7	34.5	15.0	41.2	10.1	14.2	252.8	7
Total	607.8	365.5	380.2	349.3	384.9	665.4	288.3	331.2	3,372.6	100

Figure 3. Voting Comparison and Totals

Product Name: _____

Application: _____

Criteria/Baseline	Test	Results		Weight	Rank	Total
Toxicity				0.13		
Flammability	Ignitability			0.13		
VOC Potential				0.09		
Residue	NVR			0.03		
Cleaning Efficiency	OSEE			0.09		
Contaminant Solubility				0.05		
Corrosion Potential	pH			0.07		
Evaporation Rate				0.04		
Compatibility				0.09		
Bond Strength, No Grit Blast (as cleaned)	Tensile Fracture	D6AC	7075	0.07		
Bond Strength, with Grit Blast		D6AC	7075	0.19		
Material Cost				0.02		
			Total	1.00		

This rank is a rating between 1 and 10. This rating is based on the actual data and predetermined ground rules.

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Figure 4. OPTIC Team Material Selection

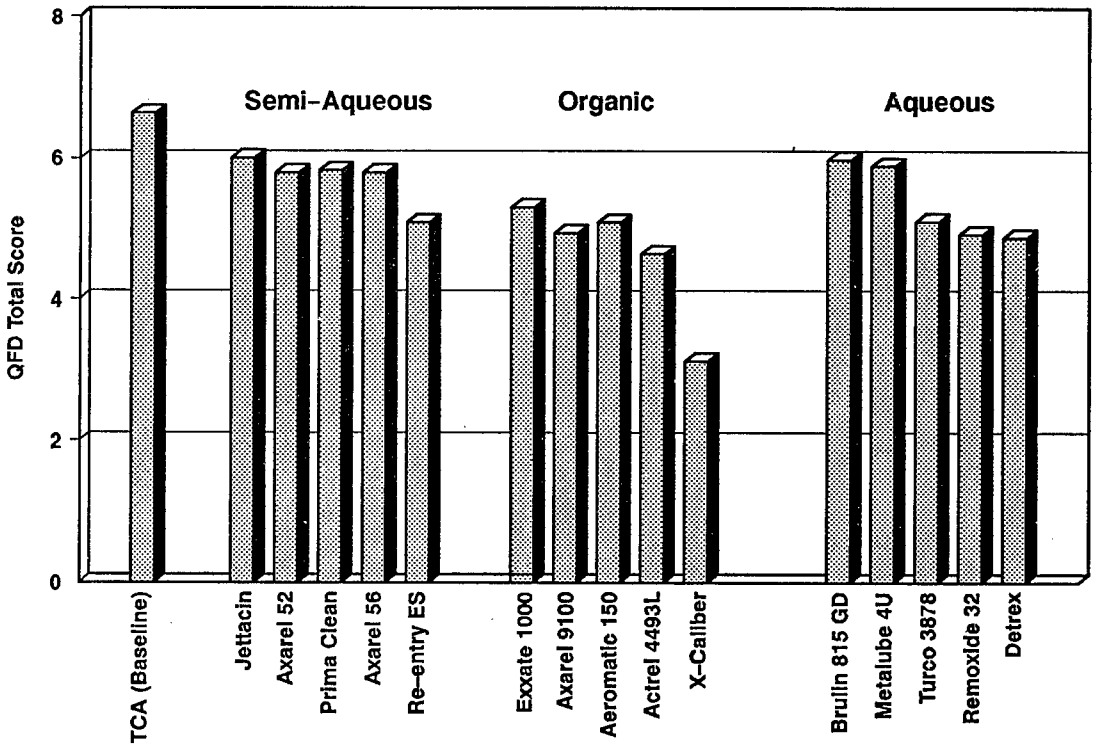

Figure 5. OPTIC Team QFD Results. Down-selection from 15 to 5. (total scores)

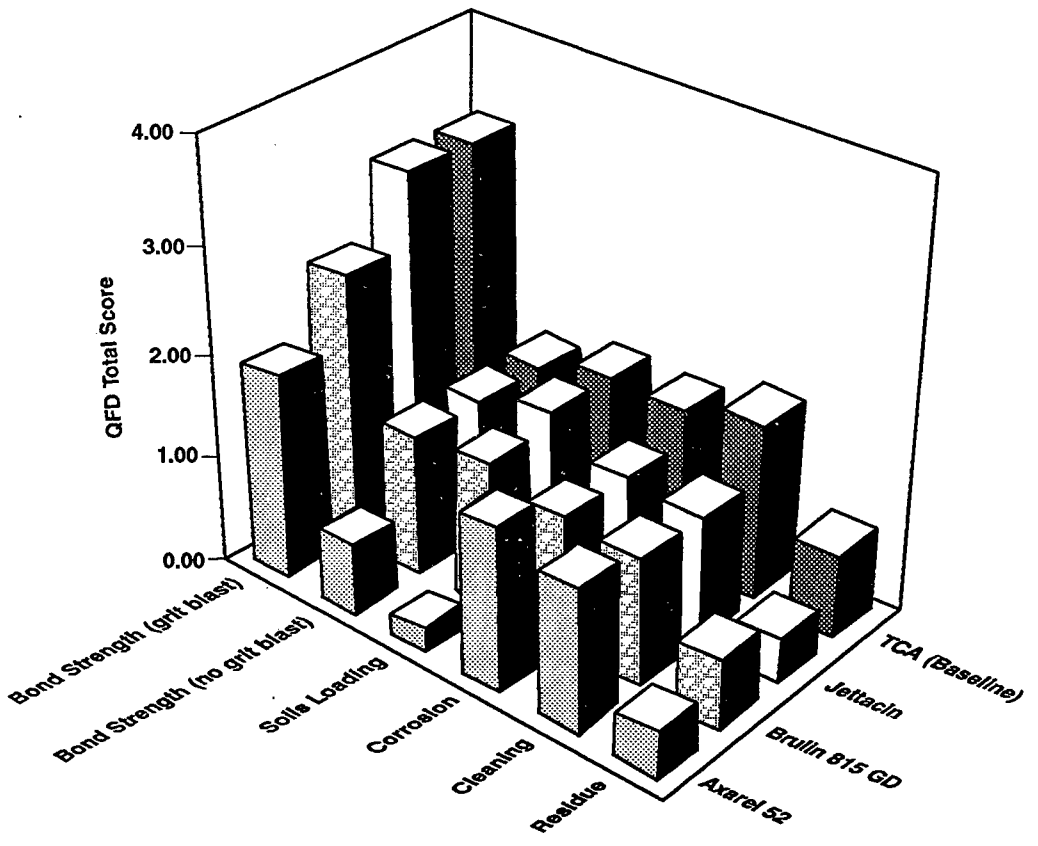

Figure 6. OPTIC Team QFD Results. Down-selection from 5 to 2. (total scores)

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For each cleaner:

Test	A	B	C	D	E	F
1	+	+	+	+	+	+
2	+	+	+	−	+	−
3	+	+	−	+	−	−
4	+	+	−	−	−	+
5	+	−	+	+	−	−
6	+	−	+	−	−	+
7	+	−	−	+	+	+
8	+	−	−	−	+	−
9	−	+	+	+	−	+
10	−	+	+	−	−	−
11	−	+	−	+	+	−
12	−	+	−	−	+	+
13	−	−	+	+	+	−
14	−	−	+	−	+	+
15	−	−	−	+	−	+
16	−	−	−	−	−	−

Variables	High Level (+)	Low Level (−)
A = Cleaner Temperature	135°F ± 5°	70°F ± 5°
B = Cleaner Concentration	30%	10%
C = Wash Density	2.3 gpm	1.5 gpm
D = Wash Pressure	250 ± 25 psi	70 psi
E = Rinse Pressure	250 ± 25 psi	70 psi
F = Lab Location	HSO	S&E
G = Cleaner	Jettacin	Brulin

Figure 7. Design of Experiments, 6 Variables (2 levels)

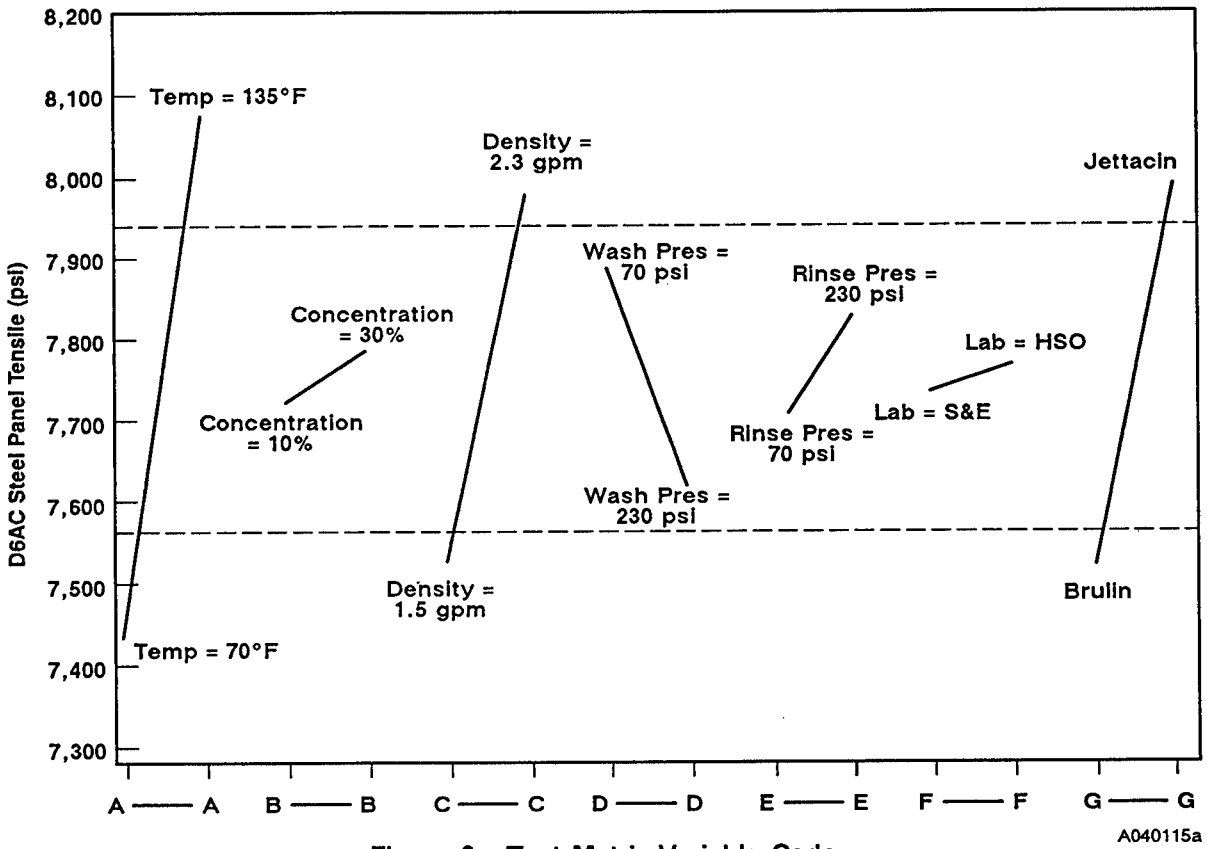

Figure 8. Test Matrix Variable Code

A DESIGN OF EXPERIMENTS TEST TO DEFINE CRITICAL SPRAY CLEANING PARAMETERS FOR BRULIN 815 GD AND JETTACIN CLEANERS

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ABSTRACT

Experimental design testing was conducted to identify critical parameters of a aqueous spray process intended for cleaning solid rocket motor metal components (steel and aluminum). A two-level, six-parameter, fractional factorial matrix was constructed and conducted for two cleaners, Brulin 815 GD and Diversey Jettacin. The matrix parameters included cleaner temperature and concentration, wash density, wash pressure, rinse pressure, and dishwasher type. Other spray parameters: nozzle stand-off, rinse water temperature, wash and rinse time, dry conditions, and type of rinse water (deionized) were held constant. Matrix response testing utilized discriminating bond specimens (fracture energy and tensile adhesion strength) which represent critical production bond lines. Overall, Jettacin spray cleaning was insensitive to the range of conditions tested for all parameters and exhibited bond strengths significantly above the TCA test baseline for all bond lines tested. Brulin 815 was sensitive to cleaning temperature, but produced bond strengths above the TCA test baseline even at the lower temperatures. Ultimately, the experimental design database was utilized to recommend process parameter settings for future aqueous spray cleaning characterization work.

INTRODUCTION

Thiokol Space Operations has been on an aggressive schedule to select non-ODC cleaners to replace the 685 thousand pounds of 1,1,1-trichloroethane currently used annually in two main vapor degreasers. Both immersion and spray processes were evaluated. For this particular application, it was determined that spray cleaning was not only superior, but also more practical. Two cleaners emerged from over 150 tested: Brulin 815 GD and Diversey Jettacin. Once the cleaner selection had been narrowed to these two, a process optimization test was defined. It was determined that a Design-Of-Experiments (DOE) matrix should be used to meet the following objectives:

- Identify critical aqueous spray cleaning process parameters
- Determine operating ranges of the matrix parameters
- Specify the cleaning process for remaining development work

TABLE 1 - TEST MATRIX

6 VARIABLES (2 LEVELS)

For Each Cleaner:

Test	A	B	C	D	E	F
1	+	+	+	+	+	+
2	+	+	+	-	+	-
3	+	+	-	+	-	-
4	+	+	-	-	-	+
5	+	-	+	+	-	-
6	+	-	+	-	-	+
7	+	-	-	+	+	+
8	+	-	-	-	+	-
9	-	+	+	+	-	+
10	-	+	+	-	-	-
11	-	+	-	+	+	-
12	-	+	-	-	+	+
13	-	-	+	+	+	-
14	-	-	+	-	+	+
15	-	-	-	+	-	+
16	-	-	-	-	-	-

Variables	High Level (+)	Low Level (-)
A=Cleaner Temperature	135° ± 5° F	70° ± 5° F
B=Cleaner Concentration	30%	10%
C=Wash Density	2.3 gpm	1.5 gpm
D=Wash Pressure	250 ± 25 psi	70 psi
E=Rinse Pressure	250 ± 25 psi	70 psi
F=Lab Location	HSO	S&E
G=Cleaner	Jettacin	Brulin 815 GD

Wash density = (Flow rate x Cleaning time)/Area of surface cleaned

Time and area were held constant; thus, wash density is expressed in terms of flow rate.

Huntsville tests were conducted by Thiokol Huntsville Space Operations. Utah tests were conducted by Thiokol Science and Engineering.

The matrix was a six-parameter, two-level fractional factorial which was executed once for each cleaner. The matrix, process parameters and the test levels are shown in Table 1. There was concern that division of the matrices at two laboratory locations may compromise the experimental control of each matrix; particularly, because the two labs utilized dissimilar dishwashers (Table 2). However, the effort was divided with confidence that experimental consistency could be achieved because:

- Historically, Huntsville and Utah bond property databases have correlated closely

- Utilization of two different dishwasher systems would demonstrate aqueous cleaning process robustness
- Both labs used the same lot of adhesive for bond specimen assembly
- Lab location was selected as a process variable

The final selection of variables included cleaner temperature, cleaner concentration, wash density, wash pressure, rinse pressure and lab location. Other parameters, deemed less critical through technical discussions, were held constant as indicated in Table 2.

TABLE 2 - CONSTANT PARAMETERS

PARAMETER		HSV	Utah
Nozzle Stand-off Distance		6 ± 1 inches	8 ± 1 inches
Wash Time		9 minutes	2-3 minutes
Rinse Water Temperature		65 ± 5°F	65 ± 5°F
Rinse Time		10 minutes	2-3 minutes
Dry Conditions		Missile grade, ambient air	Clean room grade, ambient air
Contaminants	(Steel)	Magnaflux + Diala oil + grease	Magnaflux + Diala oil + grease
	(Alum)	Grease	Grease
Water		Deionized	Deionized

NOTE: Cleaning and rinsing times and stand-off distances were corrected for Huntsville and Utah "dishwasher" differences. The Huntsville system configured the specimens horizontally on a rotating table under fixed nozzles. The Utah system configured the specimens vertically on a rack with oscillating nozzles.

RESULTS

Response tests for these matrices are listed as follows:

- Tensile Adhesion Strength (Bond line = EA 913 Adhesive/Steel and EA 913 Adhesive/Aluminum)
- Fracture Energy (Bond line = EA 913 Adhesive/Steel and EA 913 Adhesive/Aluminum)
- Surface Energy Analysis (Contact Angle)
- Surface Chemistry Analysis (ESCA/SIMS/Auger)
- OSEE Analysis

The bond lines represent actual production bond systems and are typically used for screening tests because of their sensitivity to contamination and other substrate characteristics. In addition, the fracture energy and tensile adhesion tests function well in differentiating substrate treatment effects. Essentially, there is much information to be gained from the analysis because of the response tests.

The discussion of the paper is limited to the bond line data analysis because the results of the other tests corresponded closely with the bond line data. Thus, the conclusions of the bond line data are analogous to the other tests. The TCA (1,1,1-trichloroethane) baseline data cited in this paper was processed differently than current RSRM production hardware is processed. In order to maintain similarity with the aqueous cleaned specimens, the TCA baseline panels did not receive a post clean or pre-bond grit

blast. A grit blast after aqueous cleaning would prevent discrimination between critical parameters by masking their effect; therefore, for testing purposes it was omitted.

The data from the sixteen runs of each matrix, shown in Figures 1-4, were processed through a least-squares regression analysis which assessed the main effects of high/low parameter variation on each response. In addition, the two-parameter interactive effects were calculated. Parameter variation was regarded significant to the response when the high-to-low change cause the value of response measurement to exceed experimental variability (outside the error bands). A parameter was considered critical if the main effects were statistically significant at a 95% confidence level. Table 3 shows the interactive parameters. The analysis also combined the results of the Brulin 815 and Jettacin matrices, which created a seventh parameter, cleaner. The analyses are plotted in Figures 5 to 9. The charts plot the measured response against each parameter (high and low level). The dotted lines (error bands) show experimental variability. The following paragraphs discuss the results for each bond line response tested. It is important to note that all of the main response average bond values are significantly above the baseline TCA standard database that has been constructed during the ODC testing.

Tensile Adhesion Strength (EA 913/Steel). Figure 5, the main effects chart, shows that cleaner temperature, wash density, and choice of cleaner are critical to the tensile adhesion strength of this bond line. On the average, raising the cleaner temperature to 135 °F increases the tensile adhesion strength by 640 psi. Increasing the wash density to 2.3 gpm also raises the tensile adhesion strength by 455 psi. Finally, cleaning with Jettacin results in a tensile adhesion strength of 476 psi higher than Brulin 815.

There are three significant two-parameter interactions of interest shown in Figure 6. This chart is a composite that plots tensile adhesion strength against cleaner temperature at the two wash densities for both cleaners. The data show that high temperature cleaning is independent of wash density variation. Also, high wash density cleaning is independent of cleaner temperature variation. While the Brulin 815 GD requires the high temperature setting to match the bond strengths of the Jettacin, even the low temperature setting produces bond strengths above the TCA test baseline of 6300 psi. Both cleaners are essentially equivalent at either a high wash density or high temperature setting.

Tensile Adhesion Strength (EA 913/Aluminum). The main effects chart, Figure 7, for this response test analysis reveals that cleaner temperature and type are critical. Higher temperature cleaning improved tensile adhesion strength by 1,134 psi. Also, Jettacin cleaning resulted in a 1,054 psi higher average bond strength than Brulin 815. Again, these effects was primarily due to the sensitivity of Brulin 815 at the lower temperature. The low parameter values for the 70° F and Brulin 815 cleaned specimens, around 6600 psi, was still 1500 psi above the TCA baseline of 5100 psi for this bond line.

Fracture Energy (EA 913/Steel). The main effects chart for this response property is plotted in Figure 8. This chart shows a critical effect from cleaner temperature, test lab, and cleaner type. Variation in cleaner temperature from 70 °F to 135 °F increases fracture energy from approximately 12.5 to 16.0 in•lbs/in^2. Similar to Figure 6, the two-parameter interaction analysis showed that this effect was due to Brulin 815 cleaning sensitivity to low temperature. Again, Jettacin performed essentially the same at the two ends of the cleaner temperature spectrum. All of the average bond strengths were significantly above the TCA baseline of 2.0 in•lbs/in^2.

Fracture energy also demonstrated significant sensitivity to lab location/dishwasher type. Cleaning in the Huntsville dishwasher reduced fracture energy by 2.8 in•lbs/in^2. The sixteen runs of cleaning in the Huntsville dishwasher provided an average fracture energy of 12.8 in•lbs/in^2, which is substantially higher than nominal baseline cleaning process, TCA vapor degreasing, values.

The main effects analysis also showed that fracture energy effected by the type cleaner. Jettacin cleaning provides a fracture energy of 2.0 in•lbs/in^2 greater than Brulin 815.

Fracture Energy (EA 913/Aluminum). This response demonstrated significant dependance on cleaner temperature due to Brulin 815 temperature sensitivity (Figure 9). The higher cleaner temperature increased the fracture energy from approximately 8.8 to 14.0 in•lbs/in^2. As with the other bond lines, even the low values are significantly above the TCA baseline values of 0.4 in•lbs/in^2 established during the ODC testing program.

Similar to the steel fracture energy data, lab location strongly affected this response. There was a delta 2.6 in•lbs/in^2 decrease in fracture energy when the specimens were cleaned in the Huntsville dishwasher.

Wash density demonstrated main effects on this property. Cleaning at the higher wash density improved fracture energy by 2.1 in•lbs/in^2.

Table 3 itemizes the significant and interactive effects of each of the parameters of each design of experiments matrix.

CONCLUSION

The individual parameter recommendations can be found in Table 4. To summarize, the data analysis leads to the following conclusions:

- Aqueous spray-in-air cleaning produced statistically significant higher bond properties than the baseline process, TCA vapor degreasing.
- Jettacin cleaning was relatively insensitive to process parameter variation.
- Brulin 815 cleaning was sensitive to variation of cleaner temperature, higher temperature provided higher bond strengths. However, the lower temperatures still provided bond strengths above the TCA baseline.
- Fracture energy sensitivity to the lab location parameter is probably due to differences in the dishwashers.
- Bond properties were insensitive to variation in wash pressure, rinse pressure, and cleaner concentration.
- Aqueous spray cleaning is a robust process in terms of the parameters tested.
- Because all bond line responses were significantly above the testing TCA baseline, factors other than bond strength (recyclability, OSHA, environmental) will play a more significant role in cleaner selection.

Other conclusions that were drawn from this testing included:

- The rinse and dry processes require more definition.
- Aqueous cleaning will effect OSEE readings.
- Black light inspections should be quantified with % clean and intensity of fluorescence rather than pass/fail.
- NVR should be performed concurrent with all testing.

During a mid-scale test a high degree of foaming was noted from both of these cleaners. The two cleaners tested are foaming cleaners intended for immersion type cleaning operations. Nearly identical non-foaming cleaners are available. It has not yet been decided whether work will continue with these foaming cleaners or their non-foaming "sister" cleaners.

ACKNOWLEDGEMENTS

This effort was accomplished as the result of a collaboration of many individuals. The following people played significant roles in this work: R.K. Jones, A.S. Allen, K.J. Schulte, D.E. Hutchens, H.D. Burns, P.A. Doan, T.N. Thornton, J.R. Newton, B. O. Olsen, J.A. Stevenson and R.L. Hansen.

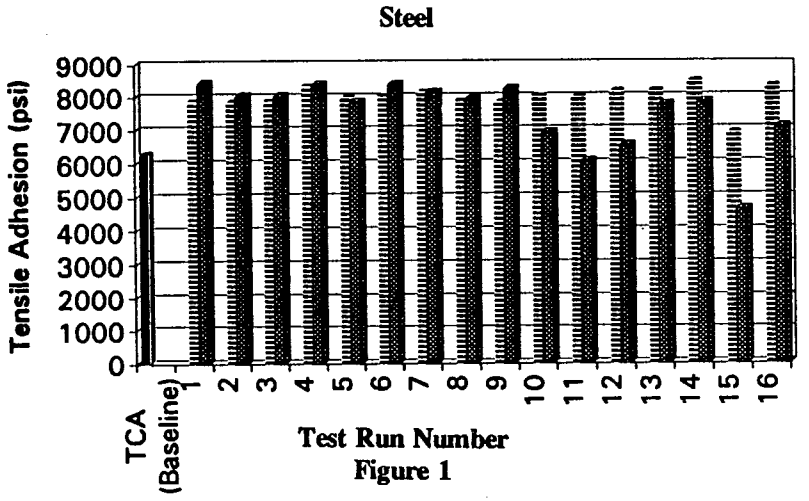
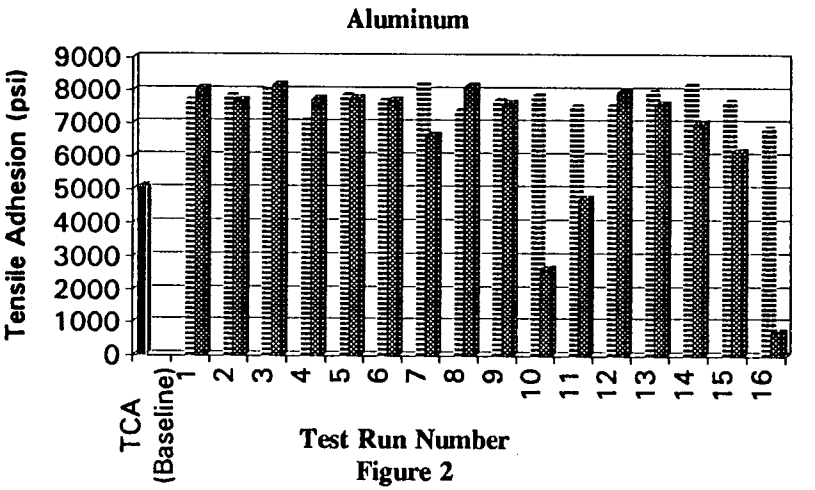


Figure 1



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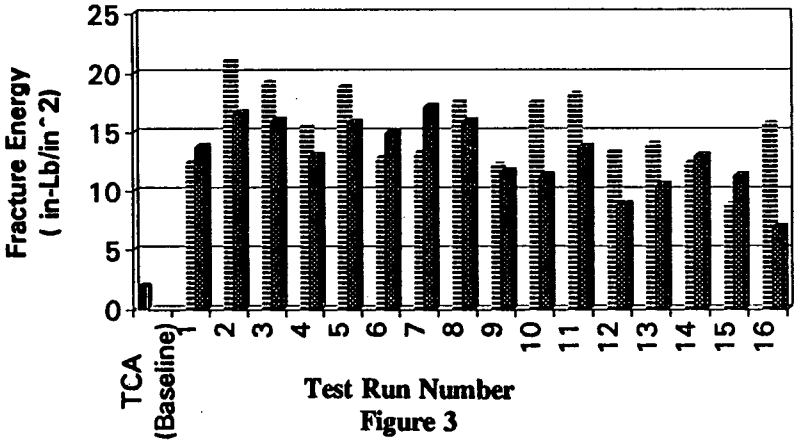

Figure 3

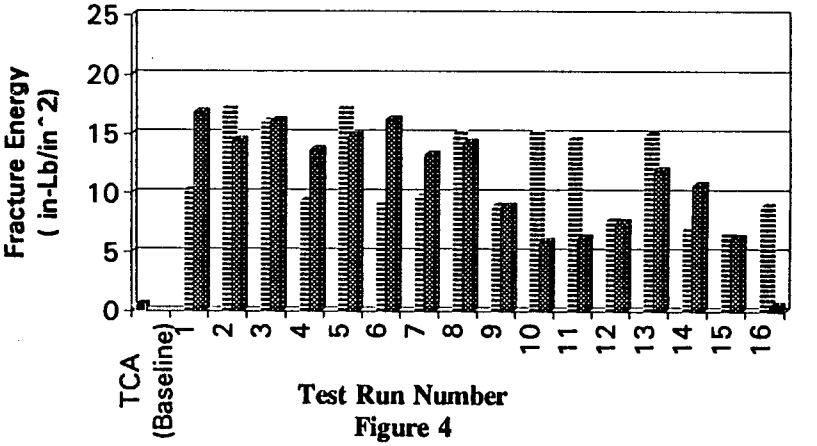

Figure 4

Table 3 - ETP G Table I Significant Main Effects and Interactions

Response Material/ Test	A Cleaner Temperature	B Cleaner Concentration	C Wash Density	D Wash Pressure	E Rinse Pressure	F Lab Location	G Cleaner
D6AC/ Tensile Adhesion	significant AG interaction AC interaction	not sig	significant CA interaction CG interaction	not sig	not sig	not sig	significant GA interaction GC interaction
D6AC/Fracture Energy	significant AG interaction	not sig BF interaction	not sig	not sig DG interaction	not sig	significant FG interaction FB interaction	significant GA interaction GD interaction GF interaction
Alum/Tensile Adhesion	significant AG interaction AF interaction	not sig	not sig	not sig	not sig	not sig FA interaction	significant GA interaction
Alum/Fracture Energy	significant AG interaction	not sig	significant	significant DF interaction	not sig	significant FD interaction FG interaction	not sig GA interaction GF interaction
D6AC panel/ConScan (post clean)	significant	not sig	not sig	not sig	not sig	significant	not sig
D6AC TDCB/ConScan (post clean)	significant AG interaction AF interaction	significant	not sig	not sig	not sig	significant FA interaction	significant GA interaction
D6AC panel/ConScan (delta pre-post clean)	significant	not sig	not sig	not sig	not sig	significant	not sig
D6AC TDCB/ConScan (delta pre-post clean)	significant AB interaction	significant BA interaction	not sig CG interaction	not sig	not sig	significant	significant GC interaction

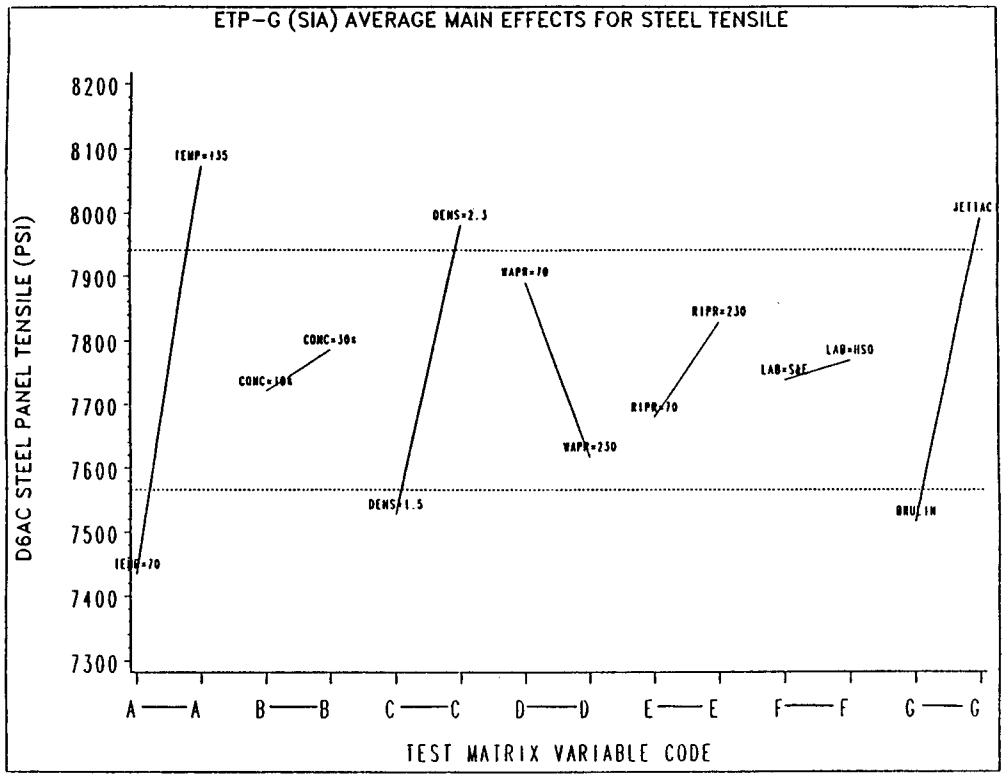

Figure 5

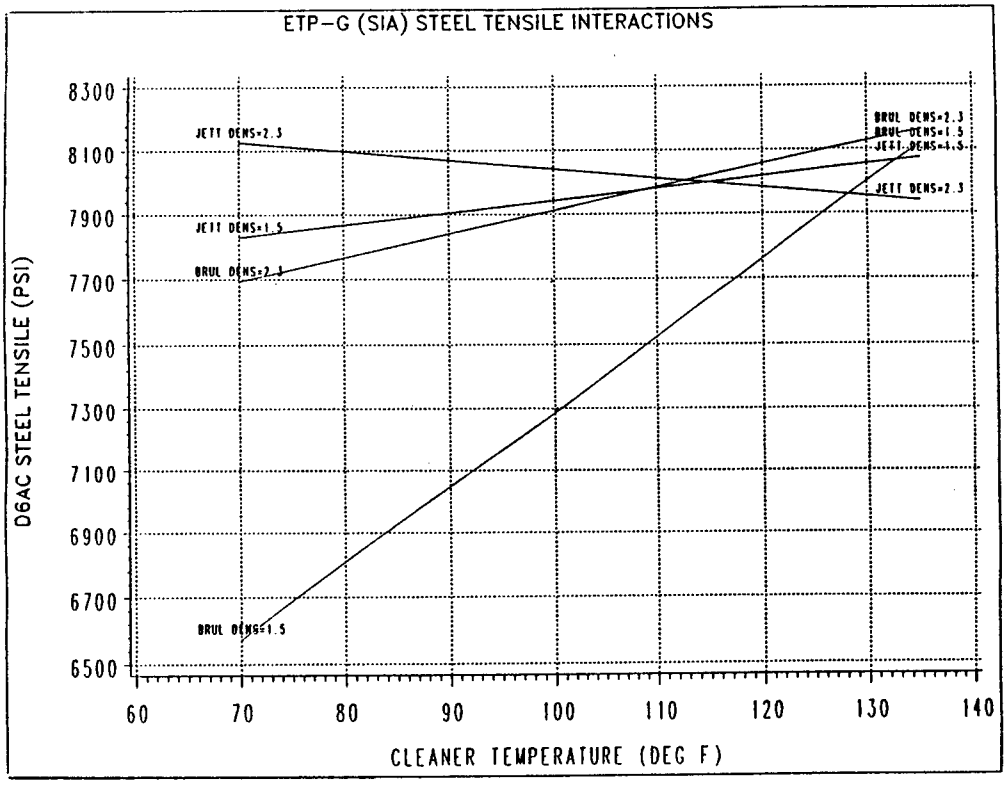

Figure 6

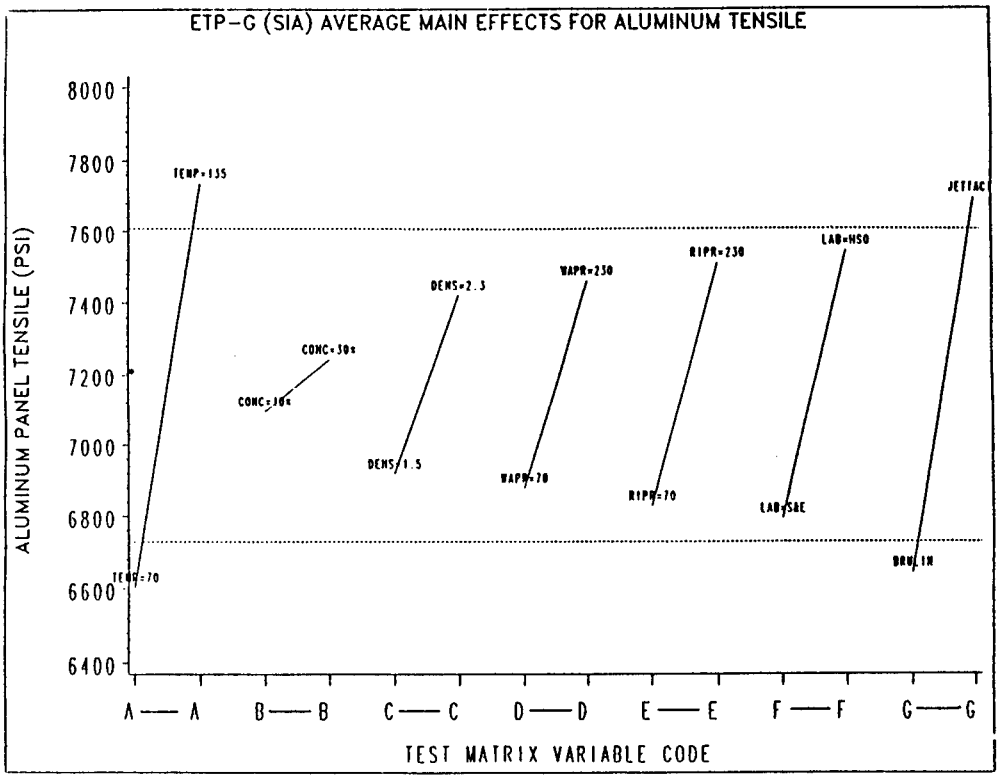

Figure 7

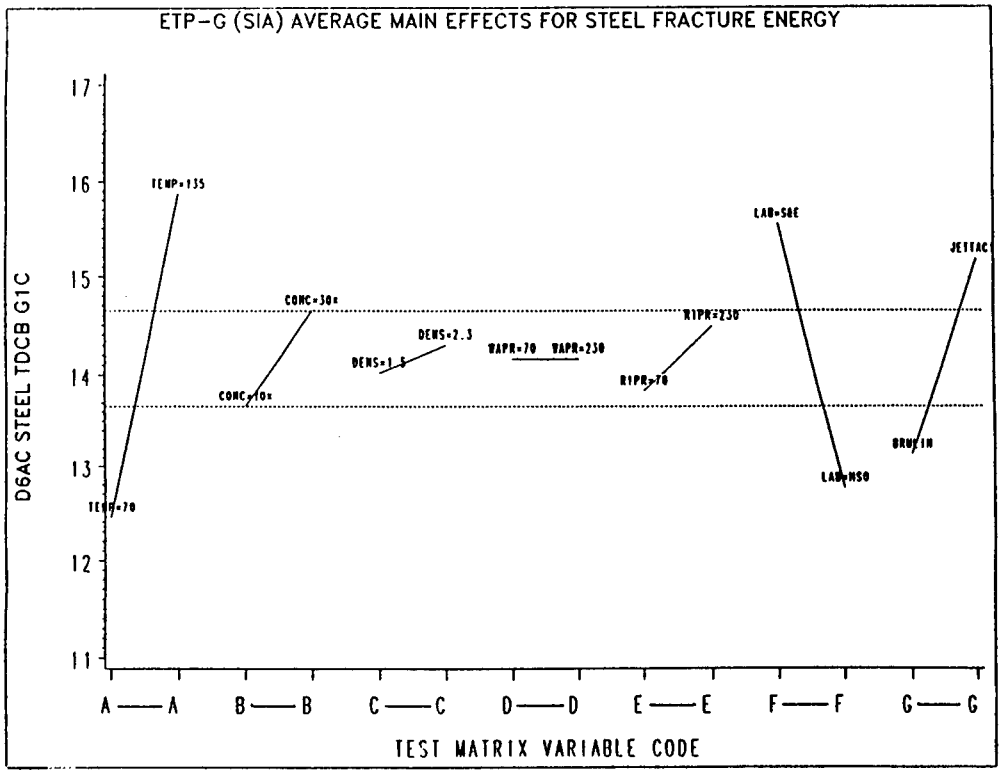

Figure 8

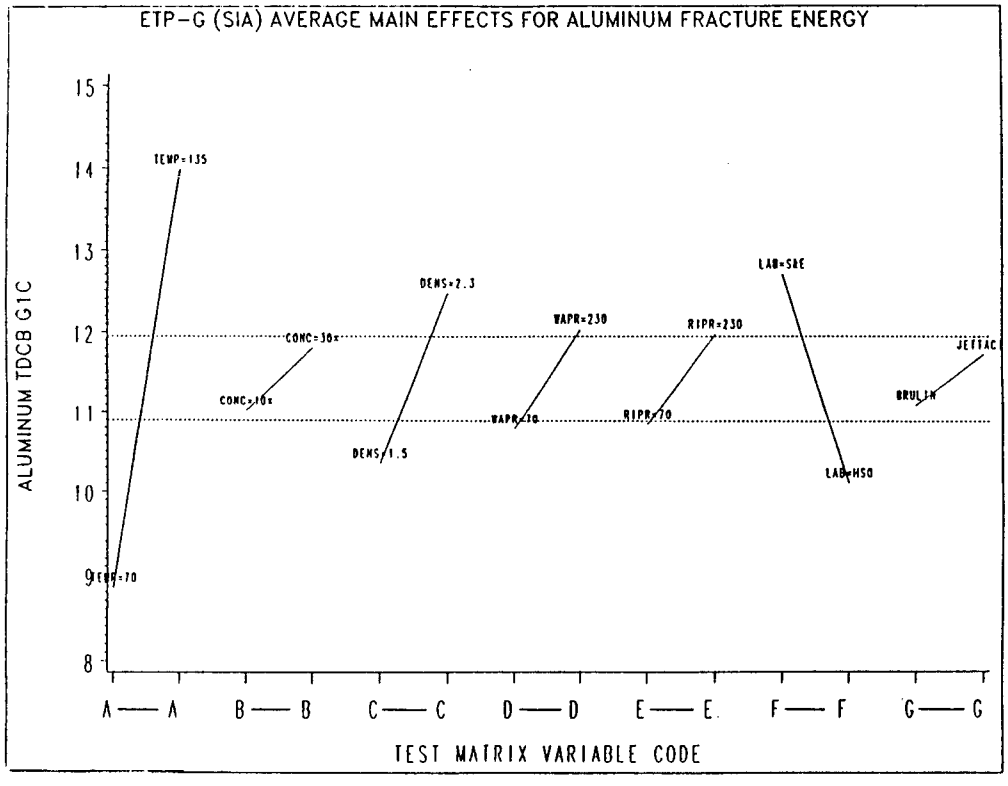

Figure 9

Table 4 Parameter Recommendations	
Parameter	Recommendation
(A) Cleaning Temperature	Fix temperature at 70° F for Jettacin, 135° F for Brulin 815 GD. No further testing needed.
(B) Cleaner Concentration	Fix at 10% for subsequent cleaning test and 15% for corrosion testing to allow for worst case.
(C) Wash Density	Fix at 2.5 gpm in subscale testing. Use comparable flow densities (gal/in^2) in full-scale facility.
(D) Wash Pressure	Fix at 100 psi. No further testing needed.
(E) Rinse Pressure	Fix at 100 psi. No further testing needed.
(G) Cleaner	Use Quality Function Deployment (QFD) method.
Potable vs Deionized Wash Water	Use deionized water.
Potable vs Deionized Rinse Water	Use deionized water.
Rinse Process	Further testing recommended.
Drying Process	Further testing recommended.

Degradation of TCE Using Sequential Anaerobic Biofilm and Aerobic Immobilized Bed Reactor

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ABSTRACT

Bacteria capable of degrading Trichloroethylene (TCE) were isolated from contaminated wastewaters and soil sites. The aerobic cultures were identified as *Pseudomonas aeruginosa* (four species) and *Pseudomonas fluorescens*. The optimal conditions for the growth of aerobic cultures were determined. The minimal inhibitory concentration values of TCE for *Pseudomonas* sps. were also determined. The aerobic cells were immobilized in calcium alginate in the form of beads. Degradation of TCE by the anaerobic and dichloroethylene (DCE) by aerobic cultures was studied using dual reactors - anaerobic biofilm and aerobic immobilized bed reactor. The minimal mineral salt medium saturated with TCE was pumped at the rate of 1 ml per hour into the anaerobic reactor. The MMS medium saturated with DCE and supplemented with xyelens and toluene (3 ppm each) was pumped at the rate of 1 ml per hour into the fluidized air-uplift-type reactor containing the immobilized aerobic cells. The concentrations of TCE and DCE and the metabolites formed during their degradation by the anaerobic and aerobic cultures were monitored by GC. The preliminary study suggests that the anaerobic and aerobic cultures of our isolates can degrade TCE and DCE.

INTRODUCTION

Trichloroethylene (TCE) is a volatile chlorinated organic compound which is used extensively as a solvent and degreasing agent (Storck, 1987). TCE and other chlorinated wastes have been shown to migrate through soils from disposal sites and threaten groundwater aquifers across the nation (Folsom *et al.*, 1990). The U.S. Environmental Protection Agency has classified TCE as a priority pollutant on the basis of its ubiquity, suspected carcinogenicity and propensity to be anaerobically degraded to vinyl chloride in groundwater (U.S. Environmental Protection Agency, 1980). Due to its widespread contamination of soil and water and its potential health threat, TCE has received much attention recently.

The application of bioremediation to solve environmental problems has increased tremendously in the last 15 to 20 years (Wackett and Gibson, 1988; Tsien *et al.*, 1989; Zylstra *et al.*, 1989; Harker and Kim, 1990; Folsom *et al.*, 1990; Folsom and Chapman, 1991; Malachowsky *et al.*, 1994). Several pure and mix cultures which possess the ability to act on TCE have been isolated and characterized from different ecosystems contaminated with these compounds (Fliermans *et al.*, 1988; Baek, N.H., and P.R. Jaffe, 1989; Folsom *et al.*, 1990; Folsom and Chapman, 1991; Alvarez-Cohen *et al.*, 1992; Malchowsky *et al.*, 1994). Bouwer and McCarty (1983) reported that the chlorinated alkenes may be converted anaerobically by reductive dehalogenation to known carcinogens such as vinyl chloride. Similarly tropic enrichment cultures can degrade TCE aerobically in the presence of certain aromatic compounds such as toluene or phenol (Nelson *et al.*, 1987). Keeping the above ongoing research in mind, a preliminary study was carried out to study the degradation of TCE by anaerobic and aerobic cultures in continuous bioreactors.

MATERIALS AND METHODS

Chemicals

Trichloroethylene, Dichloroethylene of 99% purity were purchased from Aldrich Chemical Company. Toluene and xylenes were purchased from Curtin Matheson Scientific Company, Kennesaw, GA. The gases were puchased locally. All other chemicals were obtained from Sigma Chemical Company Co., St. Louis, MO.

Media and Culture Conditions

The sterile minimal minaral salt (MMS) medium (pH 7.0) used for the isolation of aerobic microorganisms capable of degrading TCE in the presence of, xylenes and toluene contained the following (g/L): K_2HPO_4, 4.3; KH_2PO_4, 3.4: $MgCl_2.H_2O$, 0.3, NH_4Cl, 1.0, the medium was amended with 0.5 ml of the trace element solution containing the following (mg/L): $MnCl_2.4H_2O$, 1.0; $FeSO_4.7H_2O$, 0.6; $CaCl_2.H_2O$, 2.6; $NaMoO_4.\ 2H_2O$, 6.0.

MMS plates were prepared by adding 15 g of agar (Difco Laboratories, Detroit, MI) to 1 liter of the medium. Unless otherwise stated, the microorganisms were grown in the medium containing xylenes and toluene as the sole source of carbon and energy with trace amount of TCE.

Isolation and Identification of Cultures

The bacteria capable of degrading trichloroethylene in the presence of xylene and toluene were isolated from contaminated soil and water samples collected from industrial sites. A 1:10 dilution of each sample was made with sterile MMS medium and the suspension was incubated at room temperature for 1 h. One milliliter of the suspension was inoculated into sterile Pyrex test tubes containing 9 ml of the medium supplemented with different concentrations of TCE (ranging from 25 ppm to saturation concentration) and xylenes and toluene (3 ppm each). The tubes were then incubated at 25°C for 7 days and examined for turbidity. After 5 to 7 transfers, the turbid samples were streaked onto plates containing TCE and xylenes and toluene as sources of carbon and energy. Colonies that grew on agar plates containing TCE and xylenes and toluenes but not on control plates were then selected for identification.

Identification of the Bacteria

Identification of bacteria was based on the classification scheme described in *Bergey's Manual of Systematic Bacteriology* (Palleroni, 1984). Tests were performed as described in the manual (Palleroni, 1984) or as described by Smibert and Krieg(1981). Subsequently, the isolates were biochemically characterized by using commercially available diagnostic kits from the API 20E test kit (Analytab Products, Plainview, N.Y.). The identification was reconfirmed using Biolog MicroID system in Biology Department, University of Alabama, Birmingham, AL.

Growth Medium for Anaerobic Cultures

The basic growth medium for anaerobic cultures contained the following (mg/L): $(NH_4)_2HPO_4$, 80; NH_4Cl, 1000; K_2HPO_4, 200; NaCl, 10; $CaCl_2$, 10; $MgCl_2$, 50; $CoCl_2.6H_2O$, 1.5; $CuCl_2.2H_2O$ 0.2; $Na_2MoO_4.H_2O$, 0.23; $ZnCl_2$, 0.19; $NiCoO_4.6H_2O$, 0.2; $FeSO_4.7H_2O$, 1.0; $AlCl_3.6H_2O$,0.4; H_3BO_3, 0.38; Biotin, 0.02; Folic acid, 0.02; Pyridoxine-HCl, 0.1. Riboflavin, 0.05; Thiamine, 0.05; Nicotinic acid, 0.05; Pathothenic acid, 0.05; Vitamin B_{12}, 0.0001; p-aminobenzoic acid, 0.2 and Resazurin, 1.0; supplimented with 0.5% carbon source (Glucose) and saturated with TCE.

Optimal Conditions

The optimal temperature for the growth of the bacteria was determined by inoculating 50 ml of the MMS medium containing TCE and 3 ppm of xylenes and toluene into 250 ml Pyrex flasks, which were then incubated at 5, 15, 25, 35, 45, and 55°C. Growth was monitored after 72 h of incubation. The optimal pH was determined by inoculating the medium adjusted to pH 3.0 to 9.0. The inoculated cultures were then incubated at 25°C. The growth was measured after 72 h of incubation.

Minimal Inhibitory Concentrations (MIC)

Since TCE is highly toxic and can not be used as a carbon source, it is necessary to determine the levels at which the experiments could be carried out without greatly affecting the organisms. The minimal inhibitory concentration values of TCE for the isolates of *Pseudomonas* sp.s were determined by conducting the experiments in 100 ml Qorpak bottles filled with MMS medium supplemented with different concentrations of TCE (10 - 2500 ppm) and 3 ppm of xylenes and toluene as a carbon source and also inducers of mono- and dioxyganase enzymes. The medium was inoculated with 1 ml of cell suspension (A_{660} 1.0) of xylenes- and toluene-utilizing cultures. The experiment was run at 25°C for 120 h and the MIC values of TCE for the isolates were determined by monitoring the bacterial growth. The MIC is defined as the lowest concentration of the inhibitor above which no growth is observed.

Immobilization of Aerobic Cultures in Alginate

Aerobic mix culture consortium was harvested from the MMS medium supplemented with constant saturation of toluene and xylenes at exponential phase by continuous centrifugation at 15,000 x g and the pellet was washed three times with 25 mM phosphate buffer. The cell paste (300-400 mg/100 ml) suspended in 100 ml of 0.85% normal saline was mixed with 100 ml of sterile 4% sodium alginate. The alginate-cell mixture was extruded dropwise through a 25-gauge needle from a height of about 20 cm into cold 0.2 M $CaCl_2$. Each drop was hardened into a bead containing entrapped cells. The beads were further hardened by stirring them in $CaCl_2$ for 30 min and stored at 5°C for 24 h.

Optimal Conditions

Maximum growth was obtained after 120 h of incubation at 25-30°C. No growth was observed at 55°C. The isolate was found to grow well between pH 6.0 and 7.0 . However, maximum cell growth was obtained at pH 6.5 and 7.0. No growth was observed below pH 5.0 or above pH 7.0.

Immobilization

The typical yield following immobilization of cells with alginate was about 0.6-0.8 g of beads/ml of cell-alginate suspension. Individual beads had a diameter of 1-2 mm and an average wet and dry wt of 13 and 0.6 mg, respectively. At the time of immobilization, each bead contained approximately 1.5-2.5 x 10^8 viable cells, as determined by pour plate method of disrupted beads (O'Reilly and Crawford, 1989).

Minimal Inhibitory Concentration Values of TCE

The minimal inhibitory concentration values of TCE for *Pseudomonas* sp.s are presented in the Table 1. The MIC values of *Pseudomonas aeruginosa* #II and *Pseuodmonas aeruginosa* #IV were found to be 1024 ppm followed by *Pseudomonas aeruginosa* # III. The MIC values for both *Pseudomonas aeruginosa* # I and *Pseudomonas* fluorescens were found to be 32 ppm. (Table 1).

Table 1. Minimal Inhibitory Concentration Values of TCE for *Pseudomonas* Sp.s

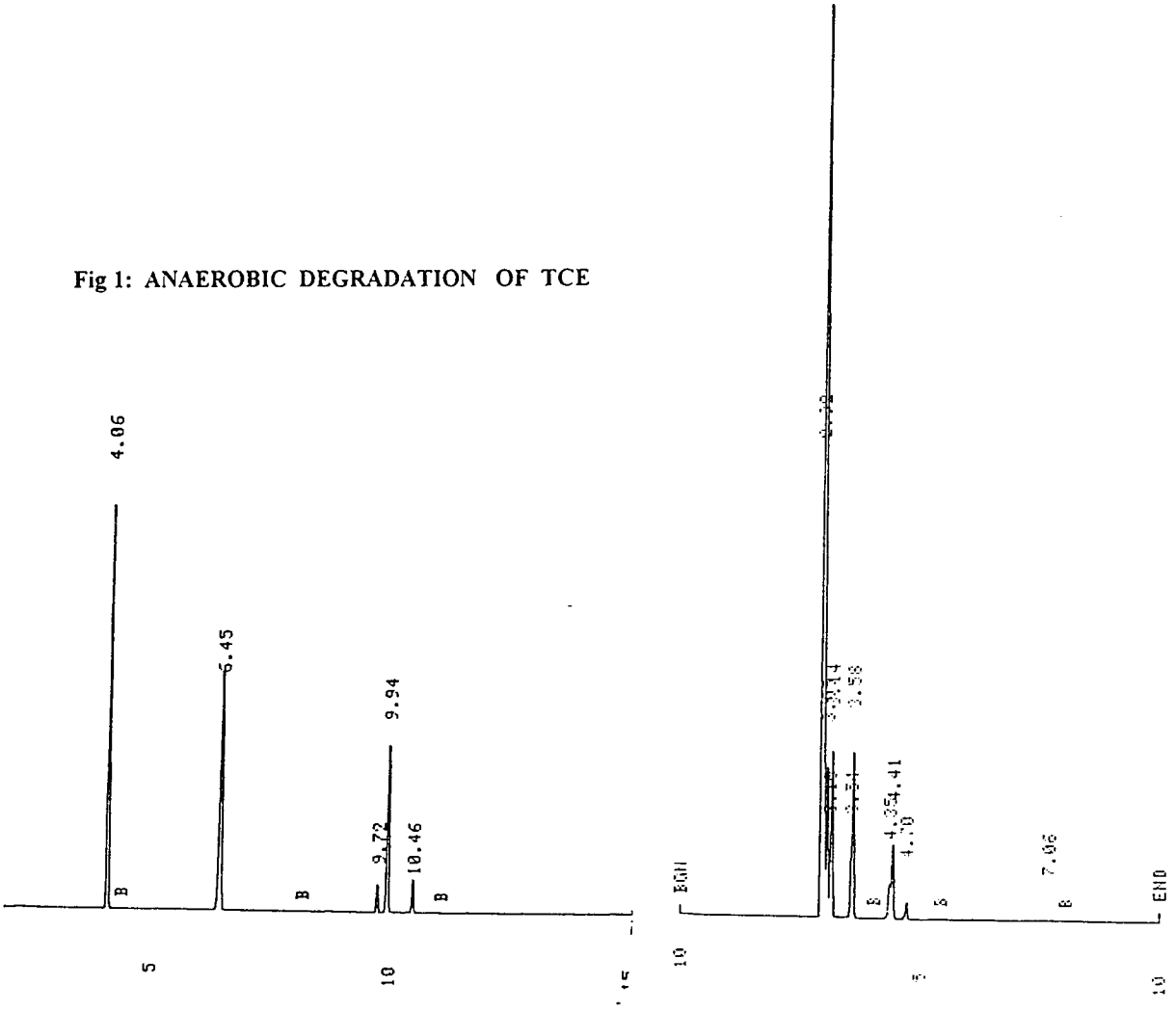
Culture #	Name of the Culture	MIC Value [ppm]
1	Pseudomonas aeruginosa	32
2	Pseudomonas aeruginosa	1024
3	Pseudomonas aeruginosa	256
4	Pseudomonas aeruginosa	1024
5	Pseudomonas fluorescens	32

Degradation of TCE and DCE

Figure 1 indicate the degradation of TCE by the anaerobic cultures. The anaerobic bacterial cells were able to degrade or dechlorinate TCE into different compounds (Fig.1) which were detected in GC. Figure 2 shows that the immobilized cells of aerobic mix cultures were able to degrade DCE. The products and concentrations of TCE and DCE have not been identified and quantified in the present investigation.

Fig 2: DEGRADATION OF DCE BY IMMOBILIZED CELLS OF *PSEUDOMONAS* Sps.

Fig 1: ANAEROBIC DEGRADATION OF TCE



DISCUSSION

Trichloroethylene (TCE), an Enviornmental Protection Agency Priority Pollutant, is widespread in the environment and relatively resistant to biodegradation in soil and the subsurface. Under aerobic conditions, TCE is usually cometabolized and thus requires the presence of a cosubstrate such as methane, ammonia, toluene, xylene. Nelson *et al.* (1988), Little *et al.*(1988), and Arciero *et al* (1989) have shown that toluene-, methane-, and ammonia-oxidizing bacteria, respectively, biodegrade TCE. It is genetically evident that toluene dioxygenase (Nelson *et al.*,1988; Wackett and Gibson, 1988) and toluene monooxygenase (Winter *et al.*, 1989) are biocatalysts active in TCE degradation (Nelson *et al.*, 1988). The results from the present study indicate the anaerobic dechlorination of TCE and degradation of DCE by immobilized cells of aerobic cultures.

The studies on the confirmation of TCE and DCE degradation and the identification and quantification of metabolites formed during their degradation are in progress. The optimization of degradation of TCE using various carbon soruces such as glucose, formate, succinate, corn syrups, etc., is also being carried out. The work on the degradation of DCE in the presence of various concentrations of xylenes and toluene which act as inducers of mono- and dioxygenases is also in progress.

ACKNOWLEDGEMENT

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REFERENCES

Alvarez-Cohen, L., P.L. McCarty, E. Boulygina, R.S. Hanson, G.A. Bursseau, and H.C. Tsien, 1992. Characterization of a methane-utilizing bacterium from a bacterial consoritum that rapidly degrades trichloroethylene and chloroform. ***Appl. Enviorn. Micorbiol.***, **58**:1886-1893.

Arciero, D., T.Vannelli, M. Logan, and A.B. Hooper, 1989. Degradation of trichloroethylene by the ammonia-oxidizing bacterium, *Nitrosomonas europaea*. ***Biochem. Biophys. Res. Commun.*** **159**:640-643.

Baek, N.H.,and P.R. Jaffe, 1989. The degradation of trichloroethylene in mixed methanogenic cultures. ***J. Environ. Qual.*** 18:515-518.

Bouwer, E.J., and P.L. McCarty, 1983. Transformation of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. ***Appl. Environ. Microbiol.*** **45**:1286-1294.

Fliermans, C.B., T.J. Phelps, D. Ringelberg, A.T. Mikell, and D.C.White, 1988. Mineralization of trichloroethylene by heterotrophic enrichment cultures. ***Appl. Environ. Micorbiol.*** **54**:1709-1714.

Folsom, B.R., and P.J. Chapman,1991.Performance characterization of a model bioreactor for the biodegradation of trichloroethylene by *Pseudomonas cepacia* G4. ***Appl. Environ. Microbiol.*** **57**: 1602-1608.

Folson, B.R. P.J. Chapman and P.H. Pritchard, 1990. Phenol and trichloroethylene degradation by *Pseudomonas cepacia* G4: Kinetics and interactions between substrates. ***Appl. Environ. Microbiol.*** **56**: 1279-1285.

Harker, A.L. and Y. Kim, 1990. Trichloroethylene degradation by two independent aromatic degrading pathways in *Alcaligenes eutrophus* JMP134. ***Appl. Environ. Microbiol.*** **56**:1179-1181.

Little, C.D., A.V. Palumbo, S.E. Herbes, M.E. Lidstrom, R.L. Tyndall, and P.J. Gilmer, 1988. Trichloroethylene biodegradation by a methane-oxidizing bacterium. ***Appl. Environ. Microbiol.*** **54**:951-956.

Malachowsky, K.J., T.J. Phelps, A.B. Teboli, D.E. Minnikin, and D.C.White, 1994. Aerobic mineralization of trichloroethylene, vinyl chloride and aromatic compounds by *Rhodococcus* species. ***Appl. Environ. Microbiol.*** **60**:542-548.

Nelson, M.J.K., S.O. Montgomery, W.R. Mahaffey, and P.h. Pritchard, 1987. Biodegradation of trichloroethylene and involvement of an aromatic biodegradative pathway. ***Appl. Environ. Microbiol.*** **53**:949-954.

Nelson, M.J., S.O. Montgomery, and P.H. Pritchard, 1988. Trichloroethylene metabolism by microorganisms that degrade aromatic compounds. ***Appl. Environ. Microbiol.*** **54**:604-606.

O'Reilly, K.T., and R.L. Crawford, 1989. Kinetics of *p*-cresol degradation by an immobilized *Pseudomonas* Sp. ***Appl. Environ. Microbiol.*** **130**:866-870.

Palleroni, N.J., 1984. Gram-negative aerobic rods and cocci. In ***Bergey's Manual of Systematic Bacteriology.*** Vol. 1 Edited by N.R. Krieg and J.G. Holt. Williams and Wilkins, Baltimore, pp. 140-149.

Smibert, R.M., and N.R. Krieg, 1981. General Characterization. In ***Manual of Methods for General Bacteriology***. Editd by P. Gerhardt. American Society for Microbiology, Washington,D.C. pp. 409-443.

Storck, W., 1987. Chlorinated solvent use hurt by federal rules. ***Chem. Eng. News,*** **65**:11

Tsien, H.C., Brusseau, G.A., Hanson, R.S., and L.P. Wackett. 1989. Biodegradation of trichloroethylene by *Methylosimus trichosporium* OB3b. ***Appl. Environ. Microbiol.*** **55**:3155-3161.

U.S. Environmental Protection Agency, 1980. Ambient water quality criteria for trichloroethylenes. Publication 440.5-80-073. ***National Technical Information Service,*** Springfield, Va.

Wackett, L.P. and D.T. Gibson, 1988. Degradation of trichloroethylene by toluene dioxygenase in whole-cell studies with *Pseudomonas putida* F1. ***Appl. Environ. Microbiol.*** **54**:1703-1708.

Zylstra, G.J., L.P. Wackett, and D.T. Gibson, 1989. Trichloroethylene degradation by *Escherichia coli* containing the cloned *Pseudomonas putida* F1 toluene dioxygenase genes. ***Appl. Environ. Microbiol.*** **55**:3162-3166.

NON-CFC CLEANING SOLVENTS, PROCESSES AND PARAMETERS 2

CLEANING WITHOUT CHLORINATED SOLVENTS

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ABSTRACT

Because of health and environmental concerns, many regulations have been passed in recent years regarding the use of chlorinated solvents. The Oak Ridge Y-12 Plant* has had an active program to find alternatives for these solvents used in cleaning applications for the past 7 years. During this time frame, the quantity of solvents purchased has been reduced by 92%. The program has been a twofold effort. Vapor degreasers used in batch cleaning operations have been replaced by ultrasonic cleaning with aqueous detergent, and other organic solvents have been identified for use in hand-wiping or specialty operations.

In order to qualify these alternatives for use, experimentation was conducted on cleaning ability as well as effects on subsequent operations such as welding, painting and bonding. Cleaning ability was determined using techniques such as X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) which are capable of examining monolayer levels of contamination on a surface. Solvents have been identified for removal of rust preventative oils, lapping oils, machining coolants, lubricants, greases, and mold releases. Solvents have also been evaluated for cleaning urethane foam spray guns, swelling of urethanes and swelling of epoxies.

Introduction

Recently many regulations have come to pass regarding the use of chlorinated solvents. Not only are solvents such as 1,1,1-trichloroethane (TCA) and 1,1,1-trichlorotrifluoroethane (CFC-113) considered ozone depleting substances and will no longer be produced in 1996, but others such as methylene chloride and perchloroethylene are also being stringently regulated. Methylene chloride and perchloroethylene are considered suspect carcinogens. Stringent emission controls are currently being proposed under the Clean Air Act for these chemicals, and their wastes are controlled under the Resource Conservation and Recovery Act (RCRA). This became a particular problem for the Oak Ridge Y-12 Plant.

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The regional Environmental Protection Agency (EPA) office ruled that wipes that had come into contact with F-listed RCRA wastes must also be handled as RCRA wastes. The Y-12 Plant handles uranium and any wipe which comes into contact with uranium is regarded a low level radioactive wastes. If one of these solvents are used to wipe uranium, the wipe is then classified as a mixed waste because it is considered both RCRA and radioactive. Currently, handling of mixed waste is very difficult. Thus, the desire of the plant was to find a substitute for the solvents being used so that the wipes would only be classified as a radioactive wastes. Since 1987, personnel at Y-12 have been active in a chlorinated solvent substitution program.

Initially, steps were taken to determine the amount of these solvents being used and how they were being used. This was done by first compiling purchase records from the plant stores for a three year time frame. Surveys were also issued to each of the areas in the plants asking for their usage. After this data were obtained, visits were made to each of the facilities to observe the operations and talk to the personnel using the solvents. The usages throughout the plant included cleaning parts prior to and after machining, inspection or operations such as welding, bonding, plating, painting, and heat treating; drying metal chips; cleaning urethane foam spray guns; and cleaning meter mix machines. A priority list was established for attacking these usages and work began.

To determine levels of cleanliness obtained from solvents or aqueous cleaning, comparitive studies were conducted using coupons which are prepared, cleaned and analyzed using X-ray photoelectron spectroscopy (XPS). This technique is capable of looking at monolayer levels of a surface. The surface is bombarded with X-rays and the electrons which are ejected are then measured. The energies at which these electrons are ejected differ for various elements or elements in different binding states. Thus, one can determine the elements present on the surface. When conducting cleaning studies, the ratio of the element most associated with the contaminant, generally carbon, to the base metal, such as iron or chromium is calculated. The lower this ratio, the cleaner the surface.

Not only does the cleaning ability have to be assessed in order to determine possible alternatives but other factors such as compatibility and effects on subsequent operations must also be addressed. Generally, compatibility tests are conducted by submerging metals to be cleaned into the cleaner for a given period of time and then examining the metal to determine if any corrosion is evident. Compatibility tests can also be conducted on nonmetallic materials using submersion techniques and recording weight gain as a function of time. Compatibility issues must be addressed not only with materials being cleaned but the materials used to handle the cleaning materials such as gloves and squirt bottles. Some solvents may not be compatible with handling materials and will leach out or partially dissolve these materials, leaving a residue upon the part being cleaned. Effects upon subsequent operations are typically measured by cleaning the part and then performing the operation. Some type of physical testing is then conducted to determine if any deleterious effects are noted.

Aqueous Cleaning

As early as 1984, personnel at Y-12 had begun testing aqueous cleaning systems as a replacement for vapor degreasers using chlorinated solvents due to concerns such as the possibility of formation of phosgene gas from welding operations in the vicinity of the

degreasers. Initially, a pressure spray washer was obtained by this particular area. However, the cleaning obtained with this system was not adequate and other systems were then pursued. One aqueous cleaning technique which was found favorable was ultrasonic aqueous cleaning.

Ultrasonic cleaning works by using high frequency sound to cavitate a liquid medium. Cavitation creates micro bubbles which burst on the surface of the part being cleaned mechanically scrubbing the part. This mechanical action combined with the chemical cleaning action of the solution provides a powerful cleaning technique. There are several factors which can influence the effectiveness of ultrasonic cleaning such as frequency, liquid medium, and the coupling action between the liquid and the equipment.

Frequencies for ultrasonic equipment range from approximately 20 kHz to 90 kHz. A minimum frequency of approximately 18 kHz is required to cavitate a liquid medium. The cavitational energy is inversely proportional to the frequency. Thus, the lower the frequency, the greater the amount of cavitational energy which in turn increases cleaning ability. However, some delicate parts may not be able to withstand the cavitation forces at the lower frequencies. Electronic components are normally cleaned at higher frequencies.

The liquid medium also affects cleaning performance. The viscoelastic properties of the liquid affect its ability to cavitate. Water has been shown to cavitate more intensely than organic solvents, thus aqueous systems are an ideal choice for use in ultrasonics. Properties such as surface tension and vapor pressure play an important role in cavitation. The addition of detergent to water will lower the surface tension and increase cavitation. Heating the water to raise the vapor pressure will also increase cavitation. Optimum operating temperatures for ultrasonic aqueous detergent systems generally range from 50 to 60°C.

There are several considerations which should be taken into account when selecting a detergent for use in ultrasonics or in other aqueous cleaning techniques. If the intent is to discharge to local sanitary sewer systems, determine what the local requirements are for discharge. Many areas have limits on phosphates, silicates or other chemicals which may be found in detergents. Thus, those type detergents may not be an appropriate choice. The detergent selected must also be compatible with the parts being cleaned. For instance, highly alkaline solutions such as sodium hydroxide or sodium ethylenediaminetetraacetic acid (EDTA) are not compatible with aluminum. The pH of the solution may also affect ability to discharge to the sanitary sewer. Many detergents may leave a slight residue upon the surface. Ability to rinse the detergent could be a concern. Sodium compounds are very tenacious and difficult to rinse. If this type of residue could present a problem in subsequent operations then that type detergent should be avoided. The type of surfactant used is an important consideration and is dependent upon your particular application. Nonionic surfactants such as ethoxylates are generally better for oil removal. These type surfactants also tend to foam more so caution should be used in implementing these detergents. Detergents which foam should not be used in spray systems. Anionic surfactants such as sulfonates are better for particulate removal and generally do not foam.

As stated earlier, the operating temperature is an important factor. Higher temperatures (50-60°C) are optimal for cavitation properties and will soften or dissolve contaminants more readily. However, one must be careful not to exceed the cloud point of

the detergent. At the cloud point or the point at which the detergent becomes cloudy, the detergent micelles break and are no longer capable of attracting or sequestering the contaminant. Some detergents are considered high temperature detergents and are cloudy at low temperatures but will clear upon heating while other detergents are clear at low temperatures and become cloudy upon heating.

Rinsing is another important consideration for aqueous cleaning system. Demineralized water is preferred not only for rinsing but in making up the cleaning bath. Salts or chlorine found in tap water can cause corrosion of some metal surfaces. A portion of the detergent will also be used in capturing these contaminants found in the tap water thus decreasing the amount of detergent available to sequester the contaminants on the parts. Calcium present in tap water has also been shown to react with metasilicates or pyrophosphates found in some detergents to form calcium metasilicate or calcium phosphate. These substances are opalescent gels that are difficult to filter out and could deposit upon parts. Rinsing with hot water is also advisable because hot water tends to dissolve detergent residues more readily and evaporates more quickly decreasing the possibility of corrosion. If the part is rinsed until it becomes warm, the water will evaporate very readily. Agitation also plays a role in rinsing. More aggressive agitation such as ultrasonics will tend to knock off residues more readily than gentle spraying or submersion. However, minimal amounts of detergent residue may not affect your subsequent processes. Thus, it would not be necessary to use the more aggressive agitation.

If highly active metal is to be cleaned using aqueous methods, precautions can be taken to prevent corrosion. Use of demineralized water is a must to prevent corrosion. A thoroughly cleaned part which does not have salt deposits or chlorine present does not corrode. One can also use rust inhibitors in the rinse water to prevent corrosion. A wide variety of these are available on the market. A rust inhibitor should be chosen which will not affect subsequent steps. For instance, some inhibitors may prevent coatings from adhering properly and should not be used in applications where parts will be coated.

When using aqueous cleaning systems, drying must be considered. This step could be as simple as leaving parts out in the air to dry to as complex as a vacuum drying application. Drying is very dependent upon the type of part being cleaned. If there are nooks and crannies that water can be trapped in then vacuum drying may be required. Forced air drying may be adequate for drying many parts which do not have complex geometries.

Many studies have been conducted to determine the effectiveness of ultrasonic aqueous cleaning. Figure 1 shows the results of three coupon studies conducted to compare ultrasonic aqueous cleaning to vapor degreasing with chlorinated solvents. In each of these studies, metal coupons were initially cleaned to establish a baseline level of cleanliness. One sample was retained as a control sample. The remaining samples were contaminated with the various contaminants and allowed to sit overnight. The samples were then cleaned by vapor degreasing in either perchloroethylene (perk), 1,1,1-trichloroethane (TCA) or trichlorotrifluoroethane (CFC-113) for 15 min or were ultrasonically cleaned (US) in 5 vol% Oakite NST Aluminum Cleaner (NST) for 15 min at ~55°C, rinsed by flushing in demineralized water and blown dry with argon. The samples were analyzed using XPS with the results shown in Figure 1. As shown the ultrasonic cleaning yielded samples which were as clean or cleaner than the vapor degreasing and were more reproducible.

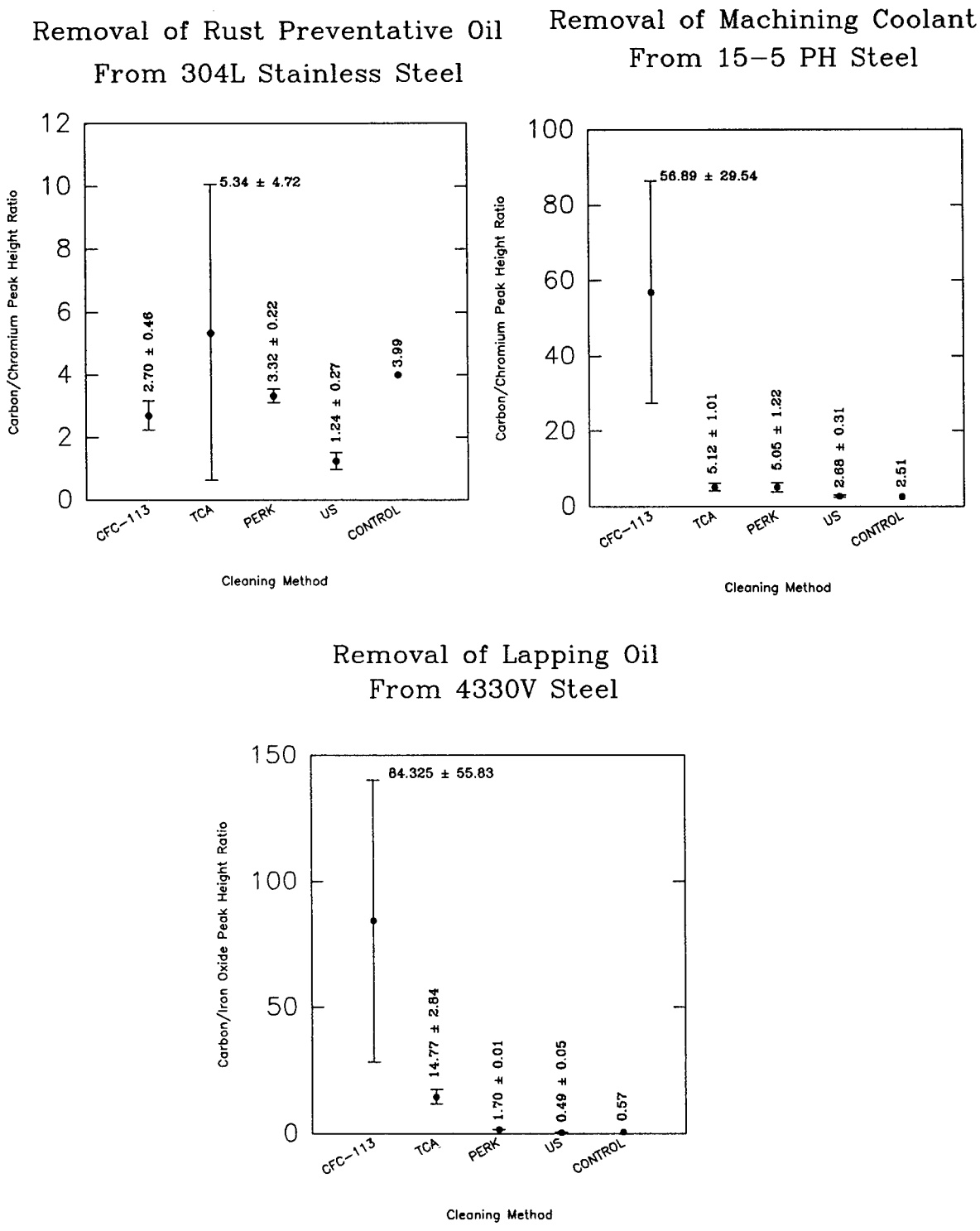

Figure 1 – Effectiveness of Ultrasonic Cleaning Versus Vapor Degreasing

Ultrasonic aqueous cleaning has been in use in the Y-12 Plant since 1984. The technique cleans well, is reproducible and generates low toxicity water waste which is treated easily. The drawbacks associated with this type of cleaning technique include noise and cost. At the 20 kHz level, irritating subharmonics are produced that require soundproof insulation and/or ear protection. Capital equipment cost is another consideration which should be taken into account.

Solvent Cleaning

Although aqueous cleaning is an attractive alternative, some cleaning requirements do not lend themselves to the batch cleaning mode or aqueous cleaning. For instance, cleaning parts at the machine or removal of materials which are not water soluble can be a problem. Personnel at Y-12 have investigated solvent alternatives for these type applications. When evaluating solvent alternatives to chlorinated solvents, the only options are other halogenated solvents which are nonflammable or combustible solvents. In order to avoid characterization as a RCRA characteristic waste, the solvent must have a flash point greater than or equal to 140°F. This was a major consideration in certain areas of the Y-12 Plant.

Several studies including cleaning efficiency, compatibility, and effects on subsequent production operations have led to the selection of two solvents for use in the plant for general cleaning purposes. These solvents are Solvent 140, a high flash mineral spirits composed mainly of C10-C13 branched and straight chain hydrocarbon molecules, and a solvent blend developed, patented and licensed by personnel at the Y-12 Plant hereafter referred to as MMK Blend. The Solvent 140 is used in moisture sensitive areas of the plant because slight amount of moisture absorbed in the MMK Blend and the presence of an -OH group in this blend can react with materials in these areas. The MMK Blend is used in the remaining areas of the plant. Solvent 140 is very effective in removing oils and hydrocarbon contaminants since it is a hydrocarbon. However, it tends to float on the surface of water and water based coolants. The MMK Blend addresses this problem and will undercut water or water based coolants. The blend also gives the added advantage of having a hydrocarbon solvent to remove hydrocarbon contaminants with a polar solvent which aids in the removal of more polar contaminants.

Several studies were conducted to determine if Solvent 140 and the MMK Blend are effective in removing substances commonly used in the Y-12 Plant for processing including rust preventative oils, lapping oils, machining coolants and fingerprints. Figure 2 shows the results of some of these studies. The studies were conducted by initially cleaning samples of various steels using ultrasonic aqueous cleaning in order to establish a baseline level of cleanliness. The samples were smeared with the contaminant until a visible layer was seen. A given amount of solvent such as CFC-113, TCA, 2-pentanol, dipropylene glycol methyl ether (DPM), dipropylene glycol methyl ether acetate (DPMA), ethyl lactate, anisole, terpene, N-methylpyrrolidone (NMP), Solvent 140 or MMK Blend was sprayed onto the sample using a squirt bottle. The sample was then wiped dry and analyzed using XPS. Solvent 140 and the MMK Blend gave the best overall results of the solvents tested.

Some concern had arisen regarding these cleaning studies since they were performed on coupons and not on actual parts. To alleviate these concerns, an analytical rinse study was

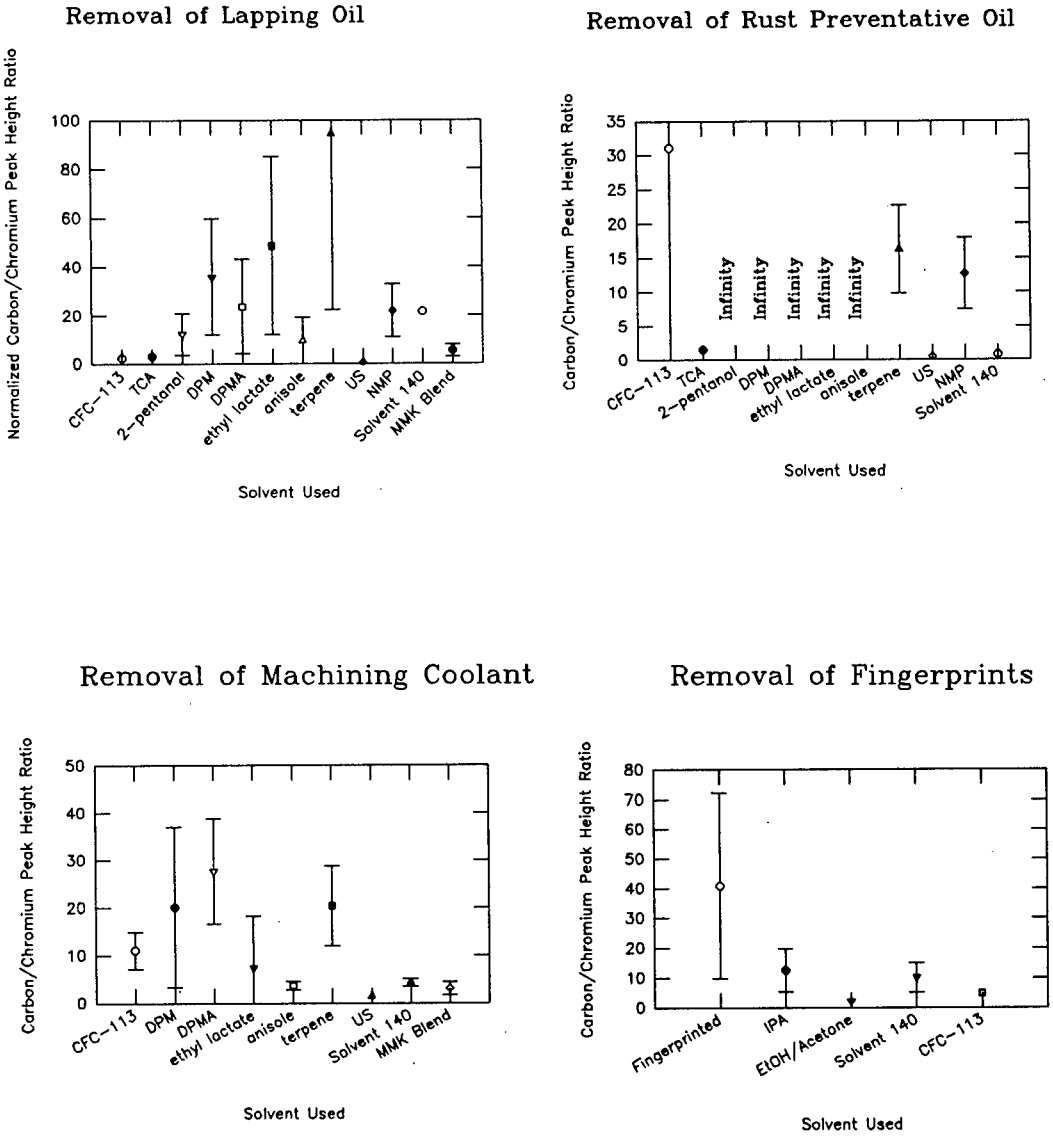

Figure 2 – Effectiveness of Solvents on Cleaning Various Contaminants

conducted on three different part types of different sizes. Four uranium parts of each type which had been coated with rust preventative oil and had been sitting on the shelf for a long period of time were randomly selected and cleaned by hand using current production processes with either CFC-113, which had currently been used in the area, or the MMK Blend. The MMK Blend was the solvent which would be implemented in this particular area. The parts were then rinsed in distilled methyl chloroform to extract any remaining oil left on the part. The rinse solution was evaporated to dryness, dissolved in distilled carbon tetrachloride and analyzed using infrared absorbance. The results of this experiment are shown in Table One. The parts cleaned in the MMK Blend had much less oil present than those cleaned in CFC-113.

Table One - Results of Analytical Rinse Experiment

Part Type	CFC-113 Cleaned μg Oil Remaining	MMK Blend Cleaned μg Oil Remaining
1	1922 $\pm$ 868	674 $\pm$ 189
2	2413 $\pm$ 1067	1419 $\pm$ 355
3	609 $\pm$ 206	387 $\pm$ 107

Compatibility experiments were conducted on the materials on which the solvent would be used as well as materials which are used to handle the solvent or may have incidental contact with the solvent to determine if there would be any problems related to the solvent use. Metal compatibility tests were conducted using a 72 hour immersion test with an artificial crevice. Both Solvent 140 and the MMK Blend were tested in this matter on depleted uranium (D-38) and its alloys, uranium-6% niobium and uranium-0.8% titanium; the aluminum alloys 1100, 7075 and 5083; iridium; the steel alloys 15-5 PH, 4330V, 1010, and HP 9-4-20; and beryllium. Slight oxidation was noted on the D-38 sample in Solvent 140 but was not perceived to be enough to be of concern. No corrosion was observed on the other metals and the solvents were approved for use. Other nonmetallic materials such as lithium hydride and beryllium oxide (BeO) were submerged in Solvent 140 with no effects noted.

Compatibility studies were also conducted on several polymeric materials such as polymethylpentene, polyethylene, mylar, silicone rubber, polyvinyl chloride, and diallyl phthalate which may come into contact with the solvent. These tests were conducted on Solvent 140 since it would be the solvent of choice in these areas as compared to methyl chloroform which was the solvent that was being used. The Solvent 140 had much less effect on the materials than did the methyl chloroform which was being used.

Long term compatibility issues were also addressed using two different means. A test unit was built using Solvent 140 for cleaning purposes replacing the methyl chloroform and CFC-113 which was being used in this area. This unit was subjected to temperature cycles under standard operating conditions. The unit exhibited no ill effects from the use of Solvent 140.

Compatibility of gloves used in handling the solvent was also addressed due to workers' health concerns and to possible contamination resulting from the use of the gloves. Weight gain studies were initially conducted on polyethylene, neoprene, butyl, latex, nylon, nitrile and vinyl gloves. Permeation studies were conducted on nitrile and latex gloves which had the best compatibility results. Tests were also conducted to determine possible contamination which may result from use. From these tests, nitrile gloves were recommended for long term or submersion use while latex was recommended for use in short exposure conditions.

Another major concern with changing solvents used in cleaning applications was the effect on subsequent production operations. Several evaluations have been conducted to determine effects on bonding, welding and painting.

Bonding studies were initially carried out that evaluated the effect on bonding of Solvent 140 or the MMK Blend when used to clean certain substances from surfaces to be bonded. Initially steel butt tensile specimens were ultrasonically cleaned in aqueous detergent, rinsed and allowed to dry in order to establish a baseline level of cleanliness. Three sets each of these samples were retained as controls. The remaining samples were coated with the substance which was to be removed and the substance was allowed to dry. Three sets each of the samples were cleaned with a given amount of solvent and bonded. The specimens were allowed to cure and tested for ultimate tensile strength. The Solvent 140 and the MMK Blend gave strengths in the same range as the CFC-113, methyl chloroform or other solvents typically used except in one instance. In this particular case, there was not adequate adhesive to cover the surface on one specimen which caused the strength to be lower then the remaining specimens and caused the average strength to be lower. If this data point were neglected, strengths were in-line with other strengths obtained.

Bonding studies were also conducted to determine the effect of Solvent 140 for a final cleaning on certain substrates. Butt tensile specimens of BeO and beryllium were initially cleaned ultrasonically in aqueous detergent, rinsed and allowed to dry. Five sets of these specimens were retained as control samples. Five sets each of the remaining specimens were cleaned with Solvent 140 or methyl chloroform which was the solvent being used in the area. The BeO specimens were bonded with an epoxy formulation while the beryllium specimens were bonded with a urethane. All of the test specimens were cured, and tested for ultimate tensile strength. No negative effects were seen from the use of Solvent 140.

Two bonding studies were also conducted on aluminum substrates using adhesives which had not been used in prior studies. These adhesives were Epon 828/Epon 871/N-aminoethylpiperazine and Accrabond PR14368. The specimens were initially treated using a standard Forest Product Laboratories (FPL) chromic acid etch. Five sets of samples were retained as control specimens while five sets each of the remaining specimens were cleaned with Solvent 140 or methyl chloroform. The samples were bonded, cured and tested for ultimate tensile strength. No deleterious effects were noted from the cleaning medium.

Welding is another operation which follows cleaning that was of concern. In order to address this concern, a study was conducted on electron beam (E-beam) welding of aluminum. Aluminum was chosen because it is known for being sensitive to hydrocarbon contamination when welding. E-beam welding is also one of the welding techniques which

is more susceptible to problems due to contamination. The major concern was that since Solvent 140 evaporates slowly that some residual solvent may be present on the surface during welding. This would increase pumpdown rates and the hydrocarbon contamination from the solvent may cause blow-outs in the weld or lead to weld porosity. A total of 30 aluminum alloy 5086 weld rings with a square butt joint with an alignment step were used for the study. A narrow weld was chosen to increase the probability of retaining any porosity in the weld. Root voids are common in narrow aluminum welds and were anticipated in this experiment. Half of the rings were to be cleaned using methyl chloroform which is the solvent that was currently in use in the production area. The remaining rings were cleaned with Solvent 140. No difference was seen in the pumpdown rates due to the cleaner used and no blow-outs were noted. The rings which were cleaned with Solvent 140 had significantly less porosity (6.47 $\pm$ 7.07 pores) than those cleaned with methyl chloroform (21.53 $\pm$ 22.488 pores).

A laser beam welding study was also conducted on stainless steel parts by personnel at Lawrence Livermore National Laboratory which compared Solvent 140 to CFC-113 for cleaning of welds. Hydrostatic burst pressure tests of weld qualification coupons were performed to verify the integrity of the welds for each cleaning method. The burst pressure values were independent of cleaning procedures for the welds.

Painting studies have been conducted on two different substrates, aluminum and nickel. Aluminum test panels were cleaned with Solvent 140 and a urethane coating applied. The panels were then submitted to a steam test. No loss of adhesion was noted due to cleaning with Solvent 140 as compared to prior cleaning techniques using methyl chloroform. Nickel panels were also cleaned with Solvent 140 and then coated with an epoxy primer followed by a urethane topcoat. Steam tests were again conducted with no differences noted in adhesion.

Due to the success of these tests, these solvents were implemented at the Y-12 Plant and have been successfully utilized since 1991. No major problems have been noted with their use. As with any alternative, there are some drawbacks associated with these solvents. These are higher flash point solvents and they do evaporate much slower than the chlorinated solvents. This requires adjustments in handling. These solvents are also combustible and require different handling techniques to comply with Occupational Safety and Health Administration (OSHA) regulations. However, these drawbacks can be overcome.

Summary

In implementing alternatives, consideration should be given to levels of cleanliness, compatibility issues, effects on subsequent production operations and compliance with various regulations. Testing should be conducted for specific applications as one technique may not work for all applications or contaminants present. Personnel at the Oak Ridge Y-12 Plant have been able to successfully implement ultrasonic aqueous cleaning and cleaning with alternative solvents in a production environment. Some drawbacks are associated with the alternatives but these drawbacks can be overcome and a successful substitution program can result.

Replacement of Ozone Depleting and Toxic Chemicals in Gravimetric Analysis of Non-Volatile Residue

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Abstract

The standard tests for determining non-volatile residue accretion on spacecraft surfaces and in clean processing facilities rely on the use of halogenated solvents that are targeted for elimination because of their toxic or ozone-depleting natures. This paper presents a literature-based screening survey for candidate replacement solvents. Potential replacements were evaluated for their vapor pressure, toxicity, and solvent properties. Three likely candidates were identified: ethyl acetate, methyl acetate, and acetone. Laboratory tests are presented that evaluate the suitability of these candidate replacement solvents.

Introduction

Control of contamination during processing and integration of spacecraft and launch vehicles is fundamental to insuring mission performance and longevity. Molecular contamination, or non-volatile residue (NVR), is limited by selection of materials and the control of procedures and facilities. Diagnosis of NVR accretion rates is accomplished using witness plates as described ASTM E 1235-88 ("Standard Test Method for Gravimetric Determination of Non-volatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft"). A solvent wipe test documented in USAF Space Systems Division TR-89-63 ("Standard Method for Measurement of Non-volatile Residue on Surfaces") is used to assess hardware cleanliness. These documents, or tailored versions, often define contractual requirements for US spacecraft procurement and launch (Farren *et al*, 1987, 1989; Borson, 1993). These practices rely on the use of dichloromethane (methylene chloride), which is targeted for reduction under the EPA 33/50 program and the Clean Air Act, or a mixture of ethanol with 1,1,1 trichloroethane (methyl chloroform or TCA), which is a "Class 1" ozone depleting chemical.

This paper describes a literature-based screening and laboratory tests of candidate "drop in" replacement solvents for these two tests. To insure a well understood heritage to existing practice, materials' solvent properties, vapor pressure, cleanliness and stability, safety and health issues, and environmental issues were evaluated.

Some general guidelines were followed in selecting the initial set of solvents for screening. Materials that are Class 1 ozone depleting chemicals were not considered as viable replacements for methylene chloride and TCA, for obvious reasons. Only pure materials, not commercial mixtures were considered. Aside from a philosophical desire not to endorse one vendor's mixture over another, relying on a proprietary mixture (which may be subject to unannounced changes in formulation) is undesirable in a standard practice.

These two NVR tests were designed originally to provide a method for comparing facilities and ascertaining facility cleanliness trends, but not necessarily to provide an absolute quantitative determination of a specific type of NVR (Borson, 1994). Therefore, it is important to remember that the goal of finding a replacement solvent for these standard tests is not necessarily to find the "best" solvent for a specific type

of non-volatile residue. Rather, the goal is to find those replacement solvents which most closely match the solvent properties of methylene chloride and the NVR mixture. Initial screening of commonly available organic solvents relies on the "Hansen parameters" characterization of solvents (Barton, 1983). These parameters provide a quantitative representation of the "like dissolves like" rule of thumb so familiar to chemists.

Candidate solvents must have vapor pressures similar to dichloromethane or the TCA/EtOH mixture. If the vapor pressure is too high, the test cannot be completed under standard laboratory conditions. If the vapor pressure is too low, the evaporation process for the gravimetric analysis will take too long, which would result in an unacceptable turn-around rate and risk contamination of the test sample. In the extreme case, the vapor pressure of the solvent may become comparable to the vapor pressure of the "nonvolatile" residue being diagnosed. The NVR tests, as modified, may involve the use of hazardous materials, operations, and equipment. Candidate solvents are screened on the basis of 8 hour threshold limit values, compared with their room temperature vapor pressures.

The overall results of candidate solvent screening are captured in a semiquantitative selection matrix. Three promising candidates for replacement solvents emerge from this screening: ethyl acetate, methyl acetate, and acetone. Controlled evaluations of these candidate solvents, from this laboratory and elsewhere, confirm that they are promising substitutes for halocarbons in standard NVR tests (King and Giordano, 1994; Walter and Parker, 1994).

Solvent Properties Screening

In selecting a solvent for any particular application, chemists generally rely on the rule of thumb that "like dissolves like." For example, a non-polar solute, like a saturated hydrocarbon, is generally best dissolved by a non-polar solvent. Therefore, in selecting replacements for dichloromethane and the NVR solvent blend, one looks for a solvent that is as much "like" them as possible.

One quantitative approach to "likeness" is to use "solubility parameters" to describe the solvents (Barton, 1983). One of the simplest of these parameters, the Hildebrand parameter, is related to the cohesive energy density (cohesive energy per unit volume). The cohesive energy is the energy associated with the net attractive interactions of a material (as compared to an ideal vapor at the same temperature. The cohesive energy density, c, is given by

$$c = -\frac{U}{V} \tag{1}$$

where U is the total molar cohesive energy and V is the molar volume. The units of c are the same as pressure. The Hildebrand parameter, δ, is defined as

$$\delta = c^{1/2} \tag{2}$$

Barton explains the rationale for quantifying solubility in terms of molecular cohesion as follows.

> A material with a high δ value requires more energy for dispersal than is gained by mixing it with a material of low cohesion parameter, so immiscibility results. On the other hand, two materials with similar δ values gain sufficient energy on mutual dispersion to permit mixing.

A refinement of the Hildebrand parameter consists of the three-component Hansen parameters. Hansen proposed dividing the total cohesive energy into terms corresponding to dispersion forces, polar forces, and hydrogen bonding, as shown in Eq. (3).

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

The total Hansen parameter, δ_t, is equivalent to the Hildebrand parameter. The Hansen parameters do not take into account any specific chemical or ionic interactions. They provide an estimate of the properties of mixtures considering only the properties of the individual components. Barton tabulates Hansen parameters for a wide variety of organic chemicals. Figure 1 presents the total parameter, as a bar graph, for a variety of organic solvents.

The Hansen parameters are used here to identify likely candidate replacement solvents.* The most compact comparison is provided by considering the magnitude of the vector (in Hansen parameter space) from methylene chloride or NVR solvent to the candidate solvent. The length of the vector from methylene chloride (DCM) to solvent *i* is given by

$$d_i^{DCM} = [(\delta_{d_{DCM}} - \delta_{d_i})^2 + (\delta_{p_{DCM}} - \delta_{p_i})^2 + (\delta_{h_{DCM}} - \delta_{h_i})^2]^{1/2} \quad (4)$$

with the distance to NVR solvent defined analogously. Figure 2 shows the vector differences between the various solvents considered and dichloromethane and NVR solvent. The best matches appear to be methyl isobutyl ketone, methyl ethyl ketone, n-butyl acetate, methyl acetate, ethyl acetate, and tetrahydrofuran.

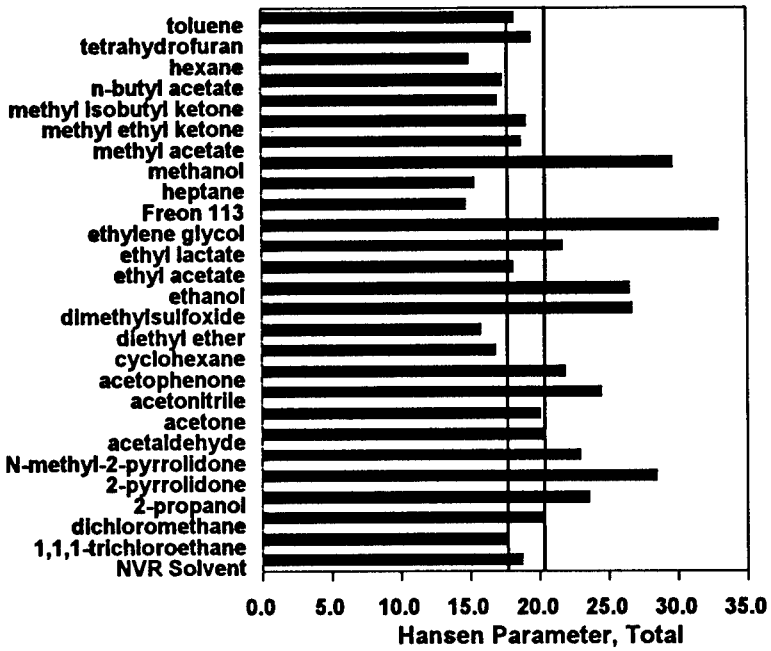

Figure 1. Total Hansen solubility parameter $(MPa)^{1/2}$ for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

* The Hansen parameters for NVR solvent were estimated using the volume weighted average of the parameters for 1,1,1 trichloroethane and ethanol.

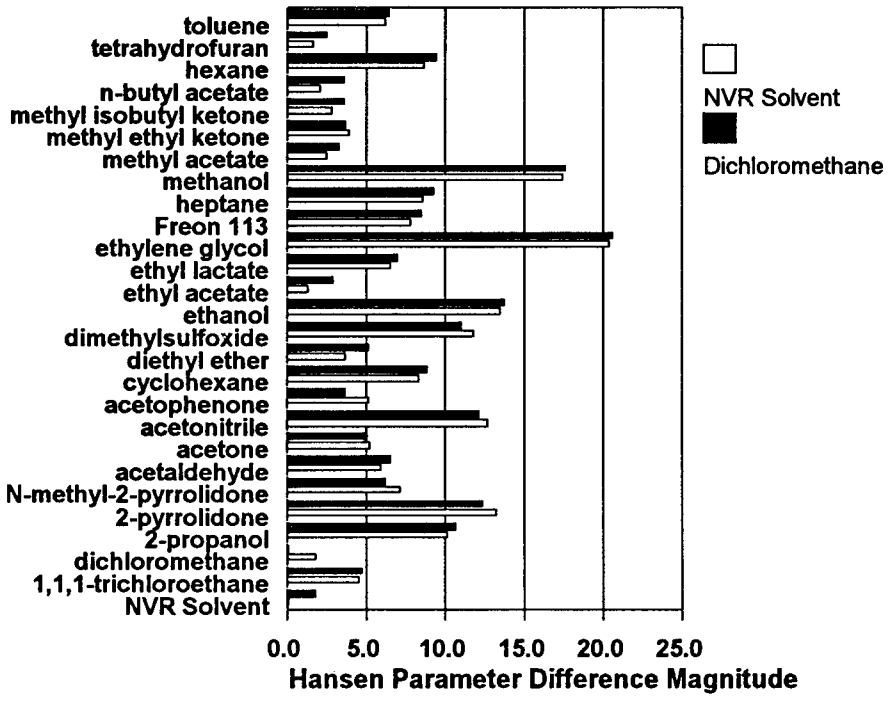

Figure 2 Vector difference in Hansen solubility parameter $(MPa)^{1/2}$ for various solvents compared to dichloromethane and NVR solvent blend.

Vapor Pressure Analysis

A solvent used for non-volatile residue analyses needs to have an appropriate vapor pressure near room temperature. The vapor pressure cannot be so high that the solvent is difficult to handle during rinsing of witness plates or wiping hardware under test. Conversely, the vapor pressure must not be so low that the near-room-temperature evaporation used in the gravimetric analyses takes an excessively long time.* Vapor pressure data were obtained from standard reference works (Lide, 1993; Stecher, 1968; Hill and Carter, 1993). Figure 3 shows the vapor pressure at 25°C for the solvents considered. The two vertical lines indicate the range of useful vapor pressures, as determined from experience. Diethyl ether is about as volatile a material as one would want to handle in the NVR tests. Isopropyl alcohol is about as non-volatile as would be desirable.

This sorting of the solvents considered suggests that diethyl ether, acetone, methyl acetate, tetrahydrofuran, hexane, methanol, methyl ethyl ketone, cyclohexane, acetonitrile, ethyl acetate, ethanol, heptane, and isopropanol are viable candidates for replacing dichloromethane and the NVR mix.

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* Note that this requirement for a moderate vapor pressure differs from what one would wish in a cleaning solvent used to wash parts (e.g. in an ultrasonic cleaner). In that case, low vapor pressure (evaporation rate) is a virtue.

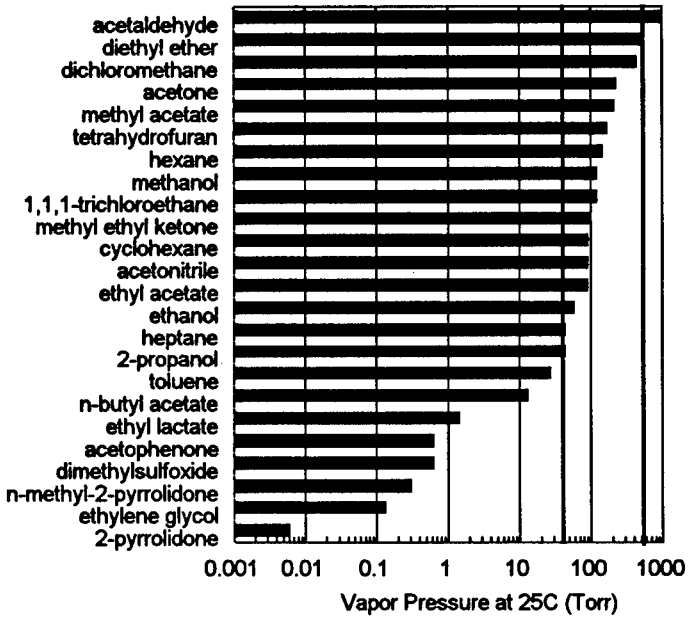

Figure 3 Vapor pressure, in Torr, at 25°C for various solvents. The bold vertical bars indicate the practical working range for NVR analysis.

Hazard Evaluation

Handling organic solvents presents both toxicity and flammability hazards. Almost all conceivable substitutes for the chlorocarbon and chlorofluorocarbons used in NVR analysis present one or both of these hazards. For the purpose of this screening, three figures of merit were examined: (1) the "Threshold Limit Value" for exposure to the material; (2) an inhalation hazard ratio (IHR, defined as the ratio of the saturated vapor concentration at 25°C to the TLV, Walter and Parker, 1994); and (3) the "Flash Point." The inhalation hazard ratio gives a feel for the degree of ventilation required for handling the material in question. Since virtually all the credible short-term replacements for ODC's in the NVR tests are volatile and flammable, the flash point data are not given significant weight in screening potential solvents.

Threshold limit value and flash point data were taken from standard literature sources (Lide, 1993; Lenga, 1988). Table 1 presents the data. TLV's and IHR's with zero values indicate that no TLV data were available for those materials (ethyl lactate, dimethylsulfoxide, and the pyrrolidones). All of the materials examined for which the TLV data are available show a lower IHR and higher TLV than dichloromethane. However, several are more hazardous, by both measures, than 1,1,1 trichloroethane, the more hazardous part of NVR solvent. Table 1 indicates other hazard information. Some of the materials are Class 1 ODC's. Several are on the EPA 17 list. Dimethylsulfoxide is an efficient skin penetrant, making it particularly dangerous when contaminated with other potentially toxic materials. Dichloromethane is a suspected carcinogen. Like most ethers, tetrahydrofuran can decompose into explosive peroxides.

Table 1. Flammability and toxicity hazard assessment for various organic compounds with potential application as NVR solvents.

Solvent	Flash Point	TLV ppm	Inhalation Ratio	Comments
1,1,1-trichloroethane	none	350	451	Class 1 ODC
2-propanol	12	400	140	
2-pyrrolidone	110			no TLV data
acetone	-19	750	386	
acetonitrile	6	40	2888	
cyclohexane	-18	300	396	
dichloromethane	none	50	11184	carcinogen, EPA 17
diethyl ether	-45	400	1806	
dimethylsulfoxide	88			skin penetrant, no TLV
ethanol	12	1000	74	
ethyl acetate	-4	400	288	
ethyl lactate[10]	49			no TLV data
ethylene glycol	111	50	3	
Freon 113	48	1000	434	Class 1 ODC
heptane	-4	400	141	
hexane	-22	50	3816	
methanol	11	200	796	
methyl acetate	-16	200	1375	
methyl ethyl ketone	-6	200	630	EPA 17
n-butyl acetate	22	150	112	
n-methyl-2-pyrrolidone	86			no TLV data
tetrahydrofuran	-14	200	1086	explosion hazard in distillation
toluene	4	50	703	EPA 17

Screening Summary

In this section a semiquantitative combination of screening data is presented, and candidate replacement solvents are identified. The rating scales were designed to give heaviest weighting to the solvent properties, as described by the Hansen parameters. Roughly equal weighting was given to vapor pressure and toxicity.

To put the Hansen parameter analysis on a roughly "one to 10 scale," the following figures of merit for solvent *i* were calculated. [See Eq. (4).] A quantity *Hansen NVR* is defined analogously.

$$Hansen\ DCM = \frac{(20 - d_i^{DCM})}{2} \tag{5}$$

Table 1 shows that virtually all of the solvents under consideration require some degree of ventilation. Therefore, the TLV, not the IHR was used as a rating parameter. To put the data on a 1-10 scale the TLV in volume ppm was divided by 100. If a candidate solvent is on the EPA 17 list, the toxicity rating was arbitrarily assigned a value of -5. Materials for which no TLV data were available received a zero score in this category. A fairly insensitive rating scale for vapor pressure was chosen, the logarithm to base 10 of the 25°C vapor pressure of the material, in Torr. This provided a scale spanning roughly -3 to +3. The individual rating data (rounded to integer values) are presented in Table 2. The

total ratings are shown in Figure 4. The chosen scale provided benchmark values for NVR solvent and dichloromethane of about 25. Five potential solvent replacements rated above 20 on this scale: acetone, diethyl ether, ethyl acetate, methyl acetate, and tetrahydofuran.

The hazard properties of the two ethers (diethyl ether and tetrahydrofuran) militate against their use in NVR testing. Diethyl ether is at the extreme high end of the range of useful volatility, and presents a severe fire and explosion hazard. Tetrahydrofuran, a cyclic ether, shares a property common to many ethers: it can decompose to form explosive peroxides. "Inhibited" materials are available, but this involves contamination, for example with 250 ppm of butylated hydroxytoluene, which is a solid with a 69°C melting point (Anon, 1992).

In the overall rating, acetone scored among the top candidates. This rating is somewhat misleading in that acetone scored high in the toxicity benchmark, but lower in the solubility benchmarks. Furthermore, it is substantially more polar than the solvents for which replacements are sought. However, this difference may not be as significant as it appears. Barton has pointed out that the polar forces are much less important than hydrogen bonding forces. Testing has shown that acetone is not as effective for some greases as other solvents (King and Giordano, 1994; Walter and Parker, 1994). However, it has some advantages. It is readily available at many laboratories. Indeed, it is already an approved material for use at many US launch sites. (This is a significant bureaucratic hurdle.) Its toxicity and vapor pressure range are attractive. Finally, it has often been mentioned as a candidate for cleaning and NVR diagnosis, so additional data on its utility will likely turn out to be useful.

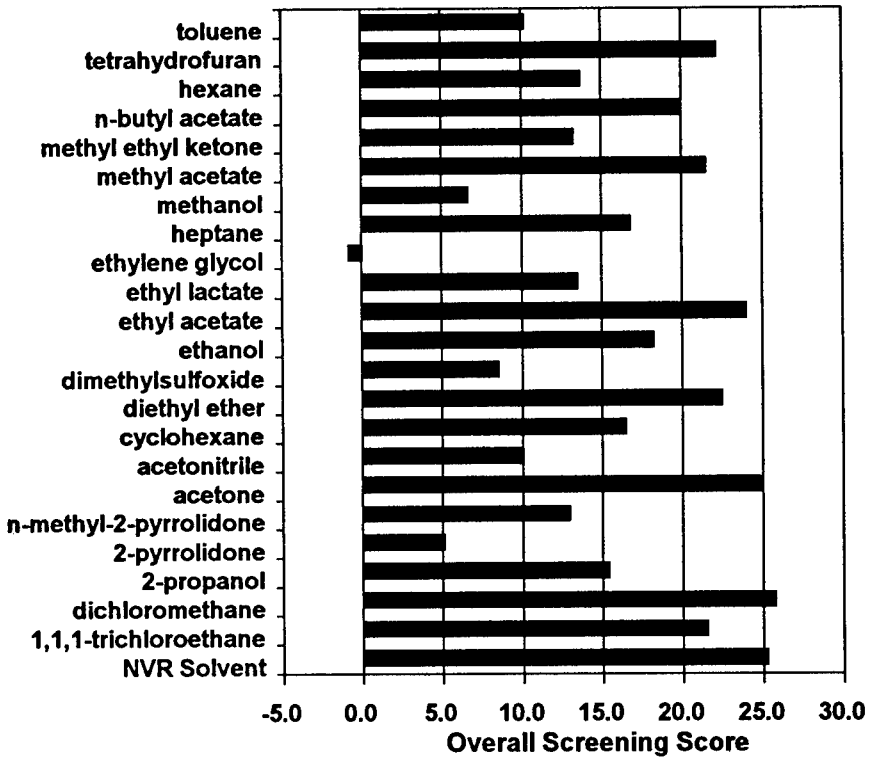

Figure 4 Overall screening score for various current and potential NVR solvents. See text for details.

Table 2. Summary of "figures of merit" for solvent properties, toxicity, and vapor pressure.

Solvent	Hansen DCM	Hansen NVR	Toxicity	Vapor Pressure	Total
NVR Solvent[a]	9	10	4	2	25
1,1,1-trichloroethane	8	8	4	2	22
dichloromethane	10	9	4	3	26
2-propanol	5	5	4	2	15
2-pyrrolidone	4	3		-2	5
n-methyl-2-pyrrolidone	7	6		-1	13
acetone	8	7	8	2	25
acetonitrile	4	4	0	2	10
cyclohexane	6	6	3	2	16
diethyl ether	7	8	4	3	22
dimethylsulfoxide	5	4		0	8
ethanol	3	3	10	2	18
ethyl acetate	9	9	4	2	24
ethyl lactate	7	7		0	13
ethylene glycol	0	0	1	-1	-1
heptane	5	6	4	2	17
methanol	1	1	2	2	7
methyl acetate	8	9	2	2	21
methyl ethyl ketone	8	8	-5	2	13
n-butyl acetate	8	9	2	1	20
hexane	5	6	1	2	14
tetrahydrofuran	9	9	2	2	22
toluene	7	7	-5	1	10

a. Assuming 1,1,1 trichloroethane vapor pressure.

Experimental Results

The first part of experimental testing was to ascertain the availability of solvents of suitable purity for this application. A review of organic chemical vendors revealed that ACS HPLC grade materials are available for both acetates (at < 3 ppm evaporation residue specification) and acetone (< 10 ppm). The price for these solvents is approximately $20 per liter. Table 3 shows examples of laboratory tests, following the procedure in ASTM E 1235 to evaluate the achieved cleanliness for some samples of the esters, compared to HPLC dichloromethane and "anhydrous" TCA. Note that these data evaluate both the purity of the solvent and the "technique" of the experimenter. The data shown in Table 3 justify the use of the "as received" HPLC grade solvents, without further purification, in the laboratory test program.

The suitability of the candidate replacement solvents is being tested using both adventitious contaminants obtained by exposing witness samples to various controlled and uncontrolled environments and by using samples prepared with known amounts of pure and mixed contaminants. The model contaminants include lubricants used in the Titan IV program, hydrocarbons, siloxanes, and phthalate esters. Test plates of 1 sq. ft. area that can be precontaminated by evaporating prepared solutions were fabricated for controlled surface wipe tests.

Table 4 presents an example of an ASTM E1235-88 stainless steel witness plate test for samples that were exposed in the Aerospace Corp. machine shop for about 1 month, then bagged together for ~3 months. The agreement between the results for the standard solvent and ethyl acetate is strikingly good.

Table 3. Solvent NVR tests, 60 ml samples.

Solvent	Test 1				Test 2			
	Residue (g)	ppm	Mean	Std. Dev.	Residue (g)	ppm	Mean	Std. Dev.
Dichloromethane	0.00007	0.9	0.9	0.1	0.00013	1.6	2.0	0.31
	0.00008	1.0			0.00019	2.4		
	0.00006	0.8			0.00016	2.0		
Ethyl Acetate	0.00026	4.8	4.0	0.68	0.00003	0.6	0.6	0.00
	0.00017	3.1			0.00003	0.6		
	0.00022	4.1			0.00003	0.6		
Methyl Acetate	0.00002	0.4	1.6	1.2	0.00008	1.4	0.7	0.58
	0.00007	1.3			0.00000	0.0		
	0.00018	3.2			0.00004	0.7		
Trichloroethane	0.00034	4.2	3.5	0.56	0.00033	4.1	4.4	0.99
	0.00028	3.5			0.00046	5.7		
	0.00023	2.9			0.00027	3.4		

Table 4. ASTM E 1235 test comparison between dichloromethane and ethyl acetate

Measured Mass (g)	Solvent	
	Dichloromethane	Ethyl Acetate
Sample	0.00093	0.00147
Blank	0.00029	0.00072
NVR	0.00064	0.00075

Table 5 presents results from a controlled surface wipe test experiment. In this case, the test plates were contaminated with an aliphatic hydrocarbon, squalane, dissolved in heptane (certified to an evaporation residue of less than 1 ppm). These initial results are not quite as promising as those for the ASTM test. Further experimentation with a variety of contaminants is clearly required. Also, in performing these tests, it was observed that the methyl acetate evaporated very rapidly, while the wipe was being performed. This observation, and the fact that methyl acetate is somewhat more toxic than the other solvents, may militate against its use for the wipe test.

Table 5. Test results for NVR wipe of test samples pre-contaminated with squalane

Solvent	Applied NVR (g)	Sample NVR (g)	Blank NVR (g)	Test NVR (g)
Methyl Acetate	0.00364	0.00265	0.00110	0.00155
Ethyl Acetate	0.00362	0.00306	0.00218	0.00088
"NVR" Solvent	0.00369	0.00514	0.00209	0.00305

Summary and Conclusions

The standard tests for determining non-volatile residue accretion on spacecraft surfaces and in clean processing facilities rely on the use of halogenated solvents that are targeted for elimination because of their toxic or ozone-depleting natures. A literature-based screening survey for candidate replacement solvents has been described. Potential replacements were evaluated for their vapor pressure, toxicity, and solvent properties. Three good candidates were identified: ethyl acetate, methyl acetate, and acetone.

Laboratory tests have confirmed that commercially available materials, in ACS HPLC grade, are adequate for this task, for the esters. Laboratory testing using model and adventitious contaminants has shown that the esters are promising candidate materials for replacing halocarbons in the standard spacecraft NVR tests. This general conclusion is supported by, other testing of potential NVR and cleaning solvents at Martin Marietta (King and Giordano, 1994; Barrows, 1994) and elsewhere (Walter and Parker, 1994).

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References

Anon., Aldrich Catalog Handbook of Fine Chemicals, Aldrich Chemical Co., Milwaulkee, WI, 1992.

Barrrows, R., Martin Marietta Astronautics Group, Private Communication, 1994.

Barton, A.F.M., CRC Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, FL, 1983.

Borson, E.N., "Contamination Control Documents for Use in Statements of Work and Contamination Control Plans for Spacecraft Programs," TOR-93(3411)-5, The Aerospace Corporation, El Segundo, CA, 30 September 1993.

Borson, E.N., private communication, 1994.

Farren, D.B. *et al.*, "Titan IV System Contamination Control Plan- ETR," MCR-86-2550, Martin Marietta Astronautics, Denver, CO, December 1987.

Farren, D.B. *et al.*, "Titan IV System Contamination Control Plan- WTR," MCR-88-25245, Martin Marietta Astronautics, Denver, CO, 30 January 1989.

Hill, E.A. and K.D. Carter, "Using Ethyl Lactate for Precision Cleaning of Metal Surfaces," Microcontamination, Nov. 1993, pp. 27-31.

King, E. and T.J. Giordano, "Cleanliness Verification Process at Martin Marietta Astronautics," JANNAF Interagency Propulsion Committee, Environmentally Benign Cleaning and Degreasing Technology Workshop, Indian Head, MD, 14 June 1994.

Lenga, R.E., (ed), The Sigma-Aldrich Library of Chemical Safety Data, 2nd Ed., Sigma Aldrich, 1988.

Lide, D.R., (ed), CRC Handbook of Chemistry and Physics, 74th Ed., CRC Press, Boca Raton, FL, 1993.

Stecher, P.G. (ed), The Merck Index: An Encyclopedia of Chemicals and Drugs, 8th Ed., Merck and Co., Inc, Rahway, NJ. 1968.

Walter, A.E. and J.W. Parker, "Selecting and Handling CFC-Alternative Critical Cleaning Solvents," Microcontamination, April, 1994, pp. 27-33.

Evaluation of Control Parameters for Spray-In-Air (SIA) Aqueous Cleaning for Shuttle RSRM Hardware

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ABSTRACT

HD-2 grease is deliberately applied to Shuttle Redesigned Solid Rocket Motor (RSRM) D6AC steel hardware parts as a temporary protective coating for storage and shipping. This HD-2 grease is the most common form of surface contamination on RSRM hardware and must be removed prior to subsequent surface treatment. Failure to achieve an acceptable level of cleanliness (HD-2 calcium grease removal) is a common cause of defect incidence. Common failures from ineffective cleaning include poor adhesion of surface coatings, reduced bond performance of structural adhesives and failure to pass cleanliness inspection standards. The RSRM hardware is currently cleaned and refurbished using methyl chloroform (1,1,1-trichloroethane). This chlorinated solvent is mandated for elimination due to its ozone depleting characteristics. This report describes an experimental study of an aqueous cleaning system (which uses Brulin 815 GD) as a replacement for methyl chloroform. Evaluation of process control parameters for this cleaner are discussed as well as cleaning mechanisms for a spray-in-air process.

Testing documented in MSFC Technical Report EH33/92-5, published previously, determined that an acceptable level of cleanliness can be achieved with application of a spray-in-air (SIA) process which utilizes aqueous based cleaner formulations. HD-2 contaminated D6AC plates were cleaned using this aqueous method and subsequently bonded for tensile adhesion testing. The test specimens produced cohesive failures within an EA913NA adhesive bond line. The RSRM nozzle fixed housing bond line utilizes EA913NA adhesive and is considered "sensitive" to HD-2 Calcium grease surface film levels above 5 mg/ft^2.

This report documents a study to further evaluate the spray-in-air process utilizing Brulin 815 GD cleaner and the mechanisms of this cleaning method. The ultimate goal is to qualify an environmentally compliant cleaner such as Brulin 815 GD to replace the current chlorinated cleaning system, methyl chloroform.

The test objectives of this study were as follows:

1) Evaluate the main effects and interactions of the following control factors used in spray-in-air aqueous cleaning of D6AC steel: pressure, cleaner temperature, cleaner mix ratio, and cleaner soak time.

2) Determine if cleaning with ambient temperature cleaner solution will yield acceptable bond strengths with the other factor settings optimized.

3) Determine effects of any residual cleaner and HD-2 grease on an Optically Stimulated Electron Emission (OSEE) measurement and on tensile adhesion strength.

The aqueous cleaner used in this study was Brulin 815 GD (Brulin & Company Inc. of Indianapolis, IN). The cleaner is a biodegradable liquid which is mixed with tap water to desired mix ratios for various cleaning applications. The cleaner contains no "butyl" or petroleum solvents but does contain a ferrous metal flash rust inhibitor for temporary corrosion protection. The chemical composition includes detergents, nonylphenoxypolyethyleneoxyethanol (5-10%) and alkaline cleaners.

The adhesive, EA-913NA, is supplied by Dexter Hysol and is currently used to bond nozzle insulation components in the RSRM . The manufacture date of the test adhesive (Lot 0064) was August 7, 1993 with an expiration date of August 7, 1994. This adhesive was chosen because it is extremely sensitive to minute amounts of HD-2 grease contamination on metal substrates..

The silane primer used in this study is a Thiokol formulation designated UF-3296. This primer was used only on the button side of the specimens to drive the failure mode down to the test panel. The detailed formulation is described in Thiokol specification STW5-3215.

The equipment used to wash the test panels in this study was an enclosed high pressure parts washer. The washer (Model 550) is a spray-in-air type unit manufactured by ADF Industries and was modified to prevent the cleaner solution from being recycled. Therefore, when panels were cleaned they were always sprayed with "virgin" cleaner solution. The machine also has a pressure adjustment valve which allows the user to adjust the pressure from 75 to 675 psi. The corresponding flow rates at these pressures were approximately 0.5 and 4 gpm, respectively. The spray gun used a fan type nozzle (Binks nozzle no. 1508) which produced a 4 inch wide fan at a standoff distance of approximately 8 inches.

The specimens used in these tests were 4 X 8 inch D6AC steel plates. Silane primed tensile adhesion buttons having 1.0 square inch bonding area were bonded to each plate. A total of seven tensile adhesion buttons were bonded to each plate with one plate representing one run of the test matrix shown in Table 1.

D6AC steel test panels were placed in a methyl chloroform vapor degreaser conforming to MIL-T-81533. The degreasing time was 15 minutes. Surface preparation grit blast was performed using 60 mesh silicon carbide grit at 80 psi and a 90 degree grit blast angle. The grit blast operation was intended to achieve a 125 Ra nominal finish. Following the blasting operation D6AC steel test specimens were placed in a vapor degreaser with methyl chloroform conforming to MIL-T-81533. The degreasing time was 15

RUN NO.	PANEL NO.	TEMPERATURE (DEG. F)	SOAK TIME (MINUTES)	CONCENTRATION (PERCENT)	PRESSURE (PSI)
1	2	72	2	10	75
2	3	72	2	30	675
3	7	140	2	30	75
4	9	140	2	10	675
5	13	72	10	10	75
6	10	140	10	30	75
7	12	140	10	10	675
8	5	72	10	30	675
9	14	140	2	10	75
10	15	72	2	30	75
11	16	72	2	10	675
12	8	140	2	30	675
13	11	140	10	10	75
14	6	72	10	30	75
15	4	72	10	10	675
16	17	140	10	30	675

Table 1 Spray-In-Air Cleaning Test Matrix Including Factors

minutes. The specimens were removed from the degreaser and checked for stains. Additional degreasings were permitted if stains were found. Bonding surfaces were prepared by grit blasting surfaces of each test specimen using "virgin" 100 to 200 mesh Zirclean grit. A grit blast pressure and angle of 80 psi and 45 degrees was used. A 4 to 5 inch standoff distance for the blast gun was also used. The resulting speed of travel was approximately 3-4 inches per second. The grit blast dust was removed using missile grade air.

It should be noted that normally the nozzle grit blast pressure, angle, and standoff distance for RSRM nozzle hardware is 40-70 psi, 45-90 degrees, and 12 to 15 inches. However, due to differences in this test grit blasting chamber the pressure and standoff distance were adjusted (as stated above) to produce the uniform dull white bonding surfaces called out in the RSRM manufacturing instructions.

Baseline OSEE inspection was performed within 5 minutes of grit blasting and the readings were documented. A heavy layer of HD-2 grease was applied to the test panels using a poly-foam brush. The test panels were placed in an oven for 24 hours at 100±5 °F to allow grease to flow into the micro crevices of the test panels. Excess grease was scraped from each test panel using wooden tongue depressors. More than one pass with the tongue depressor was necessary. Each panel was cleaned according to the factors shown in Table 1. The panels were placed vertically for cleaning. Figure 1 illustrates the parameters of the cleaning cycle. The panels were rinsed using deionized water pressurized to 75 psi in a small pressure rinser. The test panels were dried using missile grade air. The test panels were placed in a nitrogen purged plastic bag for transport to the OSEE laboratory. They were situated such that the bag surface did not contact the bonding substrate of the panels.

OSEE inspection was performed and the measurements were documented. Visual and black light inspection was performed and the approximate amount of grease remaining on the surface of the panel was documented. Coverage was estimated and documented in terms of percent. The test panels were placed in a nitrogen purged bag and transported to the lay-up facility.

The adhesive was prepared in accordance with Thiokol specification STW5-3292 followed by vacuum mixing for 15 minutes (mix time was recorded). Seven tensile buttons were bonded to each prepared tensile plate for each run from the Table 1 matrix. All tensile buttons had a 30 ± 5 mil bond line thickness. Lay-up start times and lay-up finish times were recorded. The test specimens were cured at 105±5°F for 72 hours minimum.

Figure 2 is a flow diagram of the fabrication process used for these test specimens.

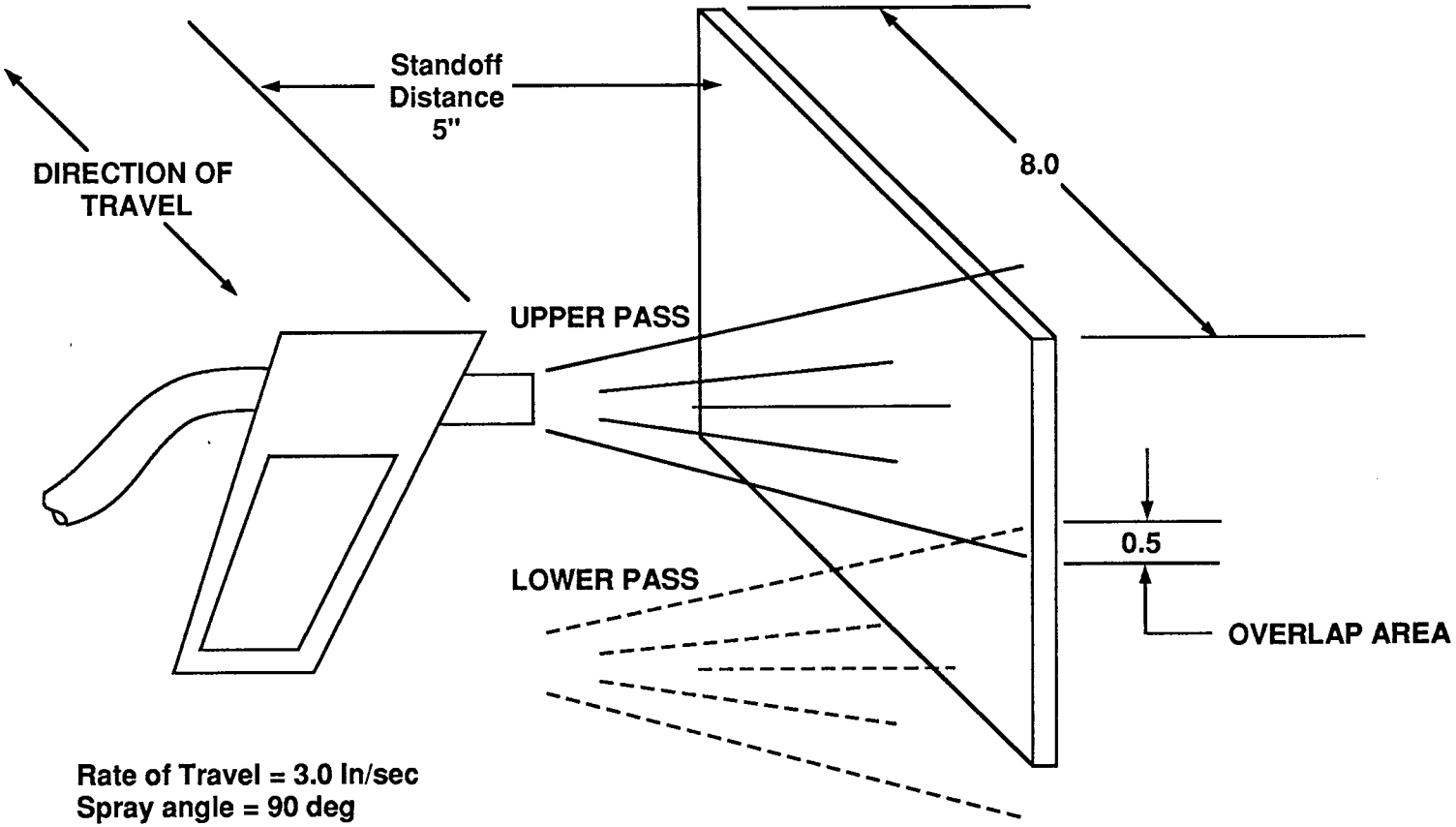
All sixteen of the test panels used in this study were processed in a controlled manner so that the elapsed time from operation to operation was the same for each panel. For example, each panel was un-bagged, grit blasted, OSEE inspected, and re-bagged before the next panel was un-bagged. The cleaning, rinsing and bonding processes used for the panels were also performed in this manner.

OSEE inspection was also performed for each panel. The data were reduced to a difference between the baseline OSEE reading taken when the panel was clean and freshly grit blasted and after the panel had undergone its designated cleaning cycle. The data were reported in terms of centivolts which indicated the amount of ultraviolet light reflected off of the surface of the test panel.

Visual and black light inspection was performed on each of the panels to quantify the amount of grease remaining on the surface of the panels. Grease coverage was estimated and documented in terms of percent coverage.

Tensile adhesion testing was performed to determine the effect of the specified cleaning process on bond strength for each of the panels. As mentioned Hysol EA-913NA adhesive was used in this study because of its high sensitivity to HD-2 grease contamination. Seven tensile buttons were bonded to each test panel using Teflon spacers which yielded a 0.030 inch bond line thickness. The specimens were pulled at 72 ±5°F with a crosshead speed of 0.05 inch per minute.

Visual inspection of the test panels indicated that eight of the panels were successfully cleaned using the described factors. A successful cleaning was defined as a panel in which no grease remained on the bonding surface (as evident from the black light inspection). In addition, panels which were



1 PASS CONSISTED OF AN UPPER AND LOWER PASS TO SPRAY THE ENTIRE PANEL
1 CYCLE CONSISTED OF 2 PASSES SEPARATED BY THE SOAK TIME

Figure 1 Test Panel Spray Cleaning Parameters

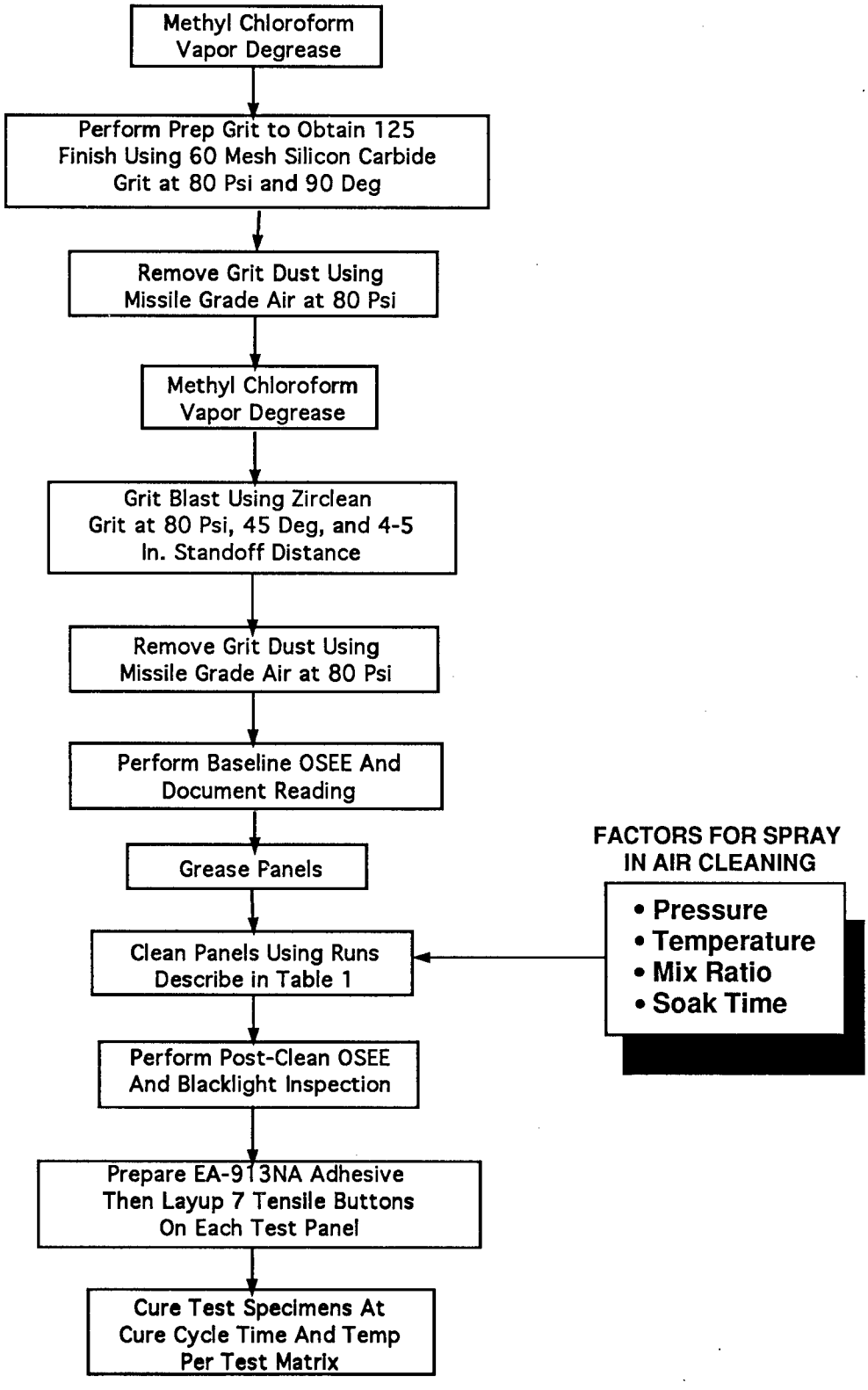


Figure 2 Test Specimen Preparation Flow Diagram

successfully cleaned also exhibited fast dry times following the rinsing operation. Six of the test panels appeared visually clean following the cleaning sequence and also yielded high tensile adhesion strengths.

Optically Stimulated Electron Emission readings were taken to provide a delta value between the baseline OSEE reading taken when the panel was clean and freshly grit blasted and after the panel had undergone its designated cleaning cycle. These values are shown in Table 2.

Also listed in Table 2 are the results from black light inspection of the panels. This method provided a more striking indication of the residual grease remaining on the panels. Each panel was inspected and given a percent residual grease value (0 - 100%).

The results of the tensile adhesion testing are tabulated in Table 2 and graphed in Figure 3. The panels which appeared "clean" through visual and black light inspection had the highest tensile adhesion strengths as expected. Panel to panel comparison of these "clean" panels shows individual tensile button strengths with less variation from button to button on a panel. The failure modes for these panels were almost exclusively cohesive failures. The panels with a percentage of residue remaining typically resulted in adhesive failure modes. The tensile strengths from these panels depended primarily on location of button bonding on the panel.

Initial intentions on measuring the foaming affects of Brulin 815 GD consisted of spraying the cleaner onto a vertically oriented 8 X 12 inch clean steel plate and catching the solution in a transport pan as it drained off. Once this was done the solution was to be transferred into a 3500 ml graduated beaker where the amount of liquid and foam could be measured. However, during the test it was surprising to observe that foaming of this cleaner at 10% or 30% and 675 psi yielded a post spray solution which consisted entirely of foam. The foam varied in density as part of the slurry could be poured while other parts were more like soap suds. Due to a lack of a controlled method for characterizing the ability of the Brulin 815 GD to foam the factor was not investigated further in this test.

As shown in Table 2 the factor having the greatest effect on black light, OSEE, and tensile adhesion strength was spray pressure. This is due primarily to the mechanical energy of the spray stream which breaks the grease down into a very thin layer allowing the Brulin 815 GD to effectively interact and remove the remaining grease. This displacement ability of pressure can be seen in the high and low pressure condition of the post cleaned panels. Inspection of these low pressure panels revealed streaks which in some cases appear clean and in others appear streaked with grease. The scraping was not performed with a "true" straight edge across the width of the scrape, thus an uneven grease layer was produced for the cleaner to interact with. The thin layers of grease were effectively cleaned (at 75 psi spray pressure) while adjacent thick areas of grease were not. A button-to-button comparison on individual panels sprayed at low pressure revealed a high coefficient of variation for tensile strength values. This variation was significantly lower with the high spray pressure test runs.

It should also be noted that in the previous study (documented in NASA report EH33/92-5) 75 psi pressure was effectively used to clean several test panels. In this study 75 psi was not effective. This is due to the fact that two different cleaning cycles were used in the previous study. Two continuous one minute washes which were separated by a 5 minute soak time resulted in a very high volume of cleaner per unit area of test substrate for the wash cycle. In the present study the cycle was changed and reduced to effectively evaluate the factors of mix ratio, temperature, pressure, and soak time. This new cycle was also more representative of the RSRM motor case spraying process being proposed by Thiokol.

As previously mentioned the factor of pressure had the most significant positive effect on the responses of black light and tensile adhesion strength results. The primary "cleaning" or grease removal mechanism identified was material displacement. This displacement reduces the thickness of the HD-2 grease layer enough so that the Brulin 815 GD can effectively remove it for the given cleaning cycle. The results of test runs using high pressure illustrate the insignificance of cleaner temperature, concentration, and soak time for these test runs. The results of test runs using low pressure illustrate the importance of the other factors. Temperature, cleaner concentration, and cleaner soak time affect the process with significance in the order listed herein. To further understand the contribution from these other factors additional testing should include a uniform amount of contamination applied across the test substrate. This

RUN NO.	PANEL NO.	TEMPERATURE (DEG. F)	SOAK TIME (MINUTES)	CONCENTRATION (PERCENT)	PRESSURE (PSI)	BLACK LIGHT % RESIDUE COVERAGE	OSEE DELTA (CENTIVOLTS)	TENSILE ADHESION (PSI)
16	17	140	10	30	675	0	441	8743
2	3	72	2	30	675	0	425	8584
8	5	72	10	30	675	0	360	8568
7	12	140	10	10	675	0	476	8554
12	8	140	2	30	675	0	484	8512
11	16	72	2	10	675	0	293	8277
15	4	72	10	10	675	0	444	7939
4	9	140	2	10	675	0	408	7391
6	10	140	10	30	75	15	481	7038
10	15	72	2	30	75	25	290	4478
3	7	140	2	30	75	30	407	4476
13	11	140	10	10	75	20	417	4349
5	13	72	10	10	75	40	283	2420
9	14	140	2	10	75	40	299	1518
14	6	72	10	30	75	40	441	1153
1	2	72	2	10	75	95	445	871

Table 2 Spray-In-Air Cleaning Test Matrix Including Factors and Responses

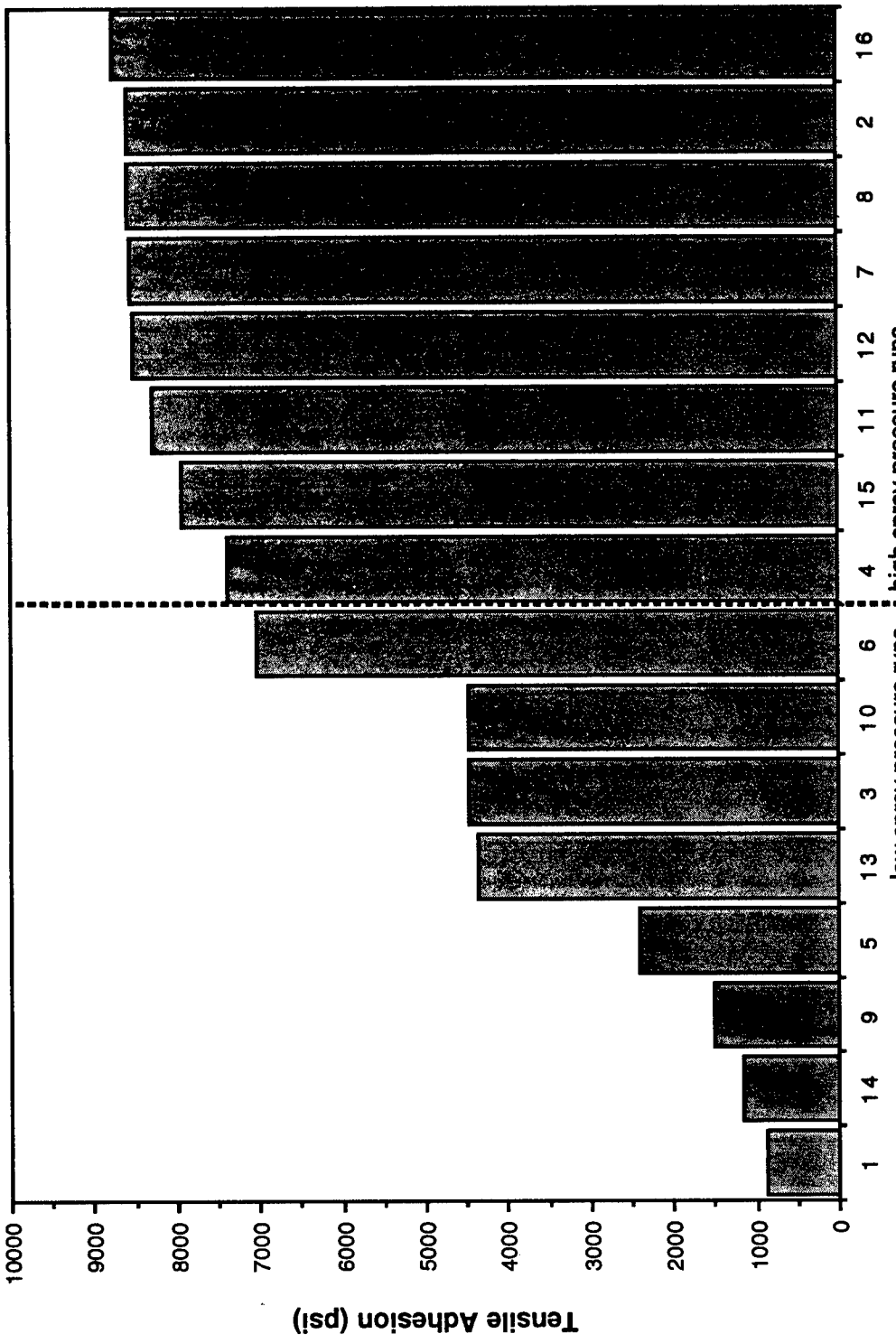


Figure 3 Graph of Tensile Adhesion Data

uniformity should enable evaluation of the cleaner's performance at lower pressure limits so that the contribution and interactions from the other factors can be fully understood.

This study reveals that room temperature cleaning is possible as long as high pressure is used to achieve the displacement discussed earlier. Runs 2,8 and 11 all yielded tensile adhesion strengths of at least 8000 psi., which represents the optimum bond strength for the EA913NA adhesive. These panels were all cleaned at 72 °F and 675 psi.

The effects of residual Brulin 815 GD not rinsed from the panels was difficult to assess because the resulting OSEE data was scattered. NVR (Non Volatile Residue) along with other surface analysis tests should be performed for a better understanding of the residual cleaner remaining. The measured responses of black light, and tensile adhesion strength dramatically displayed the effect of residual HD-2 calcium grease on the test panels (Refer to Table 2). The black light detectable residual grease contamination significantly lowered tensile adhesion strengths for the test runs

Additional testing should involve evaluating a cleaning process which uses a high pressure (< 1000 psi) "pre-rinse" with water only prior to the spray-in-air aqueous cleaning steps. This would significantly reduce recycle or reclamation problems with the contaminated cleaner solutions. The high pressure water-only pre-rinse would also ensure a uniform thickness of contamination across the test substrate, thus allowing a full evaluation of the factors and their interactions.

REFERENCES

1. C. D. DeWeese, Technical Report #EH33/92-5, September, 1992, "Solvent Replacement Studies for RSRM Internal Insulation Vulcanization / Bonding"

2. C. D. DeWeese, Technical Report #EH33/94-3, April, 1994, "Evaluation of Control Parameters for Spray-In-Air (SIA) Aqueous Cleaning for Shuttle RSRM Hardware"

Environmentally Compatible Hand Wipe Cleaning Solvents

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Abstract

Several solvents of environmental concern have previously been used for hand wipe cleaning of SRB surfaces, including 1,1,1-trichloroethane, perchloroethylene, toluene, xylene, and MEK. USBI determined the major types of surfaces involved, and qualification requirements of replacement cleaning agents.

Nineteen environmentally compatible candidates were tested on 33 material substrates with 26 types of potential surface contaminants, involving over 7,000 individual evaluations. In addition to the cleaning performance evaluation, bonding, compatibility and corrosion tests were conducted.

Results showed that one cleaner was not optimum for all surfaces. In most instances, some of the candidates cleaned better than the 1,1,1-trichloroethane baseline control.

Aqueous cleaners generally cleaned better, and were more compatible with nonmetallic materials - such as paints, plastics, and elastomers. Organic base cleaners were better on metal surfaces.

Five cleaners have been qualified and are now being implemented in SRB hand wipe cleaning operations.

Introduction

The Montreal Protocol, 1990 Clean Air Act Amendments, President Bush's edict on ozone depleters, and the forthcoming Aerospace Manufacturing and Rework National Emission Standards for Hazardous Air Pollutants (NESHAPs) have shifted aerospace industry's environmental compliance methodology from an "end of the pipe" strategy to one of prevention and elimination This is not an easy change. The aerospace community faces a special challenge since many of their materials must withstand rigorous use conditions.

USBI Co. is responsible for design, acquisition, assembly, test, and refurbishment of the nonmotor segments of the Space Shuttle Solid Rocket Boosters (SRBs). USBI was given a Technical Directive (TD) by the National Aeronautics and Space Administration (NASA) in 1991 to assess the impact of forthcoming environmental regulations on the materials and processes utilized on the Space Shuttle SRBs. The assessment indicated one of the materials/processes which would be significantly impacted by the new regulations was hand wipe cleaning. Hand wipe cleaning is a manual contamination removal procedure utilized in the processing of components with sufficient size, delicacy, or limited usage to preclude development of immersion or automated cleaning techniques. Common solvents used for hand wipe cleaning of SRB components are 1,1,1-trichloroethane, xylene, perchloroethylene, methyl ethyl ketone (MEK), and toluene. Hand wipe cleaning was found to account for approximately 27% of the total Volatile Organic Compound (VOC) emissions at the USBI production site in Florida. As a result, NASA directed USBI to define and qualify environmentally compatible replacements for the solvents currently in use.

Test Matrix / Variables

The hand wipe solvent replacement task was a major undertaking due to the large number of processes that used 1,1,1-trichloroethane and the other solvents. Cleanliness levels and possible effects on subsequent processes also had to be considered. The variables evaluated in the test program included: substrates, contaminants, and candidate cleaners. The substrates were determined by review of company drawings, and procedures. From this review forty substrates were chosen for testing (table 1).

Table 1. SRB Surfaces Selected For Testing

304 Stainless Steel	Hypalon - sealcoat
4130 Low Alloy Steel	Inconel 718 (Ni-base superalloy)
Aft Skirt Kick Ring Cover - (phenolic)	K5NA
Akzo primer (epoxy)	Low Volatile Akzo primer (epoxy)
Akzo topcoat (epoxy)	Low Volatile topcoat (epoxy)
Aluminum - anodized	MCC/USI (epoxy sprayable composite)
Aluminum - bare (2219)	MSA-2 (epoxy sprayable composite)
Aluminum - Alodined (chromate conversion coated)	MSA-3 (epoxy sprayable composite)
Aluminized tape No. 425	Nitrile rubber
Booster Trowelable Ablative (BTA)	Plastic sealant caps
Cork P50 sheet	PR 855 Foam
Deft primer (water-based epoxy)	PR 1422 (polysulfide sealant)
Deft topcoat (urethane)	PR 1770 (polysulfide sealant)
EA 934 - shim (epoxy)	Rust-Oleum primer (organic zinc rich)
Electrical cable sheath - (Teflon)	Rust-Oleum topcoat (epoxy)
Ethylene propylene rubber (EPR)	Silicone rubber
Flex hose (Resisto-Flex)	SLA-220 - TPS (silicate)
Forward Skirt Aft Seal - D Seal	Urethabond - sealcoat (urethane)
Forward Skirt Aft Seal - Neoprene	Viton rubber
Glass/Gold - electrical connector	XXX 409 - shim (phenolic)

The contaminants used in the study were identified by shop floor interviews, review of processes, and non-volatile residue witness plates. The possible sources of contamination generation are facility, process, and opportunity. Facility contaminants are generated by machinery or fixtures at the processing site. Examples are diesel exhaust, hydraulic fluid, methyl isobutyl ketone (MIBK), etc. Residues which pass from one processing step to the next are considered process contaminants. Tapes, greases, ultrasonic coupling agents, etc. are possible process contaminants. Contaminants of opportunity are those contaminants which do not have a documented presence during the normal operation of the facility or process. Fingerprints, insecticides, and hand lotion are examples of contaminants of opportunity.

The contaminant list is especially critical in any cleaner study and therefore all pertinent contaminants needed to be identified. Much of the work on SRB contaminant identification was accomplished by a previous study, "Surface Preparation and Verification For Bonding" (1). In order to simplify the test program, several contaminants were omitted due to chemical similarity to other contaminants. In addition, some of the contaminants tested, specifically the particulates, were combined to form a "cocktail" or mixture. This mixture consisted of facility dust, dirt, MSA-2 dust, cork dust, paint dust, Insta-Foam dust, and Hypalon dust. The final number of contaminants utilized in the test program was 23 (table 2). Determination of the substrate/contaminant combinations for the test matrix followed the flow diagram in Figure 1.

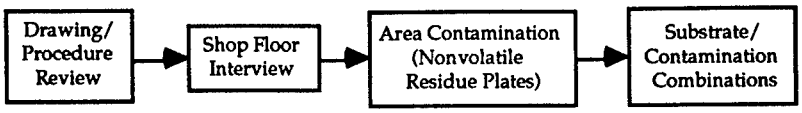

Figure 1. Flow Chart of Methodology for test matrix

Table 2. Contaminants Selected For Testing

880 C&C Grease	Molybdenum grease
Ardrox dye penetrant	Particulates:
Chalk	Cork residue/dust
Echo Ultragel II	Facility dust
Fingerprints	Hypalon dust
Flight grime	Insta-Foam dust
Glo Bright	MSA-2 residue/dust
Grease pencil	Paint dust
HD Conoco Grease	PR 1422
High temperature tape	Teflon spray
Hydraulic fluid	Vacuum pump oil
Magnaflux dye penetrant	Vinyl tape
Marking ink	Walnut hulls
Masking tape	

Several criteria were used to select the candidate cleaners. Material Safety Data Sheets (MSDSs) from possible candidate cleaners were reviewed for toxicity; worker safety hazards, physical properties (including flash point and vapor pressure); and storage, disposal, and shipping requirements/restrictions. The cleaning ability of potential cleaners was initially evaluated by vendor interviews and review of their data sheets. The chemical components of the cleaners were also reviewed by MSDS, data sheets, and vendor interview. Nineteen cleaners were chosen for testing (table 3).

Table 3. Cleaners Selected for Testing

CLEANER	VENDOR
409 Cleaner	Clorox
815 GD	Bulin & Company, Inc.
815 MX	Bulin & Company, Inc.
Allied Signal Volatile	Allied Signal
Axarel 6100	Du Pont
Blue Gold	Modern Chemicals Inc.
D. K. Solvent	DuBois
D99 Cleaner	Tiodize Co. Inc.
Fantastik	Dow Chemical
Jettacin	DuBois
Key Chem 01000	Stuart - Ironsides, Inc.
Key Chem 06000	Stuart - Ironsides, Inc.
PF Degreaser	PT Technologies, Inc.
Prime	DuBois
Propanol/Ethanol	-------
Reveille	DuBois
Siloo Glass Cleaner	Siloo
Simple Green	Sunshine Makers, Inc.
Solvo Cleaner 68-FD	Quaker Chemical Corporation

A full factorial of the three variables, substrates, contaminants, and candidate cleaners, would have consisted of over 17,000 combinations. Therefore, the experiment was designed to examine only those contaminants which were pertinent for a given substrate. The total number of combinations was thereby reduced to approximately 3,000.

Methods

The hand wipe solvent replacement program consisted of three phases: down selection, qualification, and implementation. Phase I, the down selection process, included performance evaluation of the cleaners, and initial compatibility testing. The test methodology for the program is shown schematically in Figure 2.

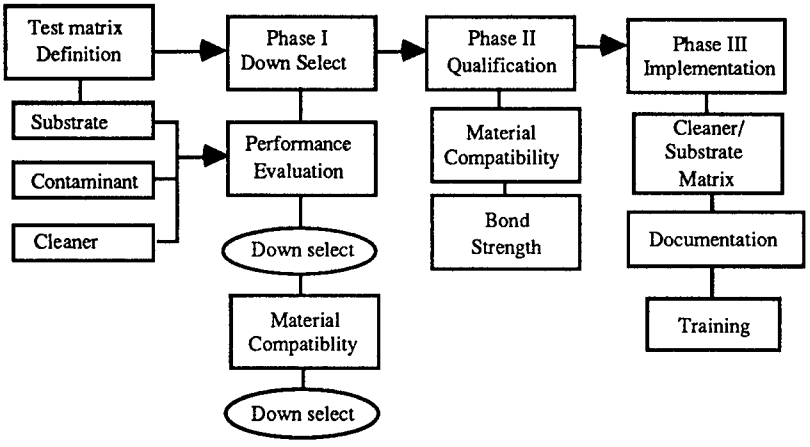

Figure 2. Project Flow Chart

The performance evaluation testing examined the cleaning ability of the candidate cleaners with respect to the substrates and contaminants. This quick and simple test was designed to identify, early in the program, cleaning weaknesses of the candidates. Performance evaluation measured the amount residue left on a substrate coupon after contaminating with a specific contaminant and then cleaning with a candidate cleaner. The residue was measured gravimetrically and, where applicable, water break free. In all tests, 1,1,1-trichloroethane was used as a control solvent. Where appropriate, other solvents were also used as controls. In addition, the performance evaluation testing also identified some compatibility concerns. By identification of the cleaning weaknesses it was possible to reduce the number of candidates examined in the next phase of testing.

After performance evaluation seven viable cleaners remained. These cleaners were then tested for compatibility using ASTM F 483: "Total Immersion Corrosion Test" (9) and ASTM D 471: "Standard Test Method for Rubber Property - Effect of Liquids" (5). Total Immersion tested the compatibility of the cleaners to the metal substrates, and "Standard Test Method for Rubber Property - Effect of Liquids" tested the compatibility of the cleaners to the non metallic materials. Because of the duration of exposure to the candidate cleaners these tests were considered very conservative compared to actual use conditions. 1,1,1-trichloroethane was used as the control solvent in all testing.

At the end of the Phase I testing, five candidate cleaners were selected for qualification (Phase II). Factors other than the test data were also considered in the final down selection process. These factors included: cost analysis, worker safety, and environmental impact.

Phase II of the solvent replacement project consisted of qualifying the candidate cleaners through compatibility and bond strength testing. Compatibility testing in Phase II was accomplished by exposures, under special conditions, of the candidate cleaners to metals and paint systems utilized on the SRB. Compatibility of the cleaners on metal substrates was qualified using ASTM F 1110: "Sandwich Corrosion Test" (6) and ASTM F 485: "Effects of Cleaners on Unpainted Aircraft Surfaces" (2). The sandwich

corrosion test was used to determine if the cleaners had an effect on faying surfaces. The "Effects of Cleaners on Unpainted Aircraft Surfaces" test was used to evaluate the cleaners potential for staining metal surfaces. ASTM F 502: "Effect of Cleaners and Chemical Maintenance Materials on Painted Aircraft Surfaces" (2) was used to determine the compatibility of the cleaners to SRB paint systems. 1,1,1-trichloroethane was used as the control solvent in all tests. Since, there are no ASTM procedures available for evaluating compatibility of cleaners to spacecraft surfaces, the ASTM aircraft procedures were used.

Bond strength testing in qualification examined the effect of the candidate cleaners on paint system adhesion and bond properties of adhesives, sealants, and Thermal Protection Systems (TPSs). ASTM D 4541: "Pull-Off Strength of Coatings Using Portable Adhesion Testers" (4) was used to assess potential effects the cleaners might have on SRB paint systems. ASTM D 1002: "Strength Properties of Adhesives in Shear by Tension Loading (Metal to Metal)" (7) was used to determine effect of the cleaners on the bond strength of adhesives and sealants. ASTM D 1623: "Tensile and Tensile Adhesion Properties of Rigid Cellular Plastics" (8) was used to determine the effect the candidate cleaners had on the bond strength of TPSs. Flatwise tensile testing was also used to assess the effect of the candidate cleaners following a long term exposure to conditions seen by the SRB hardware during processing. Specimens were bonded with 2216 epoxy were tested after six months of exposure and will be tested again after twelve months of exposure. Lastly, the specimens cleaned with the candidate cleaners were tested in flatwise tension at 150°F to evaluate to determine if the elevated temperature bond strength of 2216 epoxy was significantly affected. The elevated temperature testing was also repeated after six months of production facility exposure and will be repeated again after twelve months of exposure. 1,1,1-Trichloroethane was used as the control solvent for all tests.

Results

The tests showed that 1,1,1-trichloroethane was not the best cleaner for most of the surfaces. Prior to the down select, on most substrates 1,1,1-trichloroethane was ranked in the top 50% of the cleaners tested. Following down select, 1,1,1-trichloroethane was determined to be the worst cleaner for some of the substrates. None of the cleaners tested was found to consistently perform the best for all substrates examined. It was discovered that the organic cleaners performed better on some substrates while the aqueous cleaners performed better on other substrates. The major distinction appeared to be whether the substrate was metallic or non-metallic. Organic cleaners performed better on the metallic surfaces while the aqueous cleaners performed better on the coated and rubber based materials. An example of data from a performance evaluation test is shown in table 4.

Table 4. Data for Example Cleaner on 304 Stainless Steel

Contaminant	Sample No.	Applied (mg)	Residue (mg)	Water Break Free
Control	1	---	0	pass
	2	---	0	pass
	3	---	0	pass
Particulates	1	5.1	0	pass
	2	5.9	0	pass
	3	5.9	0	pass
Echo Ultragel II	1	416.3	1.7	pass
	2	501.5	0.7	pass
	3	321.8	1.1	pass
Glo Bright	1	37.0	0	pass
	2	42.3	0	pass
	3	28.6	0	pass
Fingerprints	1	0.3	0.2	pass
	2	0	0	pass
	3	0.2	0.1	pass
Conoco Grease	1	433.6	0	pass
	2	339.9	0.1	pass
	3	540.6	0	pass

Based on the results of the performance evaluation Jettacin, Prime, Blue Gold, Key Chem 01000, PF Degreaser, Reveille, Fantastik, and ethanol were chosen for continued testing. PF Degreaser, Key Chem 01000, Reveille, and ethanol are organic cleaners. Jettacin, Prime, Blue Gold, and Fantastik are aqueous or semi aqueous cleaners.

The results of the metallic compatibility tests show that none of the metal surfaces were affected by the organic cleaners evaluated. There were slight effects, statistically, displayed in conjunction with some of the aqueous cleaners used in the evaluation. However, all of the candidate cleaners were deemed to be compatible from a engineering viewpoint.

The results of the Standard Test Method for Rubber Property (Effects of Liquids) showed that, for each substrate tested, there was at least one candidate cleaner which was compatible. In fact, for the majority of the substrates, 1,1,1-trichloroethane did not display the highest degree of compatibility observed. The majority of the cleaners did not perform well on the cork substrate. This was apparently due to the porosity of the material. The cleaners soaked into the cork thus requiring a significantly longer dry time than was associated with the other substrates. Ethanol was the only candidate which displayed a reasonable dry time on cork.

Every cleaner was compatible with all of the paint systems used except Hypalon. Only the aqueous cleaners were found to be compatible with Hypalon. Acceptable bond strengths were exhibited by all paint systems except for Rust-Oleum and Urethabond when cleaned with ethanol.

Jettacin, Prime, PF Degreaser, Reveille, and ethanol were chosen for qualification. However, the preliminary aerospace NESHAPs incorporated vapor pressure limits of 45 mm Hg for hand wipe cleaners. This ruling meant ethanol was no longer an acceptable candidate. Isopropanol was suggested as a substitute and therefore added to the test program.

All the bonding tests showed at least one cleaner was as good as or better than 1,1,1-trichloroethane.

Conclusions

The USBI effort was successful in defining and qualifying environmentally compatible cleaners for Solid Rocket Booster hand wipe operations. The cleaners qualified were Prime, Jettacin, and Reveille by DuBois, PF Degreaser by PT Technologies, Inc., and isopropanol. Based on the test program results and direction from the end customer a matrix of cleaners versus substrates was generated. The matrix was as follows:

Metals	Reveille
Painted Surfaces	Reveille
- Hypalon	Prime
Thermal Protection Systems	Reveille
- Cork	Isopropanol
Rubber Materials	Prime
Foams	Prime
Composite Materials	Reveille
Electrical	Isopropanol
Sealants	Reveille

Hand wipe cleaning processes are used extensively throughout USBI's SRB operations. Because of this, over 600 documents were affected by the hand wipe solvent replacement task. Updating of these documents should start in the fall of 1994. As the documents are updated, the new cleaners will be incorporated into the USBI production cleaning operations. If delays are avoided, by the summer of 1995 all production hand wipe cleaning will be done with the new environmentally compliant cleaners. Training of the technicians in the use of the cleaners will be conducted as the cleaners are implemented.

The replacement of hazardous materials is an important challenge faced by today's industry. There are significant costs associated with testing, qualification, and implementation of such replacements. However, the long term costs of not replacing such materials may be even more expensive. The implementation of these cleaners has numerous benefits. Through the use of the new cleaners, an ozone depleting substance will be eliminated, hazardous waste generation will be decreased, the potential for exposure to toxic materials will be reduced, and the processing of SRB hardware will, in some cases, be improved through the use of more effective cleaners.

Acknowledgment

R.L. Imre — USBI - Materials and Processes
C.J. Venuto — USBI - Environmental and Operational Safety

References

1. Myers, R.S., and C.P. Clayton *Surface Preparation and Verification for Bonding* , USBI Report No. M&P-3026-006-92, December 1992.

2. "Standard Test Method for Effects of Cleaners on Unpainted Aircraft Surfaces," ASTM: F485-90, *Space Simulation; and Aircraft; High Modulus Fibers and Composites* , Vol. 15, ASTM, Philadelphia, PA. 1991, p. 498.

3. "Standard Test Method for Effects of Cleaning and Chemical Maintenance Materials on Painted Aircraft Surfaces," ASTM D502-83, *Space Simulation; and Aircraft; High Modulus Fibers and Composites* , Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 504-505.

4. "Standard Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers," ASTM: D4541-85, *Paints, Related Coatings, and Aromatics,* Section 6, Vol. 06.01, ASTM, Philadelphia, PA. 1992, pp. 791-797.

5. "Standard Test Method for Rubber Property - Effect of Liquids," ASTM: D471-79, *Rubber, Natural and Synthetic - General Test Methods: Carbon Black* Vol. 37, ASTM, Philadelphia, PA. 1982, pp. 112-120.

6. "Standard Test Method for Sandwich Corrosion Test," ASTM: F1110-90, *Space Simulation; and Aircraft; High Modulus Fibers and Composites* , Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 627-629.

7. "Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal to Metal)," ASTM: D1002-72, *General Products Chemical Specialties and End-Use Products, Section 15*, Vol. 15.06, ASTM, Philadelphia, PA. 1993, pp. 59-63.

8. "Standard Test Method for Tensile and Tensile Adhesion properties of Rigid Cellular Plastics," ASTM: D1623, *Annual Book for ASTM Standards for Plastics Section* 8, Vol. 8.01, ASTM, Philadelphia, PA. 1993, pp. 494-499.

9. "Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals," ASTM: F483-90, *Space Simulation; and Aircraft; High Modulus Fibers and Composites* , Vol. 15, ASTM, Philadelphia, PA. 1991, pp. 491-494.

IMPLEMENTATION OF ENVIRONMENTALLY COMPLIANT CLEANING AND INSULATION BONDING FOR MNASA

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ABSTRACT

Historically, many subscale and full-scale rocket motors have employed environmentally and physiologically harmful chemicals during the manufacturing process. This program examines the synergy and interdependency between environmentally acceptable materials for solid rocket motor insulation applications, bonding, corrosion inhibiting, painting, priming and cleaning; and then implements new materials and processes in subscale motors. Tests have been conducted to eliminate or minimize hazardous chemicals used in the manufacture of Modified-NASA materials test motor (MNASA) components and identify alternate materials and/or processed following NASA NASA Operational Environmental Team (NOET) priorities. This presentation describes implementation of high pressure water refurbishment cleaning, aqueous precision cleaning using both Brulin 815 GD and Jettacin and insulation case bonding using Ozone Depleting Chemical (ODC) compliant primers and adhesives.

INTRODUCTION

Marshall Space Flight Center MNASA motors traditionally employ Ozone Depleting Compounds (ODC) and other environmental and physiological hazards. MNASA is not a flight motor, but a static motor used for material testing purposes. The hardware is re-used indefinitely making storage and refurbishment operations a necessity. The motor is comprised of two main parts, the motor case and the four blast tube components (Figure 1). The forward ramp, the first blast tube component, reduces the diameter of the case down to the diameter of the blast tube. The forward center and aft center components add test area. The aft dome, the last blast tube component, reduces the diameter of the blast tube down to the diameter of the nozzle. The blast tube components are used for testing candidate case and nozzle insulation materials. The MNASA blast tube is stored with Cosmoline 1104, Rust Veto 266 and Rust Veto 76-HF. The grease is removed by a standard vapor degreasing process employing 1,1,1-trichloroethane and followed by a grit blast. Following the grit blast the interior bonding surface is immediately coated with appropriate primers and adhesives and the exterior is coated with a paint type primer.

The primary objective of the MNASA-RSRM #4 test was to evaluate the performance of non-asbestos insulations. The secondary test objective was to serve as a midscale demonstration of ODC-free motor refurbishment and ODC compliant bond system which are under development for the Redesigned Solid Rocket Motor (RSRM), but several years from full-scale implementation. Bond system primers and adhesives were screened and downselected under the Thiokol Non-Asbestos program in Utah. A second program for ODC Elimination in RSRM manufacture developed both high pressure water refurbishment cleaning and aqueous precision cleaning. These two technologies are described by Dillard and Keen, respectively, elsewhere in these procedings.

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*This work was performed under NAS8-38100 with NASA/MSFC.

BACKGROUND RESEARCH

RSRM is unique in solid rocketry in that after boosting the Space Shuttle Orbiter, they are recovered, refurbished and reused. Like MNASA refurbishment, RSRM refurbishment cleaning must remove paint, insulation, adhesives and preservative grease. Traditionally such refurbishment cleaning is by vapor degreasing and grit blasting. Water blast refurbishment testing in support of the RSRM program is currently underway. Preliminary results guided the selection of test parameters.

After refurbishment cleaning, both RSRM and MNASA are precision cleaned prior to bonding by again vapor degreasing and grit blasting. The RSRM ODC Elimination program performed preliminary screening on over 150 different cleaners and selected 15 promising cleaners to carry into formal testing. Five cleaners from each of three categories, organic, semi-aqueous and aqueous, were tested. The candidate cleaners were compared with respect to cleaning efficiency and bond integrity; the two leading candidates, Brulin 815 GD and Diversey Jettacin, were carried into this MNASA testing and demonstration.

A hand cleaner was also necessary to facilitate re-cleaning operations that sometimes become necessary during hardware processing. PF-Degreaser was selected for testing as a hand cleaner in the MNASA program. PF Degreaser, a mixture of aliphatic petroleum distillates and d-Limonene, has been successfully employed as a hand and immersion cleaner in manufacturing programs at Thiokol's Huntsville Division for several years.

TESTING

Lab Testing

Prior to manufacturing RSRM-MNASA #4, all proposed cleaning and bonding materials and processes were tested in laboratory adhesion testing. Witness panels (8" by 12") were prepared using a double vapor degrease, double grit blast method that has become the standard for all Thiokol ODC testing. The purpose of this preparation is to erase any "memory" of any chemicals the panels may have been in contact with and return the metal surface to a pure condition. Panels were then contaminated with the preservatives used on the MNASA hardware, Cosmoline 1104, Rust Veto 76-HF, and Rust Veto 266. Panels then were divided as to what process of cleaning they would undergo. All panels were black light inspectedand tested for non-volatile residue (NVR). Panels involved in aqueous processes were evaluated using water break free tests as well.

RSRM-MNASA #4 Testing

After successful completion of the lab testing, the various blast tube components of RSRM-MNASA #4 were cleaned and bonded according to the scheme in Table 1. The aft dome was a baseline control for this test. All standard, previously employed procedures and materials were used in the aft dome. Because the two center components are identical in configuration, they were used to demonstrate aqueous spray cleaning using Jettacin in the forward center and Brulin 815 GD in the aft center. Both components received a post clean grit blast. The ODC compliant bond system of Chemlok®205/Chemlok®236X was used in both center components on the blast tube hardware with Chemlok®236X being used at the insulation to insulation bond lines. The forward ramp received a water blast followed by a vapor degrease and grit blast. The forward ramp represented the first stage of ODC implementation currently planned for RSRM flight hardware. The aqueous bond system, Chemlok®805/Chemlok®828, was applied to the forward ramp. Because actual hardware cannot undergo the destructive bond testing before firing, 8" by 12" steel witness panels have been traditionally processed along side the hardware for testing purposes. Water blast and precision spray cleaning parameters observed during the full scale demonstration are listed in Tables 2 and 3.

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TABLE 1:
MATERIALS TEST SCHEME FOR RSRM MNASA #4

	REFURBISHMENT CLEANING	PRECISION CLEANING	PRIMER AND ADHESIVE
FORWARD RAMP	WB	VD/GB	CL805/828
FORWARD CENTER	WB	Jettacin/GB	CL205/CL236X
AFT CENTER	WB	Brulin/GB	CL205/CL236X
AFT DOME	VD/GB	VD/GB	CL205/CL236A

Legend

WB = Waterblast
VD = Vapor Degreaser
GB = Grit Blast
CL805 = CHEMLOK 805 (Aqueous)
CL828 = CHEMOK 828 (Aqueous)
CL205 = CHEMLOK 205 (Organic Solvent)
CL236A = CHEMLOK 236A (Organic Solvent)
CL236X = CHEMLOK 236A (ODC Compliant Organic Solvent)

Table 2
High Pressure Water Blast

Parameter	Setting
Nozzle	Hammelmen Rotorjet
Nozzle angle	80°
Stand off	8"
Pressure	33 ksi
Pass Rate	2"/sec/3.5" wide path
Flow Rate	10 gpm
Barochem rinse	1000 psi
Dry air pressure	70 - 80 psi

Table 3
Precision Spray Cleaning

Parameter	Setting
Nozzle	2504
# of cleaner passes	3
Stand off	8 - 10"
Cleaner spray pressure	1000 ± 20 psi
Pass rate	4"/sec/8" wide path
Cleaner temperature	150 ± 5°F
Rinse pressure	70 ± 10 psi
Dry air pressure	70 - 80 psi

RESULTS

NVR results of all refurbishment methods were in the same family and below 2 mg/ft^2, which is excellent. Figures 2 and 3 summarize the adhesion results for the lab tests, as well as witness panels accompanying the motor. In all cases, bond strength, reported as tensile adhesion and peel strength, of the ODC compliant primer/adhesive systems was roughly the same as the baseline primer/adhesive system (Chemlok®205/Chemlok®236A). All peel strengths more than an order of magnitude above the program requirement of 12 pli and more than three times the program adhesion strength requirement of 100 psi. The primary failure mode in all cases was cohesive within the rubber insulation. Some significant discoveries were that in this case, water blast followed by a grit blast produced excellent NVR results, exceptional bond results and immediately following the high pressure water blast, all panels passed water break free tests.

Figure 4 summarizes testing of the ODC compliant adhesives as insulation ply-to-ply adhesives. As with insulation-to-steel adhesion above, both candidate ODC compliant systems (Chemlok 205/Chemlok 236X and Chemlok 805/Chemlok 828) performed well. All adhesives performed about equivalently and significantly above the minimum for MNASA.

CONCLUSIONS

The program objectives were accomplished. An ODC free refurbishment process (high pressure water blast followed by precision spray cleaning and grit blast) was defined for MNASA that met and significantly exceeded program requirements. In addition, ODC compliant primers and adhesives were identified for the MNASA-RSRM #4 bond lines that met and significantly exceeded program requirements. These results help ensure a future atmosphere of acceptance for these and other ODC free processes.

Not surprisingly, a certain body of unanticipated results fall into the category of "Lessons Learned." This project is no exception:

- Since water evaporates more slowly than organic solvents with low vapor pressure, the aqueous adhesives were more prone to run and drip when applied as thick as conventional products. Therefore, operators should practice with new materials to learn to control them.

- Since the waterblast conditions are so harsh, protective maskants are easily torn, allowing the adhesive to recontaminate the hardware. Therefore, protective maskants should be avioded prior to waterblasting.

- Rust inhibitors should either be in the waterblast water, or constantly flowing over the part to be most effective.

- Water stands on all horizontal surfaces, where possible these should be shimmed unevenly to encourage drainage.

- Medium pressure missile grade dry air facilitates drying faster than a hot gun.

- While organic vapor masks are probably appropriate for all spray cleaning applications, operators find solutions such as Jettacin, which contain an organic solvent, more objectional.

ACKNOWLEDGEMENTS

This paper is the result of a collaboration of many individuals. The following people provided assistance and information: T.N. Thornton, J.R. Newton, K.B. Evans, J. Stevens and K.J. Schulte.

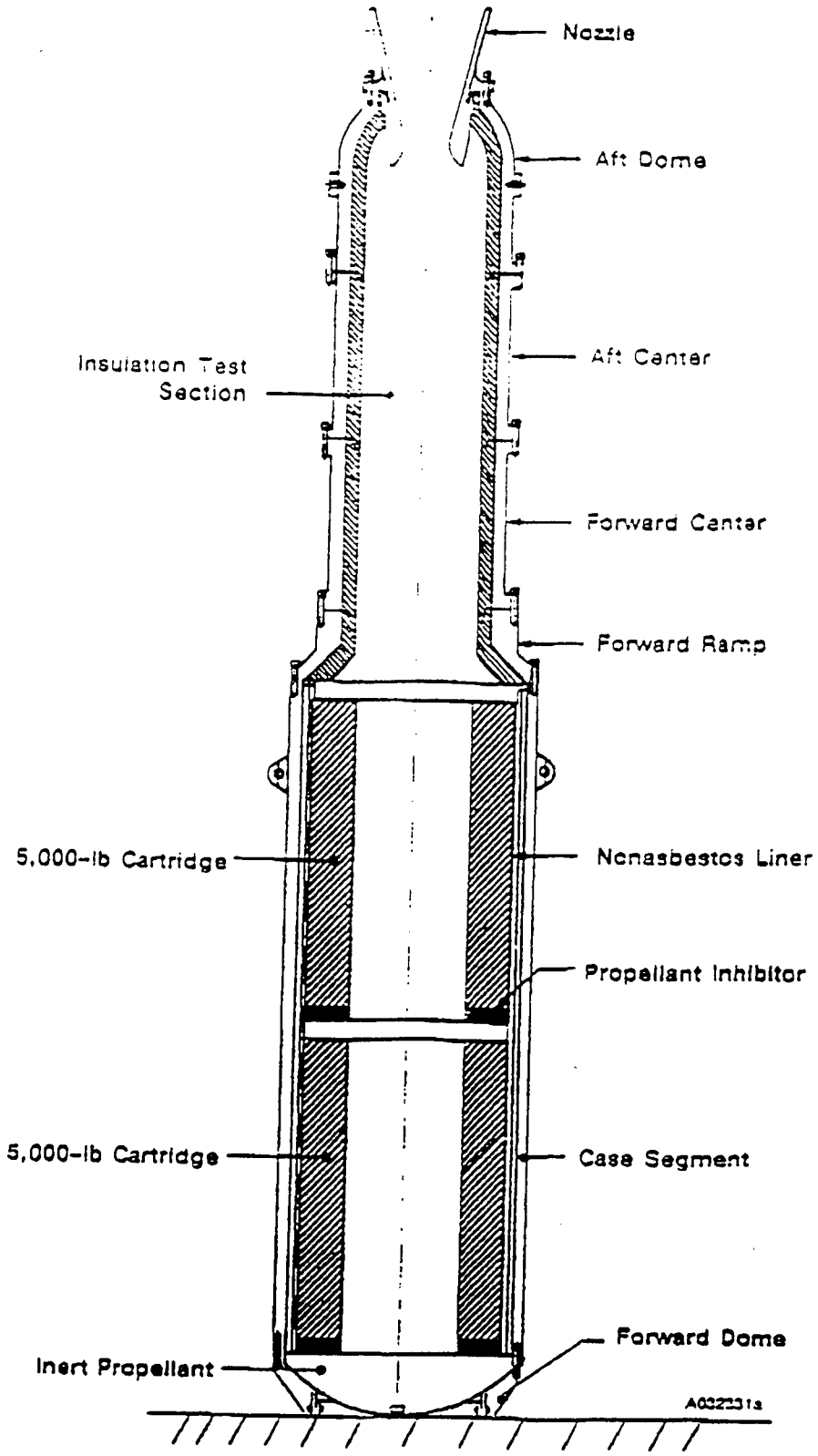


Figure 1. MNASA Motor Test Configuration (Vertical-fired Motor with Nozzle Up)

Figure 2

Tensile Adhesion of Asbestos-Free EPDM to D6AC Steel

(All Failures Cohesive in Insulation)

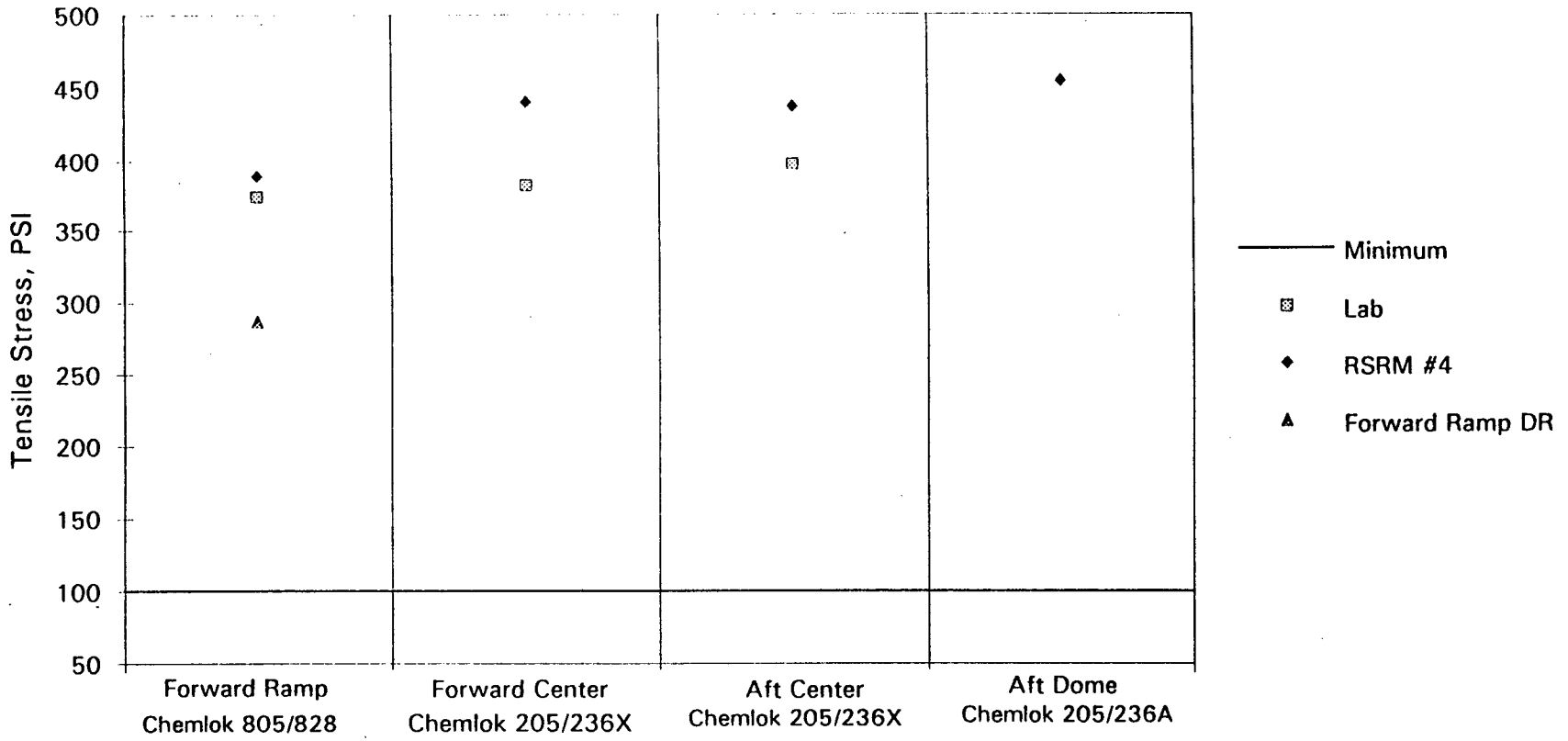
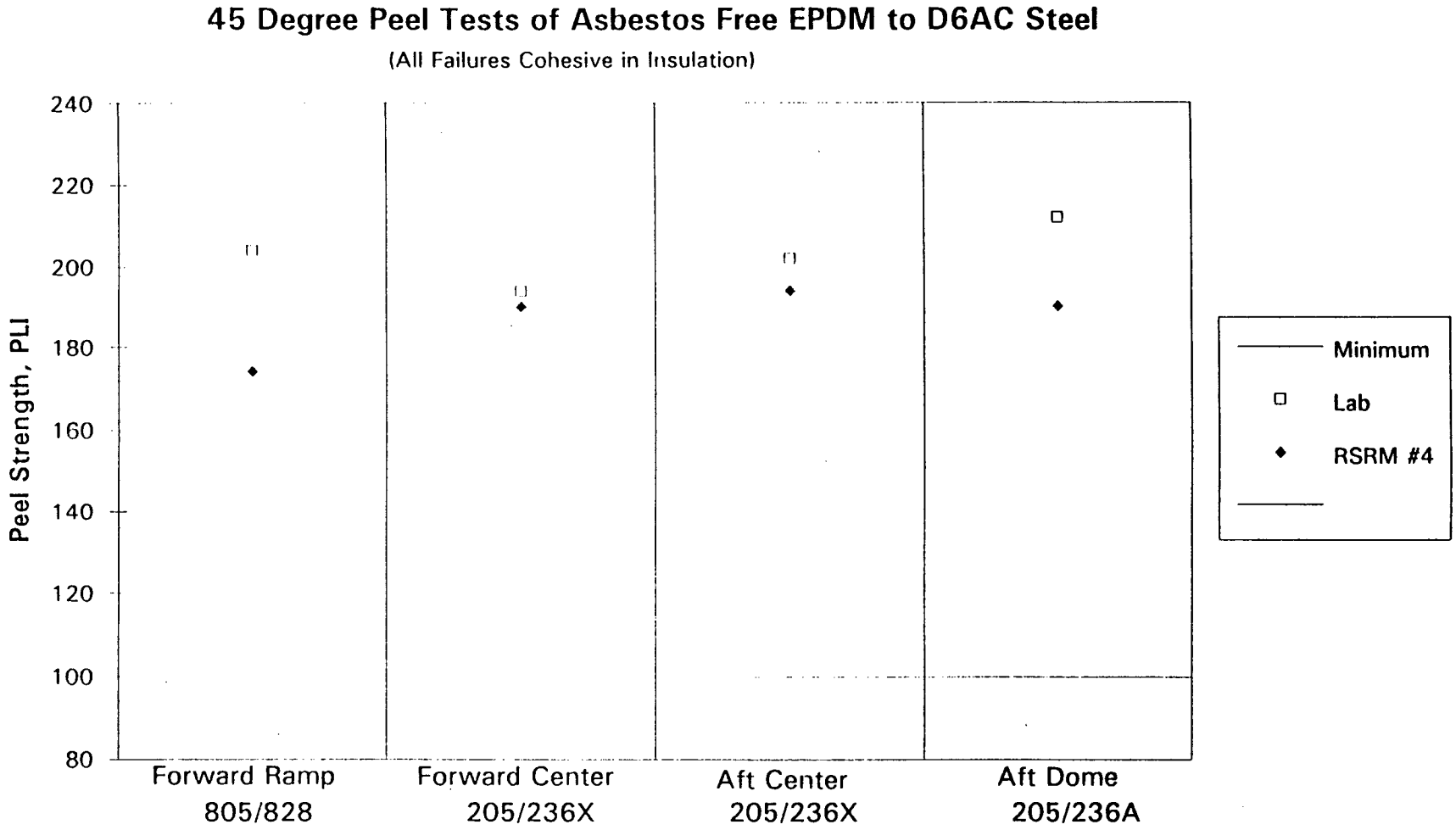


Figure 3


45 Degree Peel Tests of Asbestos Free EPDM to D6AC Steel
(All Failures Cohesive in Insulation)
Peel Strength, PLI
240
220
200
180
160
140
120
100
80
Forward Ramp
805/828
Forward Center
205/236X
Aft Center
205/236X
Aft Dome
205/236A
Minimum
Lab
RSRM #4

Thiokol CORPORATION
SPACE OPERATIONS

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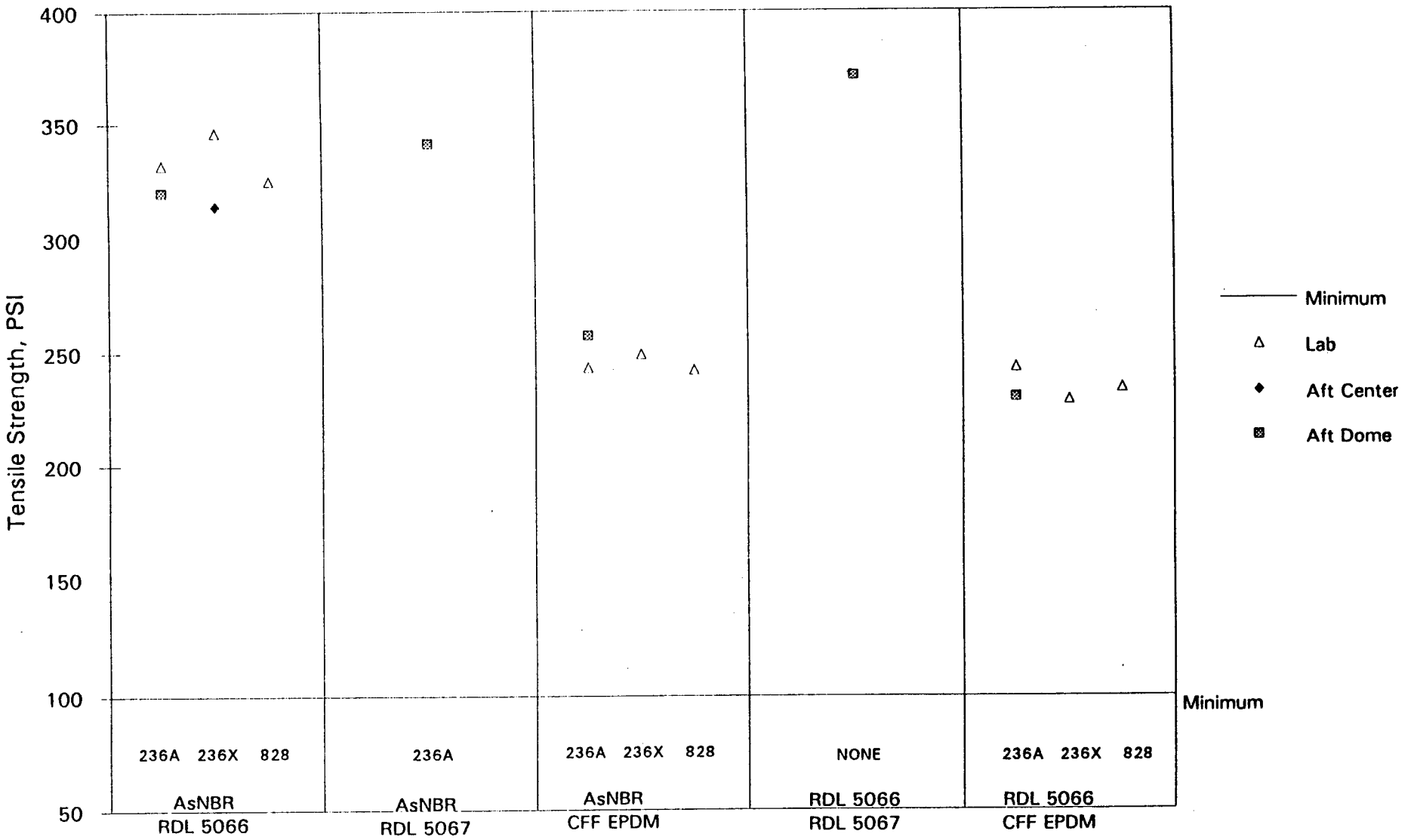
Figure 4

InterInsulation Tensile Adhesion
MNASA RSRM #4



CLEANING VERIFICATION—INSTRUMENTATION AND TECHNIQUES 1

Surface Contamination Analysis Technology Team Overview

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Abstract

A team was established which consisted of representatives from NASA (Marshall Space Flight Center and Langley Research Center), Thiokol Corporation, the University of Alabama in Huntsville, AC Engineering, SAIC, Martin Marietta, and Aerojet. The team's purpose was to bring together the appropriate personnel to determine what surface inspection techniques were applicable to multi-program bonding surface cleanliness inspection. In order to identify appropriate techniques and their sensitivity to various contaminant families, calibration standards were developed. Producing standards included development of consistent low level contamination application techniques. Oxidation was also considered for effect on inspection equipment response. Ellipsometry was used for oxidation characterization. Verification testing was then accomplished to show selected inspection techniques could detect subject contaminants at levels found to be detrimental to critical bond systems of interest. Once feasibility of identified techniques was shown, selected techniques and instrumentation could then be incorporated into a multipurpose inspection head and integrated with a robot for critical surface inspection. Inspection techniques currently being evaluated include optically stimulated electron emission (OSEE); near infrared (NIR) spectroscopy utilizing fiber optics; Fourier transform infrared (FTIR) spectroscopy; and, ultraviolet (UV) fluorescence. Current plans are to demonstrate an integrated system in MSFC's Productivity Enhancement Complex within five years from initiation of this effort in 1992 assuming appropriate funding levels are maintained. This paper will give an overview of work accomplished by the team and future plans.

Introduction

The Surface Contamination Analysis Technology team was established to address future surface cleanliness verification requirements for applicability in new manufacturing processes resulting from elimination of ozone depleting chemicals. Elimination of ozone depleting chemicals will effect shuttle hardware processing in two major areas. These areas are cleaning solvent elimination and replacement materials, i.e. primers, adhesives, and coatings. The Surface Contamination Analysis Technology team effort addresses the effect of losing solvents currently used in shuttle hardware manufacturing processes. Ozone depleting chemical elimination will effect currently used cleaning solvents, cleanliness verification solvents, and manufacturing materials containing targeted solvents. Ozone depleting chemicals identified in the shuttle program include for the largest part chlorinated solvents commonly used in cleaning processes and flight hardware cleanliness verification. Changes in processes and materials will effect future surface cleanliness verification requirements and their applicability in new manufacturing processes and inspections.

Replacement materials, which in all likelihood will be aqueous based and possibly more susceptible to contamination, when implemented may result in a bond system more sensitive to contamination. These concerns lead to the effort undertaken by the Surface Contamination Analysis Technology team. This effort, to identify alternate cleanliness verification techniques which can be applied both in laboratory and manufacturing environments, was initiated in 1992 in MSFC's Materials and Processes Laboratory. The goal was to develop a multi-purpose inspection system within five years. The new inspection system as conceived would consist of multiple techniques making up a single inspection head. The system would be used to detect, identify, and quantify contamination. Data attained would then be used to determine appropriate cleaning procedures.

Concerns

Cleaning Solvent Replacement Concerns

Cleaning solvent elimination will require replacement with alternate cleaning agents. The leading replacement candidates are alternate solvents, organic based cleaners, and aqueous based cleaners. Removal of contamination with candidate cleaners will depend on the type contaminant, its solubility / rinsability in the proposed cleaners, and cleaning process parameters. These new cleaning solutions may not remove contaminants as efficiently as solvents, i.e. residues may remain on surfaces after cleaning. If these residues prove detrimental to critical bondlines then new inspection techniques which are sensitive to low levels of contamination may be required for cleanliness verification prior to critical bonding operations.

Cleanliness Verification Solvent Replacement Concerns

Current techniques for cleanliness verification such as water break and blacklight which have been used as acceptance tests in the shuttle program have limitations since they are subjective and qualitative techniques. If future cleaning processes leave detrimental residues which are not detectable with currently used inspection techniques more sensitive quantitative inspection techniques may be required. Non-volatile residue (NVR) analysis is a commonly used quantitative cleanliness verification method utilized in the Space Shuttle program. NVR analysis utilizes solvents (freon and 1,1,1 trichloroethane) on the elimination list. NVR sampling has been used for years in the shuttle program for hardware cleanliness acceptance. Liquid oxygen systems are evaluated for cleanliness with NVR which utilizes a laboratory flash evaporation of a sampling solvent to obtain a residue. NVR is quantitative but is dependant upon the sampling solvent being able to remove the expected contaminant. If NVR is detected the data gathered indicates the amount of material removed from the surface not what remains after NVR (flush or wipe) analysis. Residue remaining on the surface is of major concern. NVR analysis is used as a sampling technique and is impractical for 100 percent acceptance testing of surfaces of the magnitude found in solid rocket motor manufacturing. Since solvent NVR analysis cannot be accomplished in a real time manner there is a need for development of new, real time, quantitative cleanliness inspection techniques which can be applied to shuttle hardware manufacturing.

Concerns with Replacement of Solvent Containing Production Materials

Adhesives and coatings which contain ozone depleting chemical components are used throughout the shuttle program. Materials which may require replacement in the near future include solvent based primers, adhesives, and coatings. Resulting formulation changes may change critical bondline response to contamination. If new materials implemented result in the bondline being more sensitive to contamination then new cleanliness inspection techniques may be necessary.

Technical Approach

Concerns stated above lead to a search for cleanliness verification techniques which could detect a wide range of contaminants on critical surfaces. Residues may consist of organic and/or inorganic components depending on the cleaning solution and method used. Due to the range of possible contaminants and surfaces requiring inspection it is expected that a combination of techniques rather than a single technique would be used for cleanliness inspection. There is currently no available single technique capable of detecting organic and inorganic contaminants on various large surface areas in real time. Candidate techniques currently used in industry as well as those under development were considered. A plan for evaluating hardware bond surface characteristics such as substrate material type, surface roughness, and oxidation for metallic substrates,was developed. Inspection implementation parameters including inspection stand off distance, required inspection rate, environmental conditions, ease of operation, data interpretation, and direct applicability to existing manufacturing processes and facilities were considered. In order to

evaluate candidate inspection technique response to contamination both clean baseline standards and contamination standards had to be developed. The philosophy used in approaching standards development was first to determine what families of contaminants present in hardware processing environments. After contaminants were identified standards were developed to use in determining detection sensitivity and later calibration of the system. Techniques chosen had to detect contamination at levels which critical bond systems or surfaces were adversely effected. Development of processes for applying consistent low level contamination had to be undertaken. Processes and standards produced for evaluating and calibrating candidate inspection techniques were developed in parallel with some of the instrumentation characterization work.

Substrate Characterization and Standards Development

Adequate surface contamination analysis requires proper characterization of the substrate to be inspected. This characterization includes determination of a baseline nominal surface resulting from the surface preparation process. The majority of effort has been with RSRM simulated surfaces, i.e. grit blasted steel and aluminum. Test panels were prepared with the same parameters as used on flight hardware as closely as possible with laboratory equipment. These panels were then used as a baseline noncontaminated data point to compare subsequent data to. Characterization of the inspection instrumentation was accomplished to verify instrument variability due to the substrate. One variable in the metallic substrates of interest was oxidation. Surface oxidation was considered for its effect on instrument detection of contamination since past experience with OSEE showed a sensitivity to surface oxidation. Aluminum surface reactivity was much higher than steel thus making it more of a challenge in characterization studies. Oxidation characterization testing was accomplished in an environmental chamber which varied temperature and relative humidity over a wide range. Test panels were prepared to simulate hardware flow then placed in the controlled environment and monitored over time. OSEE and NIR data were generated for substrate response with varying temperature and humidity levels. NIR characterization work showed a capability to differentiate between contamination and oxidation. This was an improvement over OSEE which showed a signal reduction from contamination and oxidation, i.e. OSEE could not differentiate between the two, making data evaluation difficult. This work was accomplished by UAH personnel under contract to Thiokol.[1] MSFC laboratories were used in accomplishment of these tasks.

Ellipsometry was performed on coupons exposed at various environmental conditions. Measurements were made to attempt to characterize various aluminum oxides which have been shown to effect OSEE signal from a substrate and may also effect other inspection techniques response. The problem encountered with aluminum studies has been the lack of optical property data on aluminum oxides. UAH has attempted to grow various oxides for ellipsometry characterization with some success. This work is continuing.

Substrate characterization work was paralleled with standards development for contamination response characterization and calibration. Common contaminants expected in the process had to be identified then characterized for their effect on instrument response. Major contamination sources identified included machining oils, hydraulic fluid, greases, silicone lubricants and release agents. After contaminants were identified they were grouped by chemical family. Contaminants within a family were assumed to have the same effect, i.e. degradation, on bonding. A single contaminant was then chosen from each family, normally the most prevalent in the manufacturing environment, since testing of all possible contaminants was impractical. Selected contaminants were then evaluated for ease of application and stability once applied to a substrate.

The majority of contaminants fell into two families, hydrocarbons and silicones. Some teflon release agents were used but silicones were used for the same purpose therefore silicones were assumed to simulate teflon materials adequately. Contaminants selected for standards included Conoco HD-2 grease, a tenacious heavy duty preservative grease used in RSRM production; CRC silicone oil, a silicone

lubricate; and Kaydol, a hydrocarbon mineral oil chosen to represent general hydrocarbon based materials. Kaydol was the only contaminant that presented problems with stability. The material appeared to migrate or disperse after a period of time. Paraffin wax was suggested as a contaminant since it would represent a hydrocarbon and be stable at room temperature. Application techniques were subsequently developed for chosen contaminants.

Contamination Application Techniques

Thiokol modified an off the shelf machine for applying contaminants to test panels. The hardware manufactured by Sono-tek utilized an ultrasonic spray nozzle and conveyor track system for printed circuit board processing. A number of parameters were evaluated for effects on Sono-tek contaminant deposition. These parameters included track speed, solution concentration, pump volume or flow rate, nozzle orientation, and exhaust flow. Solution concentration was a major factor in obtaining consistent uniform coating with the Sono-tek hardware. Other application techniques evaluated included air brush application and immersion techniques. AC Engineering developed air brush application techniques. Contaminant level application was verified with gravimetric measurements made with aluminum witness foil sheets during both Sono-tek and air brush applications. An aluminum foil sheet was run through the Sono-tek equipment immediately before and after bonding panels to insure proper contaminant levels were being applied. Aluminum witness foils were exposed beside panels for air brush applications. NVR analyses of contaminated panels were done initially to verify the use of witness foils for deposition level verification. An FTIR microscope was used to characterize the contamination standards developed. Results of these tests are documented in an AC Engineering paper.[2] Verification techniques have shown Thiokol and AC Engineering have uniform and consistent procedures for application of contaminants at levels below five milligrams per square foot.

Ellipsometry was investigated also for detection and verification of contamination on various substrates. A problem encountered with ellipsometry was the lack of optical constants for various contaminants being evaluated. An effort is underway which will utilize a well defined substrate, silicone wafers, to which contaminant films will be applied then studied with ellipsometers in MSFC M&P laboratories. It is hoped this testing will allow determination of optical properties of common contaminant films which may be present on shuttle hardware prior to sensitive bonding operations. Results from this testing will feed data into other testing of various techniques which may prove useful.

After contamination application technique development, the next step was to determine critical bond system sensitivity to various contaminants. Bonding studies were conducted to determine at what contaminant level critical bond systems were degraded. Adhesive bond strength and failure modes were used to evaluate bond system performance or acceptability. High strength approaching the capability of the adhesive with a cohesive failure mode were desired. Cohesive failure is considered as failure within the adhesive or within the material being bonded to the substrate of interest. Adhesive failure, failure at the adhesive/substrate interface, indicates problems generally resulting from surface preparation, processing, or contamination. Bonding tests showed epoxy bondlines were sensitive to certain contaminants at levels below five milligrams per square foot of surface area. RSRM vulcanized bonding for insulation applications was generally an order of magnitude less sensitive. AC Engineering's efforts in support of the Surface Contamination Analysis Technology team work are detailed in "Standardization of Surface Contamination Analysis Systems" .[2]

Technique Investigation

Techniques being evaluated for incorporation into an inspection system include those which analyze surfaces over a wide wavelength range. Techniques currently being evaluated include optically stimulated electron emission (OSEE), near infrared (NIR) fiber optic spectroscopy, diffuse reflectance Fourier transform infrared (FTIR) spectroscopy, and ultraviolet (UV) fluorescence. Capability determination for

most of these contamination detection techniques is currently underway. A combination of techniques may be useful in surface cleanliness verification as a replacement for currently used inspections including blacklight, water break, and nonvolatile residue sampling. Following is a brief description of each of the previously mentioned inspection techniques.

OSEE

OSEE is currently used in the RSRM program for case cleanliness inspection prior to primer / adhesive application for insulation bonding and nozzle housing inspection prior to epoxy adhesive bonding. This non-contact technique is sensitive to low level contamination on steel and aluminum substrates. Initially OSEE was implemented to detect residual grease on the internal D6AC steel motor case after vapor degreasing. The technique was sensitive to grease levels below 10 milligrams per square foot of surface area which was below the acceptance limit of 25 milligrams per square foot set at that time. OSEE was the only technique available at the time which could yield real time data on surface cleanliness of large motor case surface areas prior to subsequent processing. Other techniques were available for quantification of grease / contamination levels but data was not available in real time. OSEE detects changes in surface chemistry but can not identify what the source of change is. A complementary technique for contaminant identification would be useful when OSEE indicated a surface contaminant. A background and overview of OSEE application in RSRM manufacturing is detailed by Mattes.[3]

OSEE Third Generation Development

The original OSEE equipment implemented in RSRM manufacturing had electronics and some quality control problems. Thiokol and the OSEE equipment manufacturer, Photo Acoustic Technologies, developed a second generation, industrial hardened, OSEE system which solved some of the problems with the initial design. Langley Research Center (LaRC) became interested in the technique and evaluated the original OSEE system design. A characterization of the physics of OSEE was undertaken at LaRC under the direction of Dr. W. T. Yost. Dr. Chris Welch of the College of William and Mary conducted characterization tests on the system. Deficiencies in the system were identified and proposals for improvements made in LaRC's evaluation report.[4] A third generation OSEE system as it was referred to was designed considering LaRC's identified improvements and MSFC Surface Contamination Analysis Technology team suggestions from equipment use history. A third generation six inch sensor system was fabricated by LaRC from funding provided through NASA headquarters Code QW.[5] Preliminary testing of the OSEE III system at MSFC shows improved stability over the current system, much quicker response time, and less effect from environmental fluctuations due to the argon purge implemented as part of the redesign. The LaRC team has applied for patents on electronic improvements made in the OSEE equipment.

IR Spectroscopy Techniques

Spectroscopic techniques were evaluated for feasibility to manufacturing on-line applications. The Surface Contamination Analysis Technology team members experienced with spectroscopic techniques and their application to process monitoring included the University of Alabama in Huntsville (UAH) In-line Process Control Laboratory. A Guided Wave 260 spectrometer with fiber optic probes was used in MSFC's laboratories to characterize RSRM substrates of interest, D6AC steel and 7075 aluminum. Tests were conducted to evaluate oxidation and contamination on these substrates. Results showed NIR use was feasible for detecting contaminants on these substrates and differentiating between contamination and oxidation after applying appropriate data analysis software. Details of this testing are discussed in "Study of Surfaces Using Near Infrared Optical Fiber Spectrometry".[6]

A joint effort between Thiokol and TMA Technologies resulted in the development of a diffuse reflectance infrared instrument, the SurfMap IR, which was evaluated by Thiokol personnel in MSFC

laboratories. The instrument was proficient in detecting hydrocarbon contamination on aluminum and steel substrates. Additional information can be found in "Cleanliness Evaluation of Rough Surfaces with Diffuse IR Reflectance".[7]

Interest in a portable FTIR system with resolution and speed for real time inspection was expressed in the Surface Contamination Analysis Technology technical interchange meeting held last year. Discussions with Dr. G.L. Powell from Martin Marietta's Oak Ridge Y-12 plant led to a procurement request for a state-of-the-art portable FTIR system applicable to manufacturing line surface inspection. Specifications calling for compact size (one cubic foot) and low weight (less than 15 pounds) were written with robotic applications in mind. Proposals have been submitted and evaluations are currently underway. Advancements in microelectronics and computational software with increased data processing speed have made these type systems a possibility for real time surface inspection. Plans are to procure the equipment and test it in MSFC's Productivity Enhancement Complex robotic test bed within the next year.

Fluorescence Techniques

An ultraviolet (UV) fluorescence technique initially funded through a Small Business Innovative Research phase I contract with LaRC was transferred to MSFC and later approved for phase II funding. Phase I testing showed this technique was capable of detecting low levels, less than 10 milligrams per square foot, of contamination on different substrates common in the shuttle program, e.g. steel, aluminum, and insulation. The technique was also demonstrated as being capable of inspecting hardware from standoff distances on the order of feet while scanning as much as 15 square feet per frame. Feasibility for inspecting large surface areas in a short period of time would be a major advantage of using this system. Details on this inspection technique are available in "Contamination Detection NDE for Cleaning Process Inspection".[8]

MSFC Productivity Enhancement Complex Test Bed

MSFC, Materials and Processes laboratory has a unique facility for evaluation / development of manufacturing processes and equipment. The Productivity Enhancement Complex (PEC) located in MSFC's building 4707 contains robotic workcells and equipment for accomplishing a wide range of full scale manufacturing processes. A PEC CimCorp gantry robot will be utilized as a test bed for inspection system evaluation. The same robot was used previously to test a three axis OSEE end effector designed by Martin Marietta for RSRM nozzle hardware inspection.

OSEE III, fiber optic NIR, SurfMap diffuse IR, and ultraviolet fluorescence systems are currently under development for in-process manufacturing applications. These systems should be available for testing in the PEC test bed by mid 1995. Other techniques will be evaluated as they become available.

Conclusion

Techniques being evaluated as part of the Surface Contamination Analysis Technology team effort appear promising for applicability to shuttle hardware inspection. Availability of a technique which will allow quick inspection of large surface areas consistent with solid rocket motor bonding surfaces appears feasible. Contamination identified in an initial scan could then be evaluated with a more sensitive spectroscopic technique which could identify species present. This information would in turn allow a cleaning procedure to be defined. Applications for this technology exist throughout the shuttle program as well as in commercial applications resulting from technology transfer.

Acknowledgements

Surface Contamination Analysis Technology team members

References

1. Workman, G. L., C. Hughes, W.F. Arendale, In-line Surface Chemistry Analysis, Final report to Thiokol Corporation, Contract 3MR029, September 1993.

2. Boothe, R. E., Standardization of Surface Contamination Analysis Systems, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

3. Mattes, R. A., Background and History of OSEE in RSRM Manufacturing, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

4. Yost, W. T., C.S. Welch, N. Abedin, OSEE Science Base, Final Report, Langley Research Center

5. Yost, W.T., et al, Design and Performance Considerations for the Third Generation OSEE Probe and Associated Electronics, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

6. Workman, G.L., W.A. Arendale, C.Hughes, Study of Surfaces Using Near Infrared Optical Fiber Spectroscopy, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

7. Pearson, L.H., B.D. Swimley, Cleanliness Evaluation of Rough Surfaces with Diffuse IR Reflectance, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

8. Marinelli, W., D. Blair, V. DiCristina, Contamination Detection NDE for Cleaning Process Inspection, Aerospace Environmental Technology Conference Proceedings, August 10 - 11, 1994.

STANDARDIZATION OF SURFACE CONTAMINATION ANALYSIS SYSTEMS

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ABSTRACT

Corrosion products, oils and greases can potentially degrade material bonding properties. The Marshall Space Flight Center (MSFC) Surface Contamination Analysis Team (SCAT) utilizes a variety of analytical equipment to detect, identify and quantify contamination on metallic and non-metallic substrates. Analysis techniques include FT-IR Microscopy (FT-IR), Near Infrared Optical Fiber Spectrometry (NIR), Optically Stimulated Electron Emission (OSEE), Ultraviolet Fluorescence (UVF) and Ellipsometry. To insure that consistent qualitative and quantitative information are obtained, standards are required to develop analysis techniques, to establish instrument sensitivity to potential contaminants, and to develop calibration curves.

This paper describes techniques for preparing and preserving contamination standards. Calibration of surface contamination analysis systems is discussed, and methods are presented for evaluating the effects of potential contaminants on bonding properties.

BACKGROUND

Efforts are underway at MSFC to develop a robotic surface contamination analysis system that can examine space shuttle booster, nozzle and external tank surfaces for contamination which might affect bonding properties. The system will detect, identify and quantify contaminants, then make appropriate decisions regarding the need for cleaning. As part of this effort, surface analysis systems are being evaluated to determine sensitivity to potential contaminant types, and to develop data necessary for integrating decision making capabilities into the system.

SELECTION OF SUBSTRATES AND MODEL CONTAMINANTS

SCAT efforts are focused on analysis of hardware in the space shuttle solid rocket booster, nozzle and external tank; therefore, contamination standards were prepared with major material components from these systems. The substrates of interest were D6AC steel and nitrile butadiene rubber (NBR) insulation from the RSRM booster, 2219-T87 aluminum from the external tank, and 7075-T73 aluminum, carbon and glass phenolics from the RSRM nozzle.

Selection of model contaminants was based on comparison of oils and greases typically found in shuttle component manufacturing environments. The materials segregated into two general classes, hydrocarbons and silicones. Hydrocarbon greases are typically used as corrosion inhibitors during steel case processing. Hydrocarbons are also present as plasticizers in bagging materials and vinyls, and can degas from the plastics and deposit on bonding surfaces. Silicones, which are often components of mold release agents, are potentially more damaging to bond strength because a much smaller amount is required to affect adhesive properties.

Conoco HD-2 grease and paraffin were selected as model hydrocarbon contaminants for SCAT standards. HD-2 grease is currently used as a corrosion inhibitor during RSRM case processing, and is therefore a likely potential contaminant to the case/insulation bond. Paraffin is a relatively non-volatile wax which was selected because of its expected stability. CRC Industrial Duty Silicone was chosen because it represented typical mold release agents.

DEFINING ZERO FOR REFERENCE

Before examining a substrate for contamination, one must first define clean for reference. It is impractical to seek a truly uncontaminated surface, since typical production cleaning procedures leave behind small amounts of residues which do not adversely affect bonding properties. Therefore, the objective for preparing reference standards is to minimize surface chemistry differences between specimens, while achieving a level of cleanliness which is representative of that obtained during production processing.

Baselines for SCAT contamination standards were defined as the surfaces obtained with current space shuttle booster, nozzle or external tank cleaning procedures. 2219-T87 aluminum (space shuttle external tank) was cleaned in Turco 4215 and Smutgo #1 (deoxidizer) solutions. Steel substrates and 7075-T73 aluminum were vapor degreased with methyl chloroform to remove oils and greases, then grit blasted with Zirclean media to remove oxidation. OSEE analysis, which is extremely sensitive to oxidation on metal substrates, demonstrated that grit blast angle and environmental conditions affected initial instrument response. An enhanced signal was observed at low blast angles, and was believed to be due to less embedded grit on the surface. The environmental conditions affected the rate of oxidation buildup on the metals. Thus, equivalent blast angles and environmental conditioning were required to obtain consistent reference data for these samples.

As with the metal substrates, processing of insulations and phenolics was carried out to provide surfaces similar to space shuttle flight hardware. Glass phenolics were machined to a smooth finish, then degreased with methyl chloroform. Carbon phenolics and insulations were not machined, but were degreased with methyl chloroform. Mirrored surfaces for ellipsometry studies were purchased clean, and were not reused.

PREPARATION AND MONITORING OF CONTAMINATION STANDARDS

SCAT contamination standards were prepared by spray applying dilute contaminant/methyl chloroform solutions (for example, 5 mg/ml HD-2 grease) using an air brush or modified Sono-tek. The spray gun was similar to those used in the automotive industry (Graco model 1265, series B), and produced a fine mist which could be adjusted to an approximately 12-inch wide spray pattern. The Sono-tek, a modified ultrasonic spray system utilizing a 48 kHz nozzle and adjustable speed conveyer belt, was originally designed to spray flux onto printed circuit boards, but modifications were made to the nozzle to make it more suitable for spraying contaminant solutions. With both methods, coating levels were determined by measuring weight changes of aluminum foil witness samples sprayed along with the standards. Several passes were required to attain target coating levels, which typically ranged from 1-30 mg/ft^2. The Sono-tek proved to be a good tool for reproducibly applying low levels of contamination (down to 0.5 mg/ft^2), while the air brush was used for higher coating levels (up to 200 mg/ft^2). The solvent was allowed to "flash" off for 15-20 minutes before witness foils were weighed.

Standards were prepared with either one coating level per panel, or in a "step plate" fashion with 5 coating levels (plus an uncontaminated area for baseline) per panel. Step plate standards offered the advantage of several coatings to examine on a single plate, which reduced the effects of substrate processing variables on analysis results. Panels with one coating were better for evaluating coverage uniformity, and for subsequent bonding studies. Standards were preserved by storage in fall-out plates, in sealed containers purged with nitrogen gas, or at specific environmental conditions in a temperature/relative humidity controllable chamber.

Only singular contaminants were used on the panels, no mixtures. The reasons were that it would be impractical to prepare a complete range of mixture ratios for analysis, and the resulting homogenous mixture of contaminants would be unlikely to occur in nature. Also, instruments used in the robotic analysis system will be programmed to color code the contaminants it detects. For example, hydrocarbons may be blue and silicones red. If more than one contaminant type is present, the results will be presented as a color pattern containing elements of each class of material detected.

Contamination standards may change over time due to migration, diffusion or volatilization of the coatings, and therefore must be monitored. FT-IR microscopy was found to be an effective method for quantifying coating levels on most substrates of interest. The viability of this technique was demonstrated when it was discovered that Kaydol, a low molecular weight oil being considered as a model hydrocarbon, was migrating on the surface of aluminum and D6AC step plate standards. The panels showed linear correlations between coating levels and CH_2 peak heights immediately after preparation, but within 2 weeks the slopes of the plots changed and approached an equilibrium across the surfaces. This technique would also be expected to detect coating volatilization or diffusion, since peak height would be reduced.

INSTRUMENT PERFORMANCE TESTING

Prior to examining surfaces for background spectra or contamination, instrument performance was measured against reference standards to ensure that the instruments were working properly, and to adjust for signal response variations due to light source or detector response fluctuations.

The OSEE system was calibrated using polished nickel panels. Ultraviolet bulb intensity diminished with time, which caused a reduction in electron emission from panel surfaces. To achieve consistent quantitative results, the bulb current was adjusted to counteract the loss in intensity. Polished nickel did not oxidize appreciably over time and had an extremely electron emissive surface, which made it a good reference standard for this instrument.

Gold mirror reference standards were used to monitor signal-to-noise levels and optimize detector signal responses of the FT-IR microscope and NIR systems.

Performance testing for the ellipsometer involved determining the "true" azimuthal orientation of the polarizers and the effects of the signal processing electronics, and optimizing reflectance of the plane polarized light off of a smooth silica wafer surface. Silica was selected as the reference standard because the optical constants for this material were well known.

The eximer laser (UVF) was evaluated for beam intensity (which affected quantitative results) and wavelength.

RESULTS FROM ANALYSIS OF CONTAMINATION STANDARDS

The contamination standards were used to develop calibration curves for surface analysis systems, to develop methods for detecting and quantifying potential contaminants, and to determine instrument sensitivity limits for the various techniques and substrates.

Figure I shows results from OSEE analysis of D6AC step plates coated with HD-2 grease or CRC Silicone. The OSEE technique, which illuminates a surface with UV light and induces electron emission, was extremely sensitive to contamination on metal surfaces, detecting most coatings at levels down to 1 mg/ft^2. Signal response could be correlated to coating level over the range from 1-20 mg/ft^2 for hydrocarbons, and from 1-10 mg/ft^2 for silicone.

Figure I. OSEE Analysis of D6AC Step Plates With CRC Silicone or HD-2 Grease

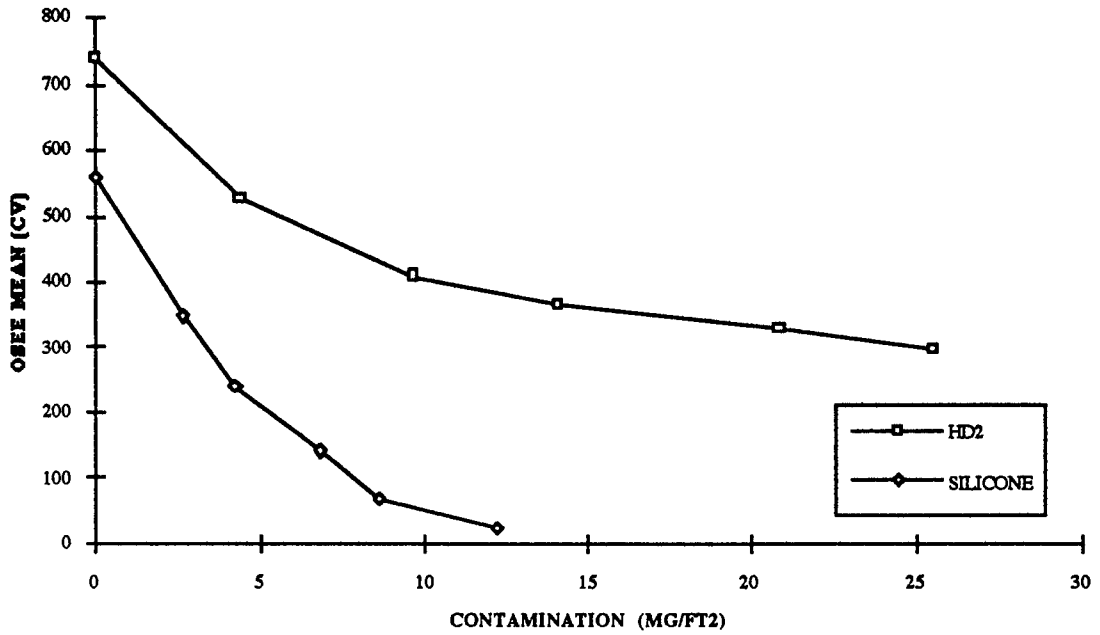
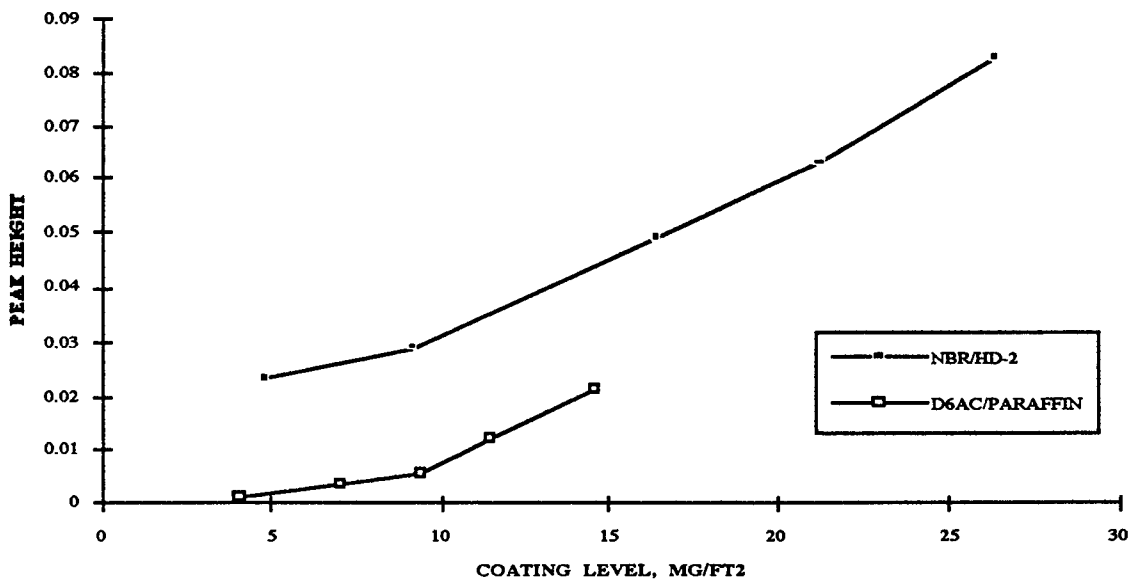


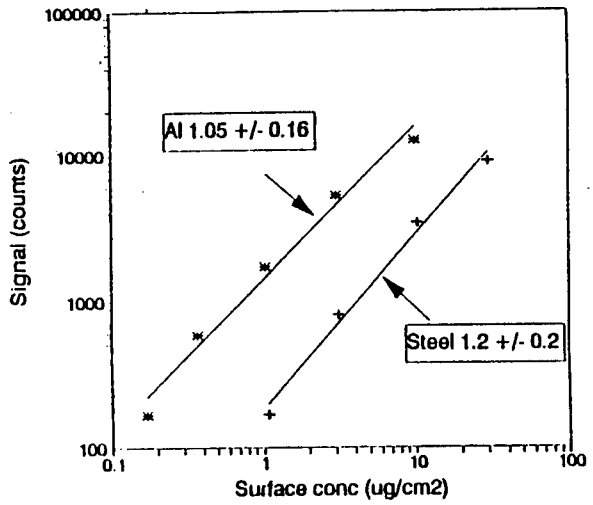
Figure II summarizes results from FT-IR analysis of NBR step plates coated with HD-2 grease, and D6AC steel coated with paraffin. The technique was acceptable for quantifying coatings above 10 mg/ft^2, but below this level peak heights approached that of baseline noise.

Figure II. FT-IR Analysis of NBR and D6AC Step plates With Paraffin



The fluorescence imaging technique illuminates a surface with a short pulse of light from an eximer laser or ultraviolet flash lamp, then captures the contaminant fluorescence with a gated image intensified camera. Figure III shows results from analysis of HD-2 grease on metallic substrates. The technique exhibited a linear response to contamination level and illumination intensity, and was independent of substrate material or shape.

Figure III. UVF Analysis of HD-2 Grease on Metallic Substrates



Ellipsometry involves measuring the change in polarization state of light reflected off of a surface, and can be used to monitor coating thickness. For example, Figure IV shows results from an experiment where baby oil was vapor deposited on an iridium surface. The technique currently works best for smooth, highly reflective materials, but methods are being developed to make it more suitable for rough surfaces.

Figure IV. Ellipsometer Measurements of Baby Oil Thickness Deposition Over Time

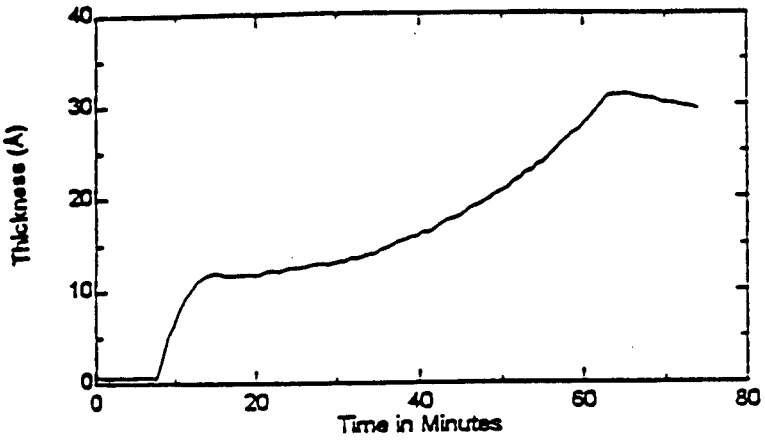
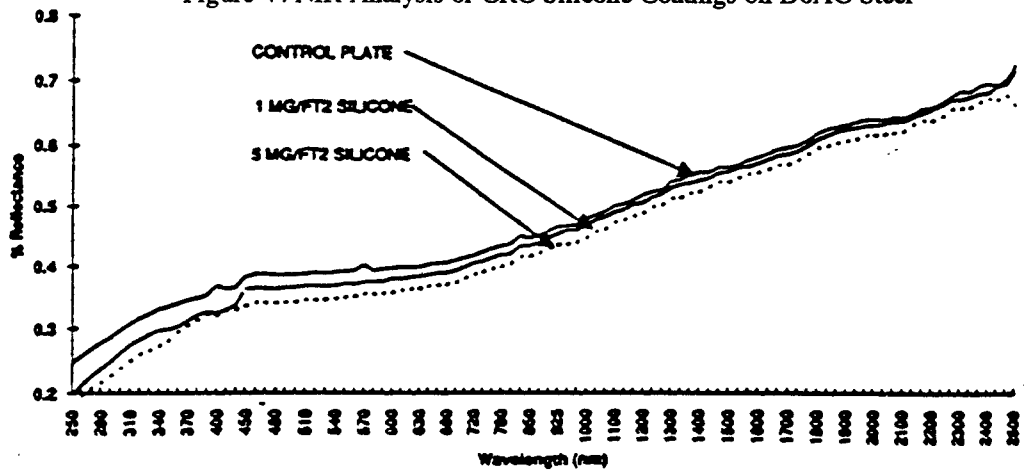


Figure V shows changes in NIR light reflectance from a D6AC panel as a function of CRC Silicone oil coating level. The technique exhibited a linear response to coating level, and could distinguish a mixture of hydrocarbon and silicone oils on metal surfaces.

Figure V. NIR Analysis of CRC Silicone Coatings on D6AC Steel



MEASURING EFFECTS OF POTENTIAL CONTAMINANTS ON BONDING PROPERTIES

Foreign material on a bonding interface is contamination only if adhesion is reduced below that of surfaces obtained with nominal cleaning procedures. Thus, if an analysis system detects potential contamination, the next step is to decide whether the material type or quantity could affect bond strength.

Peel and tensile adhesion tests are typically performed to quantify the effects of potential contaminants on bonding properties. The samples are monitored for reductions in strength, or changes in failure mode from cohesive to adhesive at the bondline.

Figure VI shows a test panel configuration typically used to measure peel and tensile adhesion of the insulation-to-case bond. Samples are pulled at a controlled rate in an Instron tester, which can be interfaced with an environmental chamber to measure temperature and relative humidity effects. Peel adhesion tests are conducted at various angles ranging from 45-135 degrees relative to the plane of the surface, while tensile adhesion is measured at 90 degrees.

Figure VI. Typical Bond Test Panel Configuration

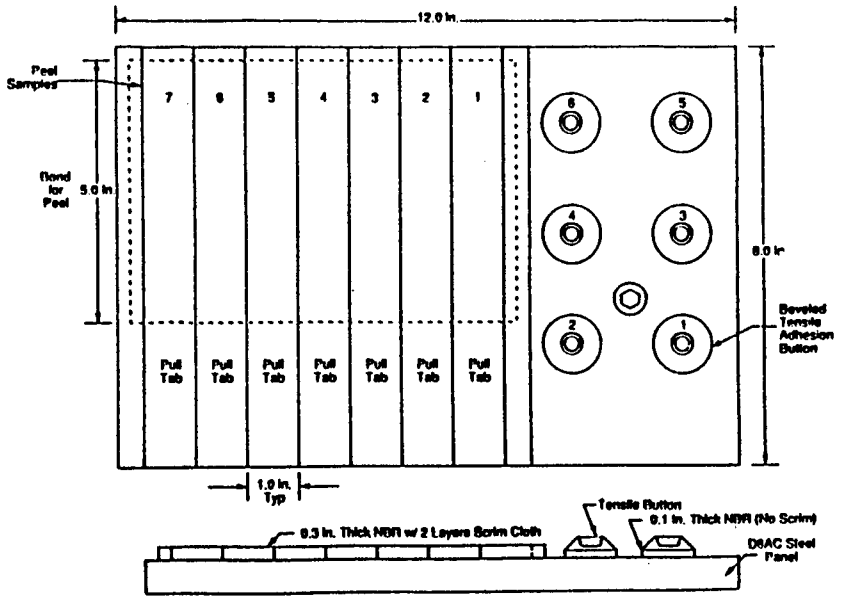


Figure VII shows results obtained from tensile adhesion testing of 2219-T87 aluminum to space shuttle external tank primer, with various levels of CRC Silicone on the substrate. Silicone acted as a contaminant to the bondline, reducing tensile adhesion by approximately 30% at a level of 1 mg/ft^2. Thus, the SCAT analysis system would be programmed to recommend cleaning of affected areas if silicone was detected at these levels.

Figure VII. Tensile Adhesion Test Results From Aluminum Coated With CRC Silicone and Space Shuttle External Tank Epoxy Primer

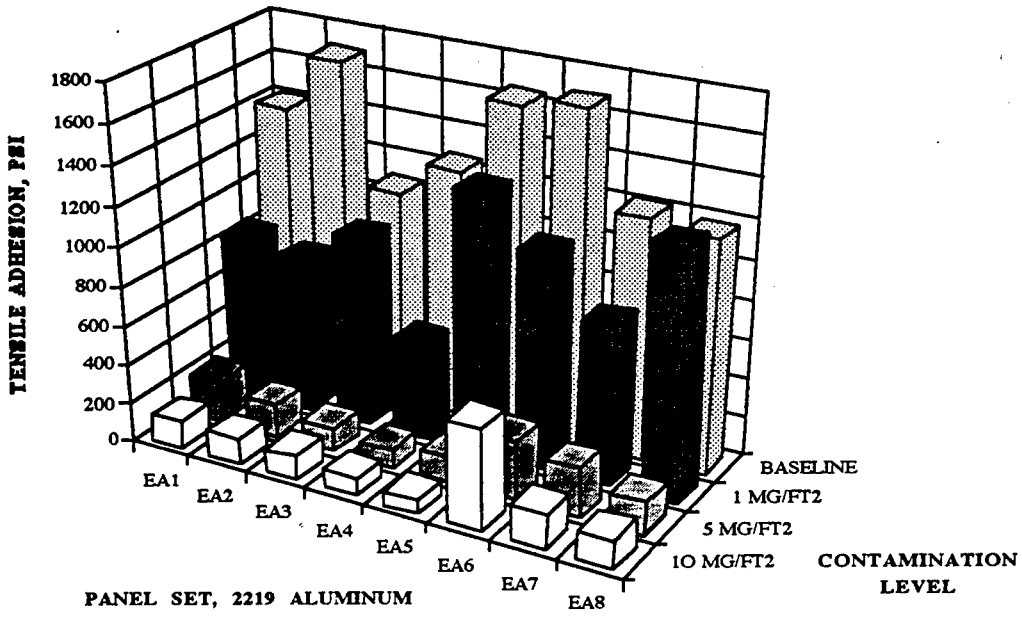


Table I summarizes results from peel and tensile adhesion testing of the D6AC steel/NBR insulation (RSRM) bondline following exposure of unprotected steel to a range of environmental conditions. The intent of the study was to determine whether the oxide formed under these conditions was a contaminant to the bond. Case-to-insulation adhesion was not affected, even after exposure to an extreme environment (29 days, 100F, 60% relative humidity). Therefore, oxidation formed under these conditions was not considered to be a contaminant to the bondline.

Table I. Effects of Environmental Exposure on D6AC/NBR Adhesion

TEMP., °F	REL. HUM., %	EXPOSURE TIME	PEEL ADHESION, PLI	TENSILE ADHESION, PSI	FAILURE MODE
-	-	-	200 TYP	700 TYP	I
50	20	3 HR	218 AVG	713 AVG	I
50	20	7 DAYS	216 AVG	759 AVG	I
50	60	3 HR	217 AVG	717 AVG	I
50	60	7 DAYS	221 AVG	742 AVG	I
100	20	3 HR	221 AVG	692 AVG	I
100	20	7 DAYS	212 AVG	668 AVG	I
100	60	3 HR	217 AVG	718 AVG	I
100	60	7 DAYS	224 AVG	802 AVG	I
100	60	29 DAYS VIS.RUST	206 AVG	697 AVG	I

CONCLUSIONS

SCAT efforts have demonstrated that a variety of analytical instrumentation is required to detect, identify and quantify contamination on space shuttle hardware bondlines. The robotic surface analysis system under development will consist of a series of instruments that can be called upon as needed to evaluate space shuttle bonding surfaces. Techniques described in this paper have proven to be effective for preparing and preserving contamination standards which can be used to evaluate instrumentation, develop analysis techniques, and establish calibration curves.

ACKNOWLEDGEMENTS

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Cleanliness Inspection Tool for RSRM Bond Surfaces

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ABSTRACT

Using optically stimulated electron emission (OSEE), Thiokol has monitored bond surfaces in process for contamination on the Redesigned Solid Rocket Motor (RSRM). This technique provides process control information to help assure bond surface quality and repeatability prior to bonding.

This paper will describe OSEE theory of operation and the instrumentation implemented at Thiokol Corporation since 1987. Data from process hardware will be presented.

INTRODUCTION

In 1987 NASA introduced a NDE method of bondline inspection to evaluate the consistency of substrate preparation prior to bonding. This technology is referred to as Optically Stimulated Electron Emission (OSEE), known at NASA Marshall Space Flight Center (MSFC) and Thiokol Corporation by the acronym "CONSCAN" for contamination scanning.

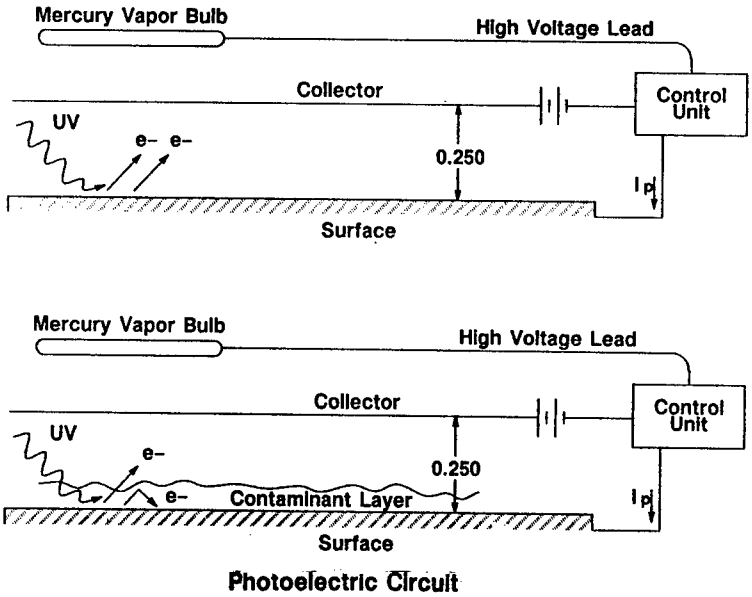
Tensile testing of the nozzle bondline has demonstrated sensitivity to contamination even at low levels of Conoco HD-2 grease (< 5.0 mg/ft^2). Tapered double cantilever beam data demonstrates that Conoco HD-2 grease in the Dexter Hysol EA913NA bondline degrades fracture toughness to critical values under 10.0 mg/ft^2. OSEE or Conscan has been baselined on D6AC steel for on-line contamination monitoring and has been used in RSRM manufacturing for the past 7 years.

THEORY OF OPERATION

OSEE is based on the photoelectric effect where electromagnetic radiation of the proper wavelength is impinged upon a substrate surface which subsequently yields electrons. The surface monitored by OSEE is irradiated with ultraviolet light with spectral lines at 2537 Å and 1849 Å. The electrons ejected from the surface are accelerated across a fixed distance or air gap by a potential on the collector around the mercury vapor lamp. The inspected surface is grounded with reference to the collector and the photoelectrons flow across the gap creating a photocurrent. The photocurrent, which is in the picoamp to nanoamp range, is detected by the sensor front end amplifier and displayed on the control unit or computer. The control unit displays the amplified signal in arbitrary units proportional to the photocurrent and are read as centivolts (CV). A contaminant on the surface will attenuate the photocurrent and produce a lower reading on the control unit.

The attenuation of the photocurrent, resulting from a contaminant on the surface is the result of the photoemitting substrate not being irradiated as strongly because of UV absorption in the contaminant covering the surface. The UV intensity is attenuated, as a function of Beer's law, as it passes through layers of contaminant. As the thickness of the layer of contamination on the a surface increases, the resulting intensity of UV on the underlying surface decreases and the photocurrent detected decreases

proportionately. Fewer photons reach the photoemitting surface and fewer electrons are emitted. The photoelectron flux passes through an accelerating field produced by the positive potential maintained on the collector ring around the UV source. See Figure 1.



Photoelectric Circuit

Figure 1

The kinetic energy imparted to an electron by an incident photon is given by the Einstein photoelectric equation

$$E_e = h\nu - \Phi_0 = \tfrac{1}{2}m_0v_e^2 \quad (1)$$

where $h\nu$ is the energy of the incident photon, Φ_0 is the energy required to remove an electron from the surface irradiated, terminating with zero velocity (known as the work function), m_0 is the rest mass of the electron and v_e is the velocity of the electron as it leaves the irradiated surface.

TECHNIQUE SENSITIVITY

There are many factors that influence OSEE measurements besides the cleanliness of the substrate being evaluated. The most significant of these is the sensor to surface distance. This causes a data variation of approximately 1% per 0.001 inch departure from a nominal standoff of 0.250 inch. This fact causes poor repeatability in data.

OSEE measurements are sensitive to not only surface contamination but oxidation/aging causes the signal to attenuate with time after grit blasting the surface. Studies of how the signal is attenuated on the same substrate with elapsed time have been conducted. See Figure 2.

OSEE response to various levels of Conoco HD-2 grease on D6AC steel was studied at NASA MSFC laboratories in 1987 under the direction of Dr. R. L. Gause[1]. These correlation studies resulted in the formulation of a functional relation between Conoco HD-2 grease contamination level and OSEE level that became known as the Gause curve. This function was utilized in the implementation of OSEE in the RSRM production facilities at Thiokol to develop cleanliness criteria in case inspection.

Tests were performed at Thiokol to correlate OSEE response to varying levels of contamination on steel and aluminum bonding substrates and bond strengths to contamination levels.

OSEE is the most sensitive instrument to date for the detection of hydrocarbons and silicones on freshly grit blasted surfaces. It can evaluate large surface areas in reasonably short time periods but does not work on irregular surfaces.

OSEE is a good process control indicator when the data are compared at equivalent time-lines in the process. OSEE cannot, however, differentiate between oxides and contamination or between various benign and bond degrading contaminants.

It has been known since the implementation of OSEE that alternative, more analytic surface monitoring techniques would be required to solve in-line process questions that arise during routine OSEE inspections.

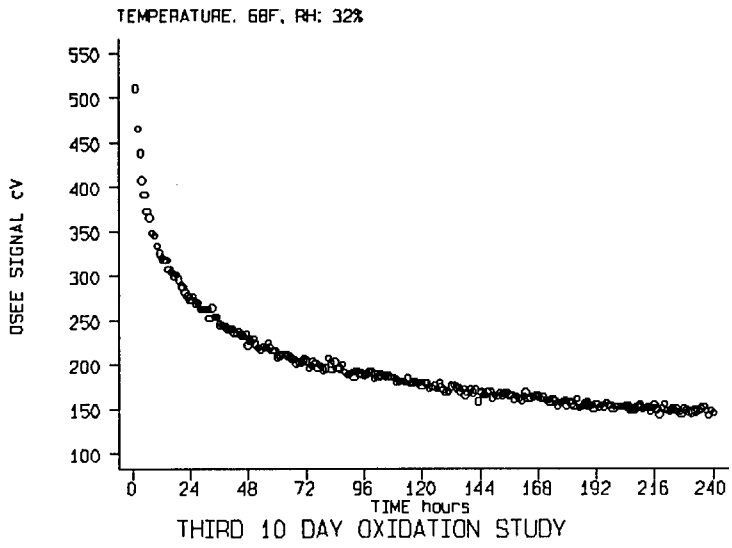


Figure 2

Over the past 7 years, other investigators have developed alternate surface contamination monitoring techniques and devices. Thiokol Science and Engineering department developed the diffuse reflectance infrared technology marketed through TMA Technologies as SurfMap II®. Bill Nerren of NASA MSFC formed the Surface Contamination Analysis Team (SCAT) in 1991. One of the goals of this team is to develop a system for surface contamination analysis composed of two or more complimentary technologies to aid in on-line decision making about the acceptability of the cleanliness of bond surfaces. Thiokol is an active participant in the SCAT team at MSFC.

RSRM APPLICATION

CASE PREPERATION

OSEE was first implemented in the case preparation manufacturing area at Thiokol. The hardware is covered with a preservative grease, for shipment and storage, that must be removed before continued processing. The case cylinders are vapor degreased allowed to cool to ambient temperature and then they are spot checked with the manual OSEE probe to verify sufficient degreaser effectiveness. If a part fails to meet the criterion limit then the part is vapor degreased again before further processing can proceed[2].

The case components are sent to the assembly stand and assembled into casting segments. In this process grease is used on the O-rings for assembly and lubrication. The grease often gets smeared on the adjacent bonding surfaces and must be removed. The casting segment is then placed in the paint pit and the top coat, a two part epoxy paint, is applied. The ends of the segments are covered during this operation to prevent overspray from depositing on the internal bond surface. The painted segment is temperature cured in the pit.

The segment is then ready for primer application, which is the first step in the process of vulcanize bonding the NBR rubber insulation to the case wall. To assure bond surface cleanliness the case is inspected with OSEE prior to the primer application. See Figure 3.

NOZZLE BONDING

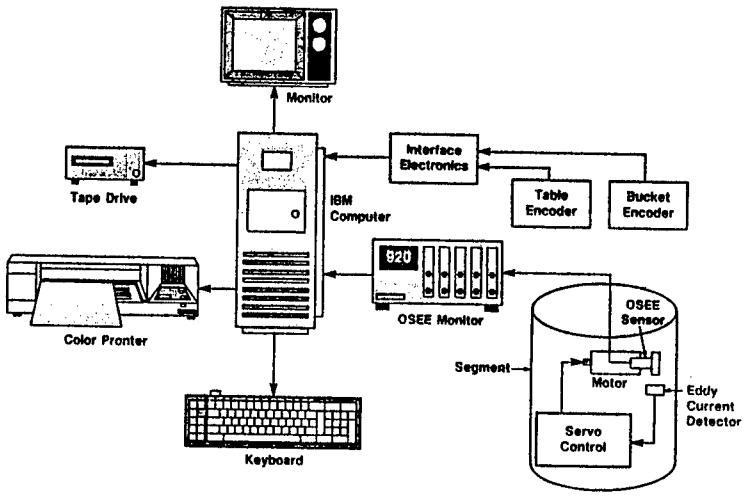
Engineering information data was collected with OSEE on metal nozzle housings to determine process criteria limits. Metal-to-adhesive bond failures in some test articles lead to extensive adhesive bond

testing. An OSEE baseline photoemission study was performed to determine what the maximum OSEE signal should be just after processing through the grit blast. These test results are still used to evaluate on-line performance. See Figure 4. The test has been performed on a daily basis recently to show OSEE values just after grit blast and 24 hours later. See Figure 5.

Three correlation studies were run to determine the functional relation between OSEE signal and contamination level. A control was run with each test and nominal levels of 5,10,20 and 30 milligrams of Conoco HD-2 grease per square foot were applied. The substrate was D6AC steel and tensile buttons were bonded using Dexter Hysol EA913NA epoxy adhesive.

The data were added to the data from the previous correlation studies and regression analysis was performed. The three new studies were also analyzed without previous data for comparison. The results were extremely similar. See Figure 6.

The regression of the whole set of data from all studies to date can be modeled with the function:



AUTOMATED CASE SCAN SYSTEM
Figure 3

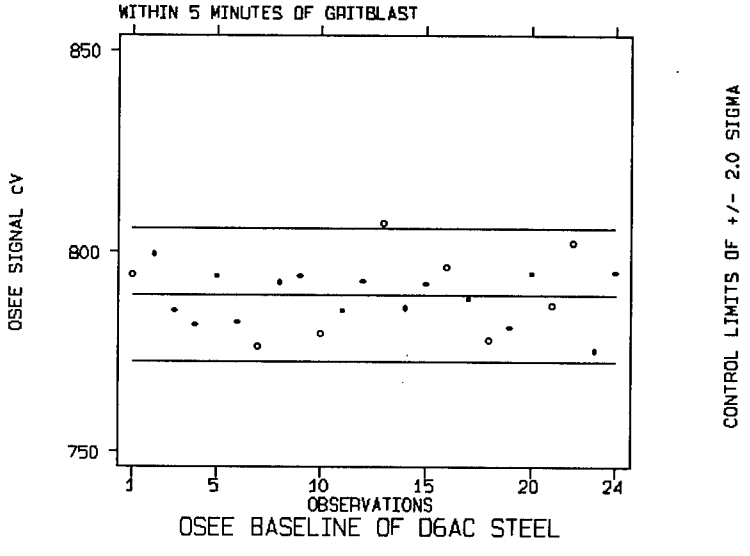


Figure 4

$$\text{OSEE} = -97 \ln [\text{contamination}] + 637. \quad (2)$$

The regression of the MSFC data alone resulted in the function :

$$\text{OSEE} = -103 \ln [\text{contamination}] + 640. \quad (3)$$

Ten milligrams of Conoco HD-2 grease per square ft. would be expected to read 414 centivolts.

The tensile strength was reduced 50% with the application of 5 mg/ft2 of Conoco HD-2 grease. The further

addition of contamination resulted in only slight further reduction of tensile strength. See Figure 7. The reason for this is not fully understood. The adhesive failure mode was greater than 50% with the application of 5 mg/ft2 of Conoco HD-2 grease, approaching 100% with 20 mg/ft2. See Figure 8.

This indicates that, although the tensile properties are not reduced catastrophically with the bondline contaminated, the failure mode is shifted to the metal-to-adhesive interface with low levels of Conoco HD-2 grease.

It was determined that cleanliness criteria should be implemented in the nozzle bonds. An OSEE limit equivalent to 10 mg/ft^2 was implemented in the process.

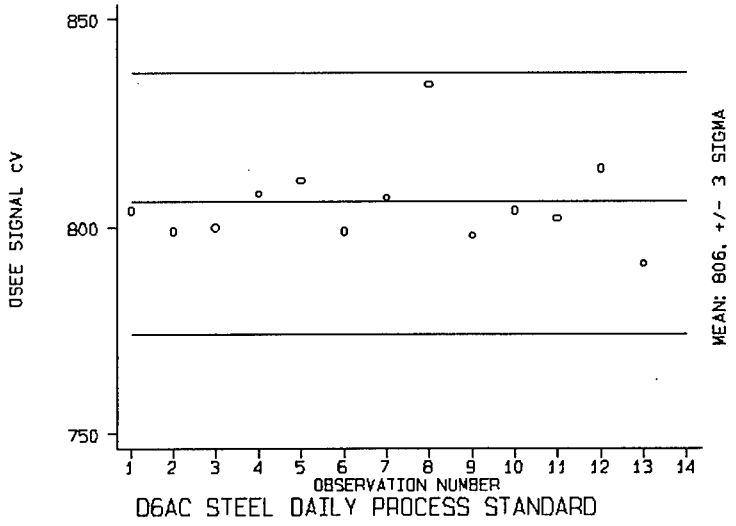


Figure 5

OTHER RSRM BOND SURFACES

OSEE has been implemented on the igniter, the weatherseal and stiffener stub and flex bearing shims.

The igniter is similar to a miniature solid rocket motor and is used to start the combustion in the full scale motor. NBR insulation is vulcanized to the internal and external surfaces of the igniter case. These surfaces are inspected for cleanliness with OSEE prior to primer application.

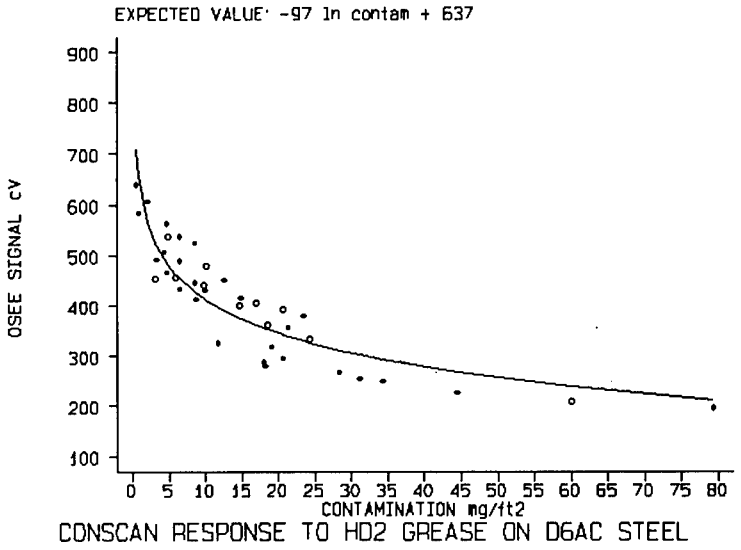


Figure 6

The weather seal is made of EPDM rubber vulcanized to cover the factory joint and seal out sea water upon retrieval operations. Each casting segment is composed of two or, in the case of the aft segment, three cylinders. These cylinders are held together with hardened steel pins which are held in place with Inconel® retainer bands. The joint area is protected with masking tape during the top coat application and must be removed and the masking adhesive

must be removed also. Grease, used to assemble and lubricate the O-rings is squeezed out when the segment is rotated in the horizontal rotator during insulation lay-up. The grease must also be removed before bonding of the weather seal. The surfaces are checked for cleanliness using OSEE after the cleaning operation before primer is applied.

The flex bearing allows the nozzle to gimbal and maintains the structural support to the aft dome. The bearing is composed of shims and end rings (concentric conic frustums) vulcanized together. To assure as clean a surface as possible the shims are checked with OSEE before primer application.

ON-LINE PROCESS DATA

The OSEE data are used to detect shifts in substrate preparation during processing. See Figure 9 for an example of mean OSEE values on the throat inlet ring bond surface for 16 housings processed.

CONCLUSION

OSEE has been used to monitor contamination on bonding surfaces in the manufacturing area for seven years at the Thiokol Corporation. The OSEE technique is still a developing technology. It has proven useful as a process aid in cleaning bonding surfaces to a clean and acceptable level. The OSEE inspection technique is an improvement over blacklight inspection because of it's lower threshold of

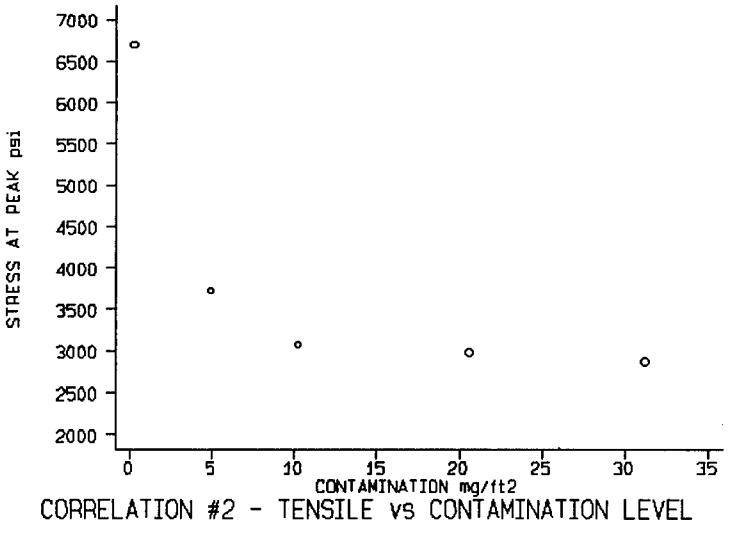


Figure 7

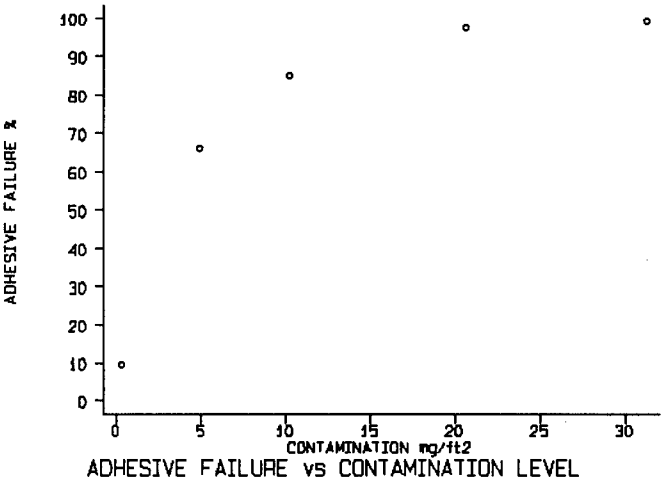


Figure 8

detection. OSEE provides an objective, documentable method of verifying bond surface cleanliness. The reliability of the OSEE equipment has continued to improve and additional improvements for industrial applications are anticipated with the third generation OSEE.

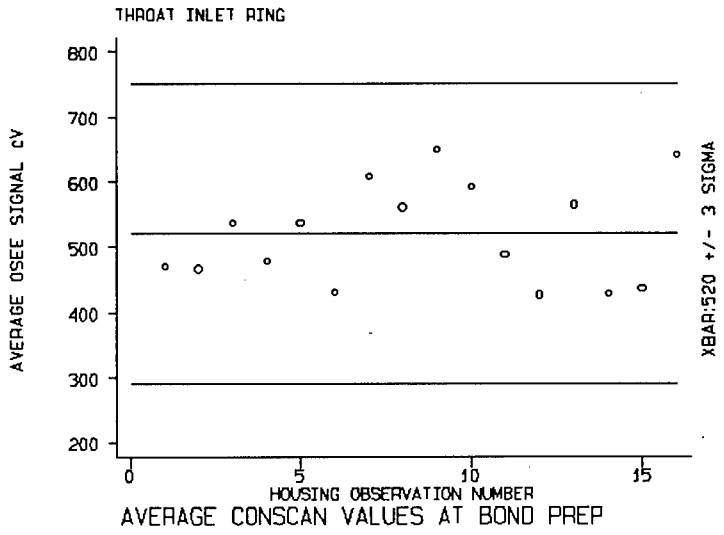


Figure 9

REFERENCES

1). Gause, R.L., "A Noncontacting Scanning Photoelectron Emission Technique for Bonding Surface Cleanliness Inspection", EH11-87-10, NASA, George C. Marshall Space Flight Center, AL 35812, December 1987.

2.) Mattes, R.A., "Contamination Monitoring of RSRM Bonding Surfaces using OSEE", Proceedings 35th Annual Technical Meeting, Institute of Environmental Sciences, 1989.

The Design And Development Of A Third Generation OSEE Instrument

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Abstract

Optically Stimulated Electron Emission (OSEE) has been used to quantify surface contamination in the aerospace community. As advances are made towards the understanding of OSEE, it is desirable to incorporate technological advances with succeeding generations of instrumentation, so that improvements in the practical application of OSEE may be disseminated among the user community. Several studies undertaken by Yost, Welch, Abedin and others [1,2,3,4,5] have expanded the knowledge base related to the underlying principles of OSEE. The conclusions of these studies, together with inputs from the user community were the foundation upon which the development of a third generation OSEE instrument was based. This manuscript describes the significant improvements incorporated into a third generation OSEE instrument as well as the elements unique to its design.

Introduction

In January 1993, an OSEE team was formed at the NASA Langley Research Center (LaRC) to design and build a third generation OSEE instrument for the inspection of contaminants on solid rocket motor casings. The focus of this effort was the detection and measurement of Conoco HD-2 grease contaminant on a D6AC steel substrate although other contaminants and substrates are applicable to OSEE inspection. The instrument was to incorporate recommended improvements from the earlier NASA LaRC

science studies as well as system requirements from the NASA Marshall Space Flight Center (MSFC) and Thiokol Corporation OSEE user community. Table 1 outlines the major design goals and performance specifications for the instrument as well as the results achieved. With these improvements and design goals, two complete instruments including spare parts were designed and built in nine months.

Table 1. OSEE Third Generation Performance Specifications, Design Goals, and Comparisons

Performance Specification	Design Goal	Measured Performance	Prev Generation Performance	Improvement Ratio (%)
Sensitivity (HD-2 grease)				
Range: 0 - 4 $\mu g/cm^2$	-------	0.04 $\mu g/cm^2$	1-2 $\mu g/cm^2$	> 250
Range: 4 - 30 $\mu g/cm^2$	-------	2.1 $\mu g/cm^2$	5-10 $\mu g/cm^2$	> 250
Resolution				
Contaminant (HD-2 grease)	< 1 nm	0.64 nm	3 nm	470
Spatial				
Vertical	2.5 cm	2.5 cm	15 cm	600
Horizontal	2.5 cm	0.41 cm	2.5 cm (est)	600
Reproducibility	< 1%	1.6%	10%	625
Electronics				
Noise and Hum	< -45 db	< -60 db	**	N/A
Collector Current (Nominal)	> 50 nA	500 nA	5 nA	10000
THD	< 1%	< 0.1%	**	N/A
Bandwidth	> 2 Khz	≈ 3 Khz	< 3 hz	≈ 100000
Probe Mass	< 1 Kg	1.8 Kg	> 4.55 Kg	> 250

** Not Measured N/A = Not Applicable

The four major recommendations for improvements cited in the science studies were a) the incorporation of a parallel electric field (PEF) configuration for the collector electrode b) a higher collector voltage c) a stable UV source and d) a dry argon atmosphere in the lamp and measurement region. The first improvement would ensure a more even distribution of the electric field thus minimizing the variation in sensitivity over the measurement region. A higher collector voltage would increase the collector current thereby improving the signal to noise ratio (SNR). Since the photo currents are linearly dependent upon the intensity of the UV source, a stable source will result in more repeatable measurements. Finally, the dry argon atmosphere is relatively non-ionizing and transparent to the UV region of interest. This will decrease the UV fluctuation due to possible absorption by oxygen and moisture in ambient air and will also decrease the photochemistry (and hence photo fatigue) on the surface of the specimen under examination. Additional significant system requirements included a) a 1" X 1" sensor area b) six channel operation for quicker inspection c) sufficient bandwidth to allow 450 in/min minimum scan rate d) a small, light weight sensor head and e) operation in an electrically noisy environment with a minimum of 80 feet of cable between the sensor head and the control unit.

Theory of Operation

In general terms, OSEE operates by illuminating the measurement region with a source of ultraviolet (UV) radiation in the presence of a direct current (DC) electric field as shown in figure 1 [6]. The UV radiation frees electrons from the surface under inspection by the photoelectric effect. The electrons are collected on the positively charged anode, and the amplitude of the resulting current indicates the level of contamination on the surface. For HD-2 grease on D6AC steel, the greater the current, the cleaner the sample.

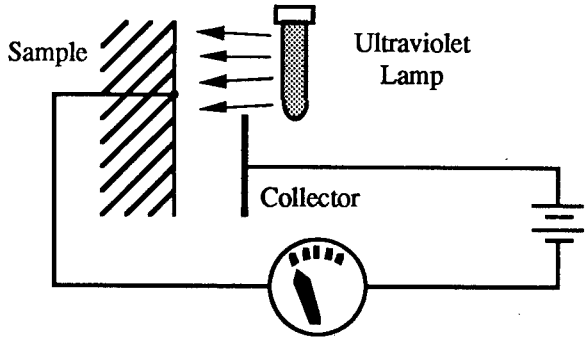

Figure 1. Basic principle of OSEE

Instrument Overview

The third generation OSEE instrument consists of a probe head and control station connected by a 90 foot umbilical. Figure 2 illustrates a block diagram of the instrument

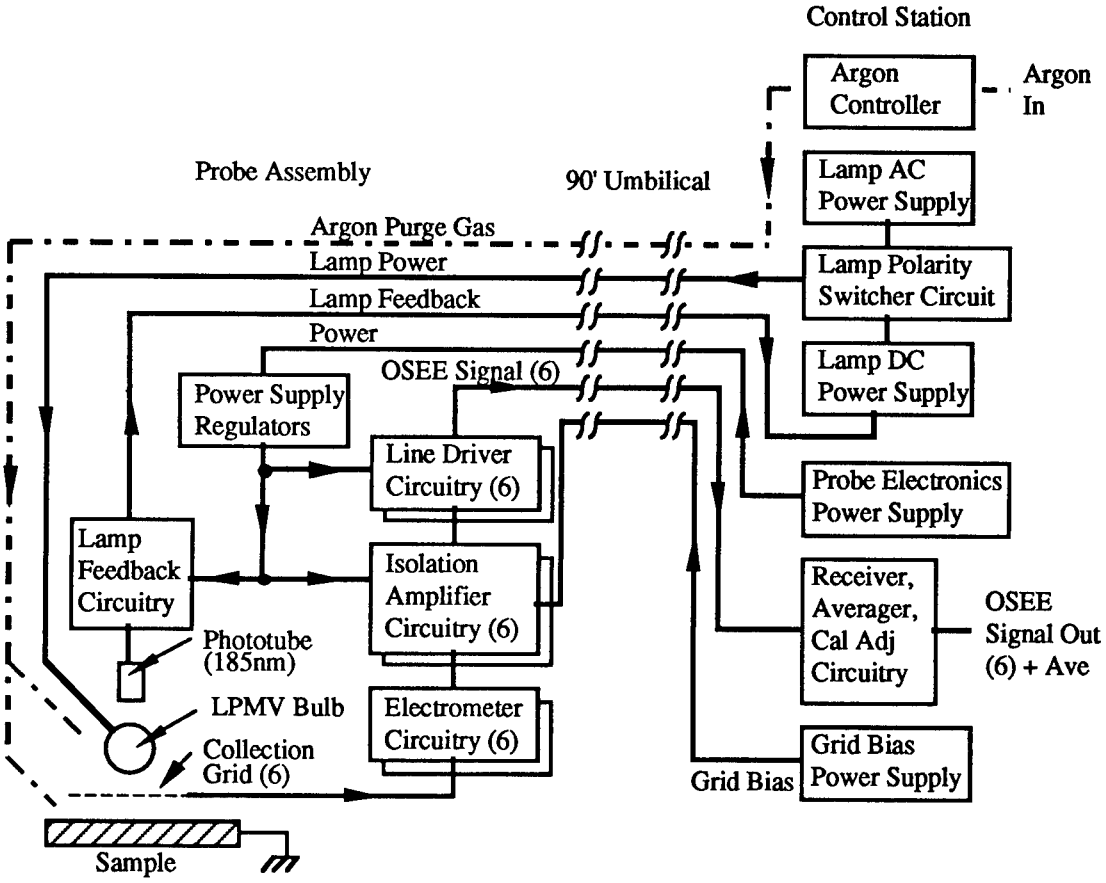

Figure 2. Block Diagram of OSEE System

The probe contains a single UV source which is controlled by a closed loop feedback circuit for lamp intensity. The UV source is common to six channels. Each channel consists of an electron collector grid, electrometer, isolation amplifier, and driver electronics to transmit the OSEE signal back to the control station. In addition, the probe also includes the power supply regulators and the necessary plumbing for the argon purge gas. The control station contains the lamp power supplies and control circuitry, the argon purge gas regulating system, the probe electrical power supply, grid bias power supply, and the signal receiver and instrument calibration circuitry. The control station also includes the switches, indicator lamps, and meters necessary to operate and monitor the system. The long umbilical allows the

probe to be mounted on a remote scanning assembly necessary for inspecting large rocket motor casings. One of the main objectives of the design was to make the probe as small and light weight as possible in order to accommodate a variety of scanning equipment including robotic scanners, which are often limited in their ability to position heavy, bulky instruments accurately.

The Probe Assembly

Figure 3 shows a cross-sectional view of the OSEE probe head.

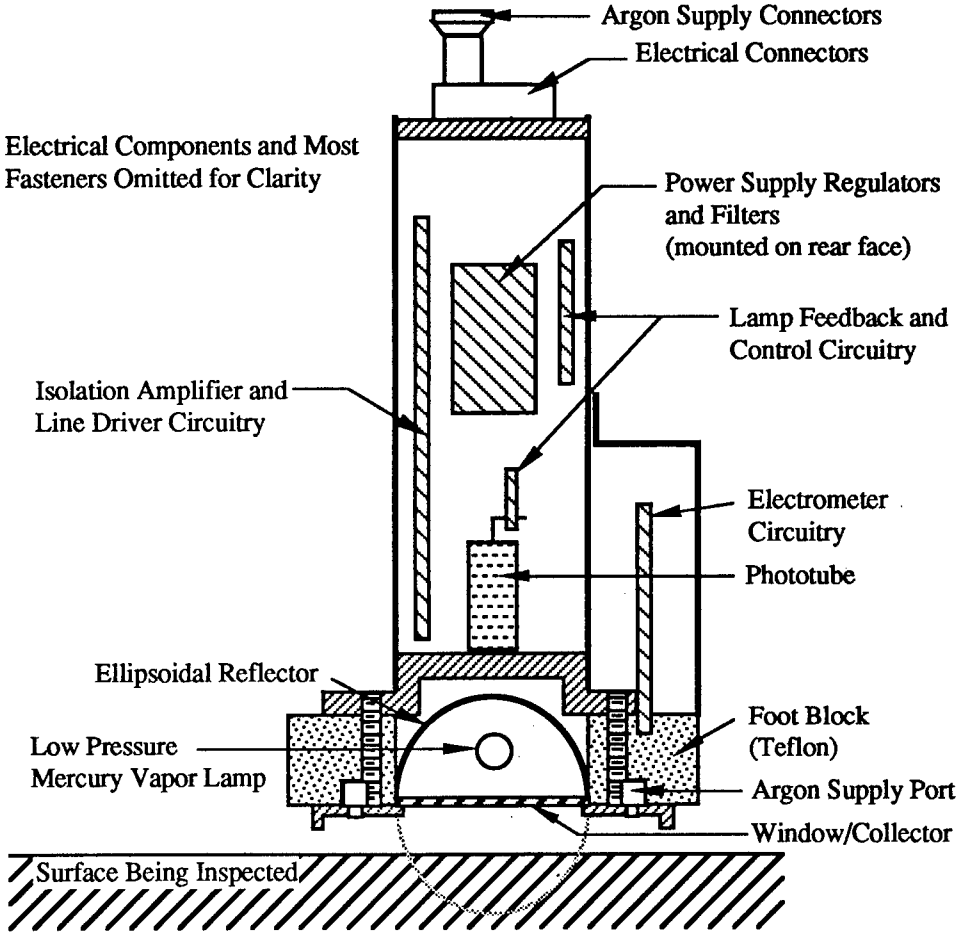

Figure 3. Cross Section of Probe Assembly

Lamp and Electrodes

A commercially available six inch long, double bore, low pressure mercury vapor (LPMV) lamp was chosen as the UV source. The LPMV lamp produces high efficiency UV light in distinct spectral lines. One of these, the 185 nm line, produces 95% of the OSEE response from the substrate and is also in the absorption spectrum of HD-2 grease. Because of the wide bandwidth of the instrument, it was decided to operate the LPMV lamp in DC mode during OSEE scanning so as to minimize interference with the low level OSEE current. One attribute of the LPMV lamp is that electromagnetic interference (EMI) emanating from the bulb is minimized by the double bore design which has a very small current loop. Additional noise reduction is achieved by surrounding the lamp chamber with an electrically grounded envelope thus shielding the sensitive probe electronics from EMI radiation. The LPMV lamp is located at the focal point of a half-ellipsoidal reflecting cavity. The reflector is fabricated with an electroformed nickel base with a highly reflective aluminum and magnesium fluoride coating. Undesirable reflections from other surfaces are minimized by coating them with a UV absorbing paint. This produces a uniform light

source and minimizes "hot-spots" on the measurement surface. The bottom of the lamp chamber is a low UV attenuating, high-quality, ES grade quartz window. Six identical one inch square anodes, slightly separated and placed side by side along the length of the window make up the collectors for the six independent channels. The collectors are formed by electro-depositing a thin translucent film of chrome over a fine line nickel grid on the outside of the window. Although this configuration reduces the maximum possible UV output from the chamber, the LPMV lamp UV generation is such that it is usually operated well below its maximum output despite this limitation. The benefit of this PEF geometry is that the electric field from the collector is more uniform over the illuminated surface.

Argon Purge System

In order to minimize photo chemical production and to reduce UV absorption possible with ambient air, the lamp chamber and measurement region are purged with dry argon. For the purposes of OSEE argon is non-ionizing, chemically inert, and transparent to the UV wavelengths of interest. The argon begins its journey from a pressure vessel adjacent to the control station. The flow rate is regulated at the control station and fed to the probe assembly through the umbilical. Two independent lines are used; one to supply the lamp chamber and one for the measurement region. Argon flows into the lamp chamber whenever the lamp is operating. In fact, when the system is turned on, the lamp is not powered up until the argon supply line and lamp chamber are properly purged. This process occurs automatically and without any operator action required. In order to conserve the purge gas, argon flow to the measurement region is switched on only when a scan is being performed. If the argon flow should be interrupted due to an exhausted supply tank or a blockage in the line, the lamp is automatically shut off.

Lamp Feedback Circuit

In order to provide a stable UV source, a feedback circuit was employed which monitors the output of the LPMV lamp at the 185 nm line and varies the input power as needed to maintain constant output intensity during OSEE scanning. A commercially available phototube with a bandwidth from 115 nm to 200 nm measures the lamp intensity. The only output from the LPMV lamp in this range is the 185 nm line. The UV reaches the detector through an aperture located at the top of the reflector with the phototube positioned just above. The output of the phototube is amplified by a Burr-Brown OPA-128 operational amplifier (op-amp) mounted directly on the phototube. The signal is then compared to a precision band-gap reference "set point." The difference becomes the error signal which is further processed before being sent to the control station via the ninety foot umbilical. Once in the control station, the signal is fed to the current limit input of a 1500V/65mA DC power supply which powers the lamp during scanning operations. The output of the power supply is sent back down the umbilical to the lamp. If the lamp intensity increases above the set-point, the current limit input to the supply is reduced, thus decreasing the input power to the lamp. If the intensity decreases, the current limit input rises and the input power increases. Typically a new lamp operates at approximately 600V @ 30mA.

Electrometer Circuit

The collector electrode is connected to the electrometer circuit through spring loaded contacts soldered directly to the electrometer printed circuit board (PCB). Each of the six identical electrometer circuits consist of one OPA-128 electrometer grade op-amp and several passive components. The input path from the collector electrode is guarded and shielded and less than one inch long. This reduces input capacitance and EMI pick-up into the 100MΩ input impedance of the circuit. The OPA-128 has a typical input bias current of only 75fA, well below the typical collector current of 500nA. This, combined with its wide gain-bandwidth product make the OPA-128 well suited for OSEE applications. The electrometer converts the OSEE current to a voltage relative to the collector bias and sends it to the isolation amplifier stage. The entire electrometer circuit is enclosed in a separate shielded compartment to one side of the probe, further reducing EMI pick-up.

Isolation Amplifier and Driver / Receiver Circuit

Because of the common mode measurement required for OSEE, the high collector voltage must be decoupled from the OSEE signal while maintaining the proper potential between the collector and measurement surface. A Burr-Brown ISO103 isolation amplifier was chosen for this task. Figure 4 shows the probe front end electronics and illustrates the isolation amplifier theory of operation. The ISO103 provides both signal and power across a high impedance isolation barrier. The Integrated Circuit (IC) contains an 800Khz oscillator driver on the output side of the isolation barrier. The driver is transformer coupled to the signal input side of the IC where it is rectified and filtered to provide an isolated power source for the internal and external circuitry. The input signal is modulated using the oscillator, transmitted across the isolation barrier, and demodulated on the output side. The ISO103 has an isolation barrier rated to 1500Vrms. The IC can provide isolated power up to ±15mA at ±15V for the electrometer. The 200Vdc grid voltage is applied to common (ground) on the input side of each isolation amplifier through 1MΩ resistors (one resistor for each channel) thus providing isolation between the high voltage grounds of any two channels. The oscillators for the six channels are externally synchronized to eliminate beat frequency interference. The output signal from the isolation amplifier is low pass filtered to minimize any residual oscillator feed through. The OSEE signal is then transmitted over the umbilical by a balanced line driver/receiver pair. The Analog Devices SSM-2142/1 driver/receiver pair together with standard Belden 8451 shielded twisted-pair cable provide a total harmonic distortion (THD) of less than 0.001% and common-mode rejection (CMR) greater then 90 db over the pass band of the system.

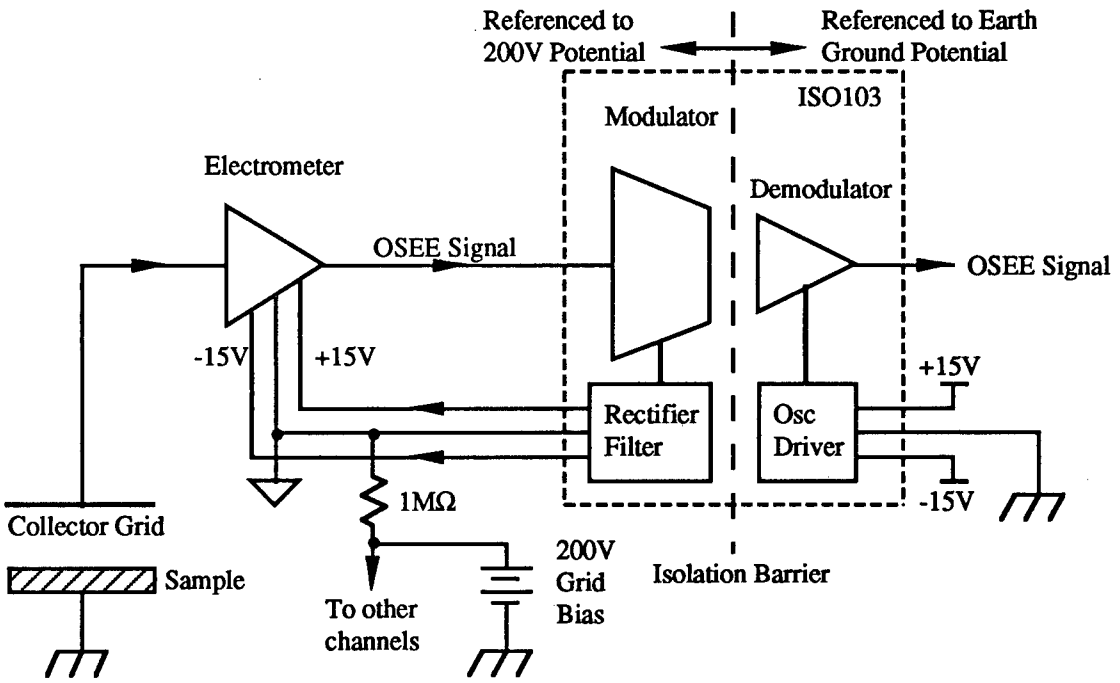

Figure 4 Block Diagram of Probe Front End Electronics

Probe Power

Electrical power for the isolation amplifier circuitry, line driver circuitry, and lamp feedback control circuitry is supplied by a regulated DC power supply located in the control station. In order to minimize EMI pickup, as well as degradation of line and load regulation performance due to the long journey through the umbilical, additional filtering and regulation are performed inside the probe assembly. This ensures ample, regulated, noise-free power for the probe in only a few square inches and one or two ounces of weight.

Control Station

The control station is housed in a 51 inch high 19 in wide standard electronic equipment rack mounted on casters. The control station has two "modes" of operation determined by a front panel switch; a scan mode and a stand-by mode. A second switch controls the flow of argon into the measurement region. When measuring surface contamination, the unit is placed in the scan mode. This allows the LPMV lamp to be operated from the DC power supply and its output regulated by the lamp feedback control circuitry. When no OSEE measurements are being made, the unit is placed in stand-by mode. This mode operates the LPMV lamp from its AC power supply, and no lamp feedback occurs. If the lamp is powered from the DC supply for more than about five minutes, then when the system is switched back to the stand-by mode, the polarity of the lamp electrodes is reversed. In doing so, the next time the unit is set to scan, the current through the lamp is reversed. By operating the lamp on AC power while idle and by reversing the polarity of the electrodes on every scan, the lifetime of the LPMV lamp may be greatly increased. Possible glitches in the OSEE signal if the polarity were switched during a scan are also eliminated.

Figure 5 provides a front and rear view of the rack. At the top of the rack, behind a blank front panel, is the controller for the argon purge gas regulators. Once the proper flow rate has been set at the time of assembly, the controller requires no further adjustment and so is normally concealed. The top rear of the cabinet contains two 5 1/4" exhaust fans to remove excess heat from the enclosure. Air is pulled in and filtered through a panel near the bottom. Below the argon controller is the control panel with the operator controls. Besides the mode and argon control switches, the control panel contains a lockable switch used to control the power to the system. "Warm-up" and "ready" indicator lamps denote system status. When first powered on, the warm-up lamp will illuminate for approximately 30 minutes to allow the UV lamp and electronics sufficient time to reach operating temperature at which time the warm-up lamp will turn off and the ready lamp will turn on until the system is shut down. Adjacent to the argon flow switch are two indicator lamps which are automatically illuminated if low argon flow is detected in either the lamp chamber or measurement region respectively. In the center of the control panel is a panel meter showing the relative condition of the UV lamp while in scan mode. Over time, as the bulb ages, the meter will move further to the right indicating that more current is being supplied to the lamp to maintain constant intensity. At sometime prior to the maximum current level, a "replace lamp" indicator adjacent to the meter will turn on, signifying that the lamp will need to be replaced in the near future (after the current scan is completed). At the far right of the control panel is an elapsed time meter which displays the accumulated time in hours that the system has been operated in the scan mode. When the system is first turned on, all the indicator lamps are powered for approximately one second so that any indicator which fails to illuminate may be identified and replaced, thus minimizing the possibility that a non-functioning indicator will jeopardize the operation of the system.

Below the control panel is the UV lamp controller and polarity switching circuit. This circuit also contains the AC lamp power supply. Below this is the DC lamp power supply, the DC power supply for the probe electronics, and the 200V DC grid power supply. All the power supplies are commercially available. A blank panel below the probe electronics power supply, conceals the rear of the receiver, signal averager, and calibration circuitry enclosure. The receiver buffers the signal from the umbilical and converts each channel to either a single or balanced output depending on the system requirements. The averaging circuit averages the six channels. The individual channel and average outputs are brought out to BNC connectors on the I/O panel at the rear of the rack. The I/O panel also contains the three electrical connectors for the umbilical and the grid bias return ground connector for the solid rocket motor casing. In order to calibrate the system, the calibration adjustment panel is removed to allow adjustment of the gain and offset of each channel. This is usually required when replacing the UV source or when using a different probe head. At the very bottom, inside the rack are the argon regulators. At the rear of the rack are the argon supply and argon umbilical connectors. All the electrical and argon connectors are unique so that the proper bulk-head receptacle is always mated with its associated connector. Just above and to the right of the argon connectors is a single standard power entry module which supplies the switched AC power to two vertically oriented power strips mounted inside the rack; one on each side.

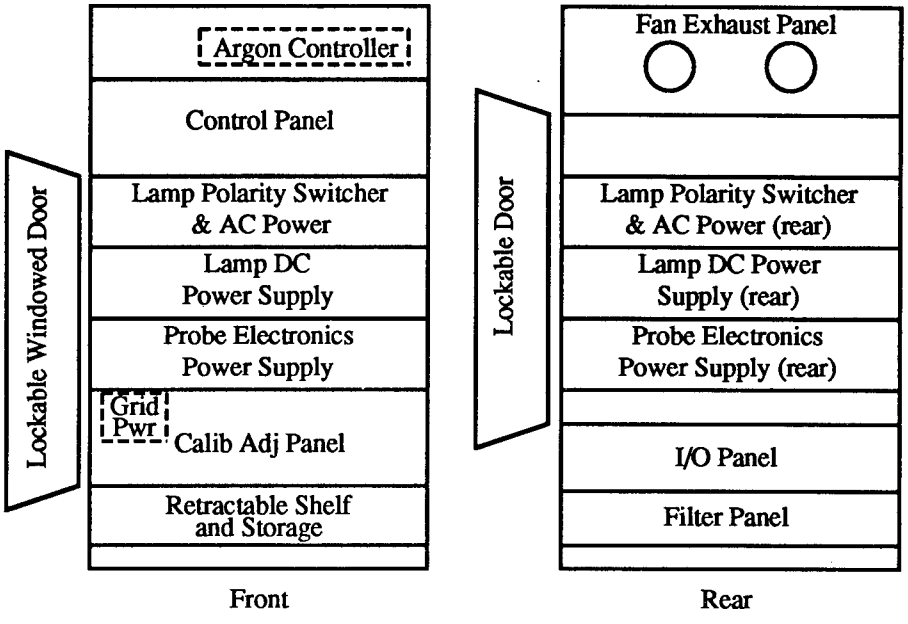

Figure 5. Front and Rear View of Control Station

Safety Issues

Because of the potential shock hazard from the high voltage lamp and grid power supplies, several safety features have been included in the design. First, the 200V DC grid bias is resistively decoupled from each exposed collector grid through 1 MΩ resistors. Not only does this provide electrical isolation between the six electrodes, but it also reduces the potential for electric shock from accidentally touching any of the electrodes. However, fingerprints and other foreign matter on the collector grid will result in erroneous readings. For the lamp power, an interlock system is employed which automatically shuts off the AC and DC lamp power supplies if any connector in the lamp power circuit path is removed.

References

1. Yost, William T., C. S. Welch and M. Nurul Abedin, "OSEE Science Base: Final Report," 85 pp (limited distribution report), December, 1990.

2. Welch, C. S., W. T. Yost and M. Nurul Abedin, "OSEE Inspection of Solid Rocket Motor Steel," Proceeding of Third Conference on NDE for Aerospace Requirements, Huntsville, AL, June 4-6, 1991, K.W. Woodis and G. L. Workman, eds, pp. 200-237, (ITAR restricted).

3. Abedin, M. Nurul, C. S. Welch and W. T. Yost, "OSEE Response on D6AC Steel due to Sample Preparation," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 11, D. O. Thompson and D. E. Chimenti, eds., Plenum Press, New York, 1992, pp. 1799-1805.

4. Welch, C. S., M. Nurul Abedin and W. T. Yost, "Optically Stimulated Electron Emission: Current-Voltage Response and Spectral Sensitivity," Review of Progress in Quantitative Nondestructive Evaluation, Vol. 11, D. O. Thompson and D. E. Chimenti, eds., Plenum Press, New York, 1992, pp. 2155-2162.

5. Welch, C. S., "OSEE Development Status," Surface Contamination Analysis Technical Interchange Meeting, Huntsville, AL September 2 & 3, 1992.

6. NASA Tech Briefs, Fall/Winter 1981, pp. 307-308

STUDY OF SURFACES USING NEAR INFRARED OPTICAL FIBER SPECTROMETRY

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ABSTRACT

The measurement and control of cleanliness for critical surfaces during manufacturing and in service provides a unique challenge for fulfillment of environmentally benign operations. Of particular interest has been work performed in maintaining quality in the production of bondline surfaces in propulsion systems and the identification of possible contaminants. This work requires an in-depth study of the possible sources of contamination, methodologies to identify contaminants, discrimination between contaminants and chemical species caused by environment, and the effect of particular contaminants on the bondline integrity of the critical surfaces.

This presentation will provide an introduction to the use of optical fiber spectrometry in a nondestructive measurement system for process monitoring and how it can be used to help clarify issues concerning surface chemistry. Correlation of the Near Infrared (NIR) spectroscopic results with Optical Stimulated Electron Emission (OSEE) and ellipsometry will also be presented.

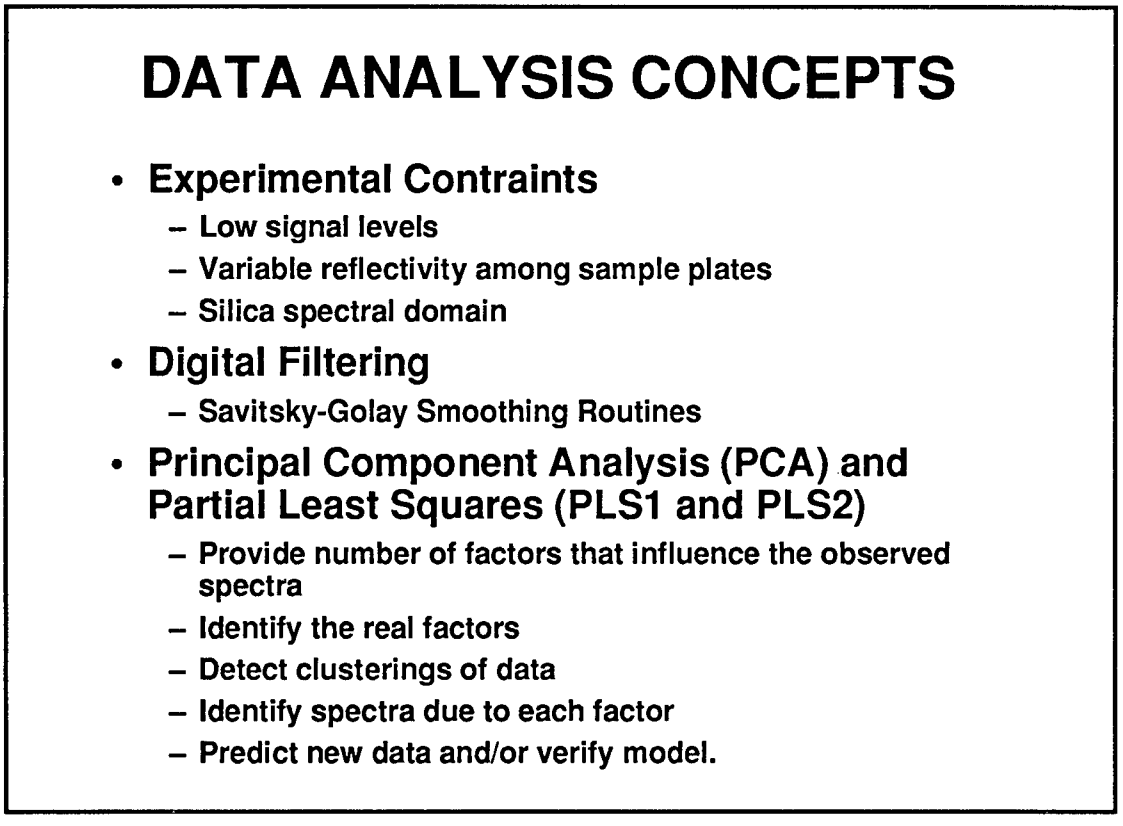
INTRODUCTION

Optical fiber spectrometry offers unique capabilities for detection and identification of contaminating species on aerospace flight hardware and other critical surfaces, either stand-alone or in conjunction with other inspection processes such as Optically Stimulated Electron Emission (OSEE). Much progress has been made in understanding spectral features observed from surface films with optical fiber probes, yet the interpretation of spectral features on surfaces continues to be the major challenge for this spectrometric tool. The complexity of the interactions due to thin film reflection/absorption phenomena still requires some chemical and physical knowledge about the surface being analyzed. In addition considerable expertise is still required to sort through the spectral features obtained, to pick out the significant features and determine the origin of these features. It is anticipated that the evolving methodologies resulting from the work presented here, will become more easily absorbed into the production arena with a little more development and implementation activities.

Continuing work with both NASA/MSFC and Thiokol has provided the opportunity to apply the capabilities of optical fiber NIR techniques to the following cases:

A summary of the path used to optimize upon an analytical approach used are presented in figure 3. The approaches most frequently used are derived from the current interest in applying chemometric techniques to solve real-world problems. All of the software packages used in this work are commercially available and used by a large number of spectroscopists and others who need to analyze large spectroscopic data sets.

Figure 3. Data analysis concepts used in this work.



The procedures follwed in obtaining spectral data and performing the analysis were fairly consistent. Deviations in the use of specific routines for data smoothing or to bring out certain anticipated features were implemented as required. Once a series of NIR spectra were obtained from the experiments described in this report, a variety of of chemometric techniques were employed to isolate significant spectral features as facators using either Principal Component Analysis (PCA) or Partial Least Squares (PLS) techniques. Iterative smoothing routines were sometimes performed back-to-back to improve the S/N ratio of the observed spectra. Complementary analysis techniques were used in order to trade off advantages over disadvantages of various techniques. For instance, optical fiber spectral scans were performed with the Guided Wave 260, which can obtain the highest resolution possible either by reducing the spectral bandwidth or by signal averaging. Either choice requires relatively longer scan times. Hence trade-offs between resolution and scan time had to be used in optimizing spectral scans with OSEE scans in the studies performed in the environmental chamber. At the level of resolution used, sequential smoothing routines would allow for good peak definition.

- HD2 and silicone films on D6AC steel and 7075 aluminum
- Mixtures of HD2 and silicone films on D6AC steel and 7075 aluminum
- D6AC steel and 7075 Aluminum plates in controlled temperature and humidity for extended periods of time.

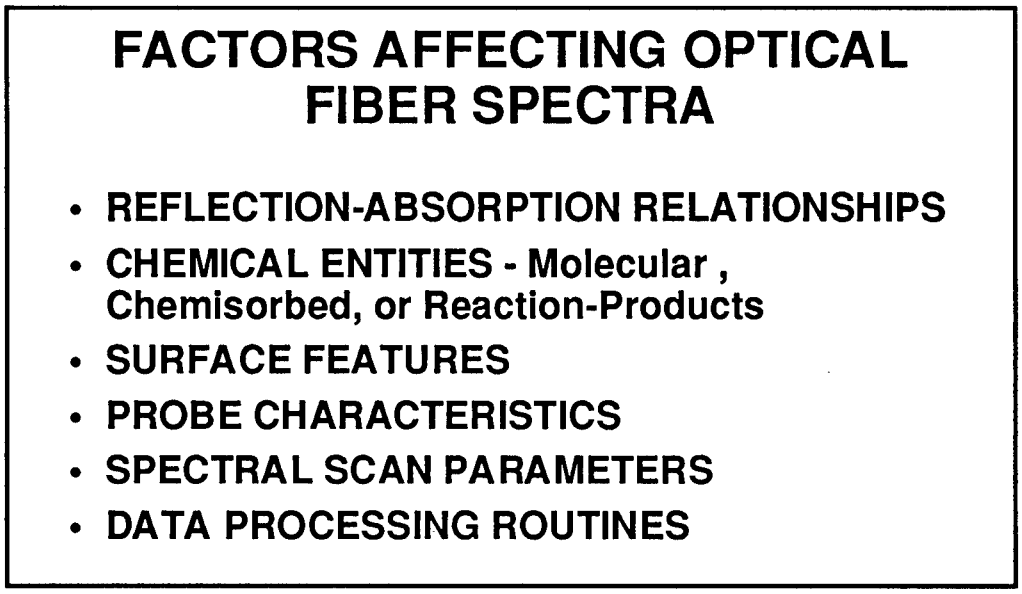
The primary results of these observations has been to show that NIR spectrometry is able to:

- Discriminate between HD2 and silicone greases in single or mixed applications, both qualitatively and quantitatively.
- Detect the various water/hydroxide species that occur on both D6AC and aluminum surfaces under variable humidity and temperature conditions.
- Detect levels of contamination by tape residues used in the manufacturing operations of the RSRM.

Optical Fiber Spectrometry Considerations:

Optical fiber spectrometry provides a number of challenges for accurate surface analysis. A number of the factors which can affect the signals observed, and correspondingly the interpretation of its chemistry, are shown in Figure 1 below.

Figure 1. Factors affecting the interpretation of spectra observed from surfaces.



The underlying physics associated with the reflection/absorption characteristics of the multitudinous films which may occur on a surface are always going to be part of the unknown in any analysis performed on solid rocket motors. Objectively, the data processing techniques used in this work, have been oriented such that these phenomena

can be factored out to provide spectral features associated with both the chemical species and physical parameters represented on the surface. These chemical entities can be oxides, hydroxides, or any other materials. In the spectral region in which this work has been performed, 1.0 - 2.5 microns, the -OH stretching vibration is the major peak observed for species which result from hydrolysis or hydration. This spectral band represents the second harmonic or combination bands of features normally observed in the mid-IR using FTIR or other infra-red instruments. In most cases, the -CH stretching vibration is also observed in this region as combination bands. This observation, for example, allows us to differentiate between HD2 and silicone greases. Spectral observations in the mid-IR can not always do as well in differentiating between similar species.

In this work, the chemical entities which are observed in the spectral scans are primarily hydrated species which result from the presence of water on the surface of the metal or contaminants purposely placed on the surface. The chemistry associated with hydrolysis of D6AC steel and aluminum 7075, obviously becomes a very important part of the interpretation of the spectra observed in these experiments. In the case of D6AC steel, very little work on hydrolysis at ambient temperatures has been found in the literature so far. Aluminum; however, provides a large number of data presented in the literature which makes the interpretation of the spectral observations somewhat easier.

The obvious goal of any spectral analysis is to obtain a quantitative measure of the interaction between the material being analyzed and the light used for interrogation. The physical features extracted in the factor analysis can be difficult to interpret with non-uniform surfaces, presenting another set of problems in the quantitative analysis of films on surfaces. Since the light may specularly reflect off the surface of the film or the surface of the metal more than once, one may obtain spurious intensity relationships from the spectral analysis. Also if the light reflected off the surface has passed through the film more than once, then one has difficulty providing a quantitative measurement of the properties of the film. In the case of the materials used in this study, solid rocket motor case materials were not intended to have mirror finishes, hence, diffuse scattering from randomly oriented surface features encompasses the primary thrust of this work. In general most the panels provided for spectral analysis had varying surface roughness and reflectivity, making calibration one of the most difficult tasks in the study.

In addition to the enhancement of the desired signals using physical improvements related to the optical and scan parameters, improved software approaches have also been used during this work, primarily in the use of chemometrics techniques to extract the useful information contained in a series of spectra acquired from the various samples under test. These methods fall under the category of multivariate analysis techniques and are used very successfully in a number of chemical and process industries. For example the idea is to analyse all the relevant spectral data at once and extract features which dominate the behavior of the data series. This is shown in figure 2 on the next page, in which the accumulated spectral data is analyzed by a multivariate analysis technique and the loadings (spectral features) and scores (influences) are extracted to determine how the system is changing chemically. This analysis is currently being performed with Unscrambler II.

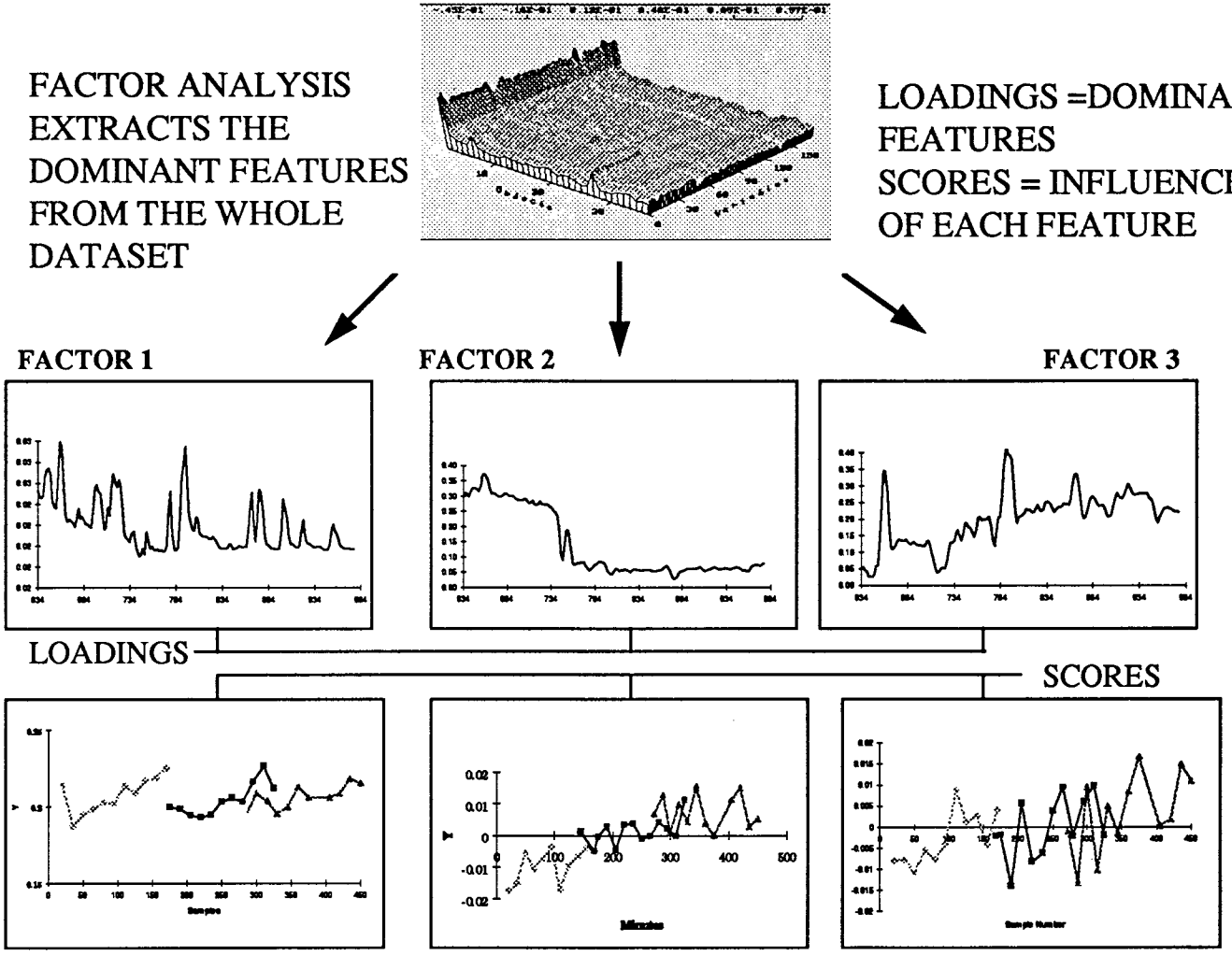
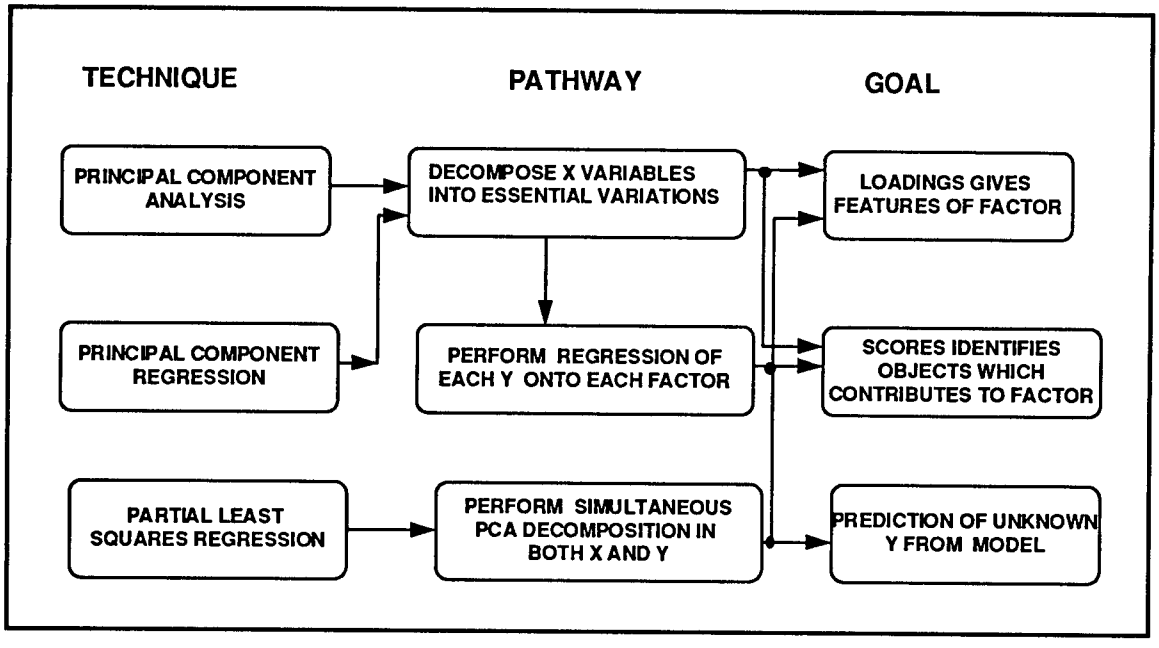


Figure 2. Loadings and scores are the dominant factors contained within a ataset.

The data handling routines for separating out the significant peaks were primarily by performing a PLS Analysis on the spectra, usually using the total spectra set to generate a model for any set of experiments. A schematic showing the possible approaches to perform either principal component or partial least squares analysis on the data sets is shown in Figure 4 below. In some cases verification of peaks and their occurrence in the experiments was obtained by taking the difference between any two spectra in a series.

Figure 4. Decision tree showing possible routes to obtain factors in the spectral analyses for this work.



In the work presented here, the philosophy was to collect all the information for a particular substrate, chemical system and build the model based upon the most complete set of varaibles possible. In this manner, the Unscrambler software was much more likely to pick out the corresponding factors from the observed spectra.

The major software used to support this work included SpectraCalc and Unscrambler II. Typically spectra were recorded in units of watts and transformed into absorbance using the relationship:

$$A = \log \frac{I}{I_{ref}}$$

Much work was spent in the beginning of the research in determining what reference surfaces to use for calculating absorbances. The major problem that arises in this type of analysis is when a spectral feature goes negative; i.e. $I < I_{ref}$ then most of the matrix multiplication techniques are not applicable. In practice, a negative absorbance is undefined, which means that the reference is not valid. Several reference surfaces used in

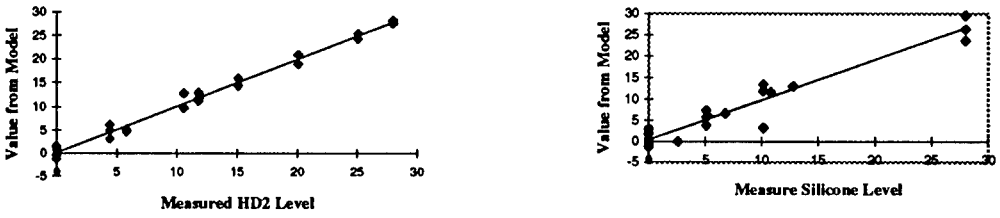
this work include an aluminum or gold mirror; i.e. totally or specular reflecting; barium sulfate i.e., diffuse reflecting, and native surfaces such as D6AC steel or aluminum.

Experimental Results:

The results of three different experiments are reported here. The first experiment is concerned with the quantitative identification of HD2 and silicone films on D6AC steel and 7075 Aluminum. A set of D6AC and aluminum 7075 panels were vapor degreased and grit blasted at 20° and contaminated at six levels with either HD2 or silicone or a combination of both. NIR spectra of the panels obtained and analyzed with PLS1 are shown in figure 5.

Figure 5. Calibration curve for HD2 and silicone contaminants on D6AC Steel

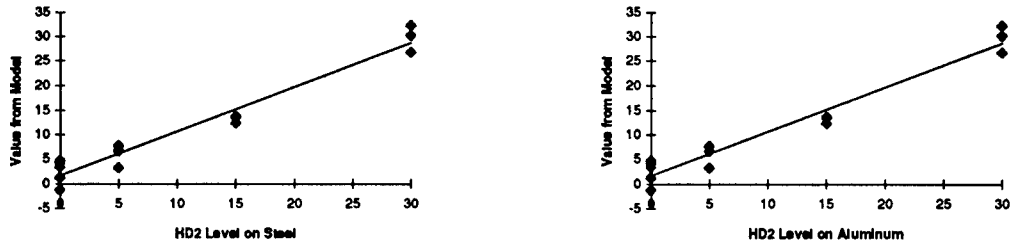
a. HD2 grease b. Silicone



Another test was performed at Wasatch as a demostration of capabilities with samples prepared by Thiokol personnel and the results are shown in figure 6.

Figure 6. Results of NIR demonstration at Thiokol Wasatch.

a. HD2 on D6AC Steel b. HD2 on Aluminum 7075



Another series of experiments looked at the surface chemistry of D6AC steel and 7075 Aluminum plates in controlled temperature and humidity for extended period of time to determine the effects of relative humidity, temperature and grit blast angle on the bonding characteristics of both D6AC steel and Aluminum 7075. In both sets of experiments,

spectra subtraction between any two spectra showed peaks in the -OH vibration region that varied throughout the experiments. In the case of the D6AC steel, the lack of knowledge of what spectra l features to expect made evaluation difficult. Aluminum has been studied substantially more and does provide spectral features which can be predicted from the literature. However, this approach does not provide much insight into the role of any of the variables in the experiment. Consequently more substance has been given to the PLS analysis in trying to interpret the observed spectral features. In each case the total collection of spectra for one substrate has been amassed into one data set to generate a PLS2 model. Then a PLS1 analysis was performed to isolate the significant features. In both cases, the principal components which appeared as the primary factor was grit blast angle. In the D6AC experiments temperature and relative humidity showed up nicely as factors 2 and 3. Spectral features that varied throughout the test then followed as the remaining principal components. For the aluminum data set, the temperature and relative humidity did not separate out quite as nicely. For that reason the interpretation for the aluminum-water chemistry is obviously quite complex. Fortunately the chemistry is better known and the literature provides more information to work with; however, the analysis of contaminating films is still difficult.

In the final sequence of experiments reported here, the residues of adhesives from four different tapes used by Thiokol in their manufacturing process were studied to determine if they could be quantitatively identified in the NIR. Data was collected from the samples of residue that might remain on a bonding surface after tape has been applied, then removed and the adhesive cleaned from the surface with solvent. The residues from four different tapes currently used by Thiokol were extracted using 1,1,1 Trichlorethane as a solvent. The four tapes studied, and their occurrence in the manufacturing process, are

1) Teflon tape, a tape used in the grit blast process;

2) P mask, a masking used in the painting operation;

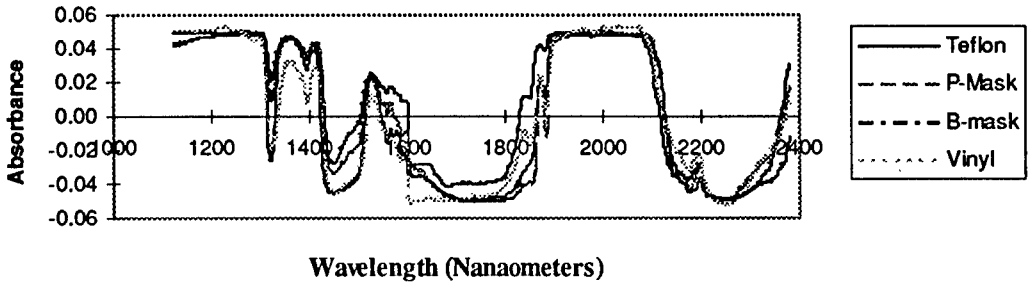
3) B mask, a masking used in the grit blast process;

4) Vinyl tape, a tape used in the cleaning operation.

The residues were sprayed concurrently on large aluminum plates and witness foils. The gravimetric weights were determined for the witness foils from which conclusions about the levels on plates were deduced. Each residue was applied in two distinct levels of contamination, yielding eight contaminated levels, two for each type of contaminant. A blank panel was also processed similarly, except without contamination.

The PLS analysis confirmed that the tape residues from the four potential contaminants could be quantitatively identified in the NIR. The close similarity of the chemistry for the adhesives, for example a common plasticizer such as a phathalate was present in each residue, made the differentiation among the four a little more difficult; however, the PLS model did a fairly good job of differentialting between the tape residues.

Figure 1. Plot of First Factor for all Four Residues



Summary

NIR spectrometry can provide a useful tool for the inspection of critical surfaces and the quantitative detection of contaminating materials. The utility of optical fiber system allows for flexible approach to using NIR in untraditional applications. In conjunction with chemometric tools, like PCA or PLS, the on-line approach is quite feasible and can provide a useful supplement to other techniques such as OSEE.

We wish to show appreciation to Ms. Yadilett Garlington, Bianca Brindley, and the other students who helped do much of the work reported here. Various phases of this work have been performed under contract NAS8-38609, D.O. 83 and Thiokol Contract #3MR029.

CONTAMINATION DETECTION NDE FOR CLEANING PROCESS INSPECTION

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ABSTRACT

In the joining of multilayer materials, and in welding, the cleanliness of the joining surface may play a large role in the quality of the resulting bond. No non-intrusive techniques are currently available for the rapid measurement of contamination on large or irregularly shaped structures prior to the joining process. An innovative technique for the measurement of contaminant levels in these structures using laser based imaging is presented. The approach uses an ultraviolet excimer laser to illuminate large and/or irregular surface areas. The UV light induces fluorescence and is scattered from the contaminants. The illuminated area is viewed by an image-intensified CCD camera interfaced to a PC-based computer. The camera measures the fluorescence and/or scattering from the contaminants for comparison with established standards. Single shot measurements of contamination levels are possible. Hence, the technique may be used for on-line NDE testing during manufacturing processes.

INTRODUCTION

The use of light-weight composite materials in structures which must function under extremes of temperature, pressure, and chemical environment presents new challenges to design engineers. Often these structures are of multilayered construction, with each layer conferring on the assembly specific properties. These types of materials range from common metals such as aluminum, matrix composites (MMC's) based on TiAl, beryllium, or copper, to ceramic reinforced carbon and silica based composites. In the joining of these multilayer materials and the welding of metals the cleanliness and structure of the interface can play a large role in the strength of the resulting bond. Contaminants may be present on these materials as a result of the manufacturing process or due to subsequent handling. Often, the simple process of oxidation during storage may substantially modify the surface structure. These contaminants may weaken adhesive bonding between layers via formation of a poor bond or via diffusion into one of the components. In the latter case the strength of the material may be compromised.

It is clear that non-destructive evaluation (NDE) techniques which can enhance the quality of bonded and welded structures in the assembly stage would greatly improve their strength and reliability. Furthermore, improved NDE techniques which enhance workplace productivity through reductions in rejected components or recognition of defective parts early in the assembly stage could substantially reduce manufacturing costs.

In this paper we discuss the development of a method which permits quantitative detection of contamination on bonding surfaces and which is capable of processing large, irregularly shaped surfaces, rapidly and in a non-destructive manner. The method is based on the principle that many of the contaminants will fluoresce when excited with UV light. However, unlike the traditional "black light" version of this principle used to detect contaminants, this method employs modern excitation and detection methods which can be readily quantified. The technique uses UV laser illumination of large surface areas to excite fluorescence in the contaminants. The use of the laser allows for much higher illumination intensities than previously employed using ordinary "black" light sources. The fluorescence excited by the laser is observed using a gated image-intensified television camera to provide a precise image of the object undergoing inspection. Thus, in a sense, a flash picture of the contaminants on the surface is recorded using this system without having to translate the item under inspection and without regard for the shape of the item. This image is collected in exposures on the order of 1s and captured

using a simple, PC-based, commercially available frame grabber system. The image may be used by process controllers to flag items for contaminant removal and the image can be filed and stored for NDE documentation purposes.

In the experiments described below we discuss the techniques used to select, quantitatively deposit, and image contaminants on a variety of manufacturing surfaces.

EXPERIMENTAL

The experimental effort followed a series of sequential steps to optimize the effectiveness and determine the sensitivity of the technique for a representative set of contaminants and substrates. Optimization of the optical technique was accomplished by determining both the absorption and fluorescence spectra of the contaminants. From these spectra, excitation and detection wavelengths were selected for examination using fluorescence imaging. Fluorescence imaging experiments were performed by recording the fluorescence signal as a function of contaminant dosing level and illumination intensity. The technique was evaluated with respect to absolute sensitivity, contrast, and linearity of response. Additional measurements were performed in which larger structures were contaminated and viewed by the imaging system.

Selection and Dosing of Contaminants and Surfaces

A specific goal of these measurements was the detection of Conoco HD-2 Calcium grease on D6AC steel, which is relevant to the bonding of the propellant liner to the Space Shuttle solid rocket motor (SRM). The full matrix of materials evaluated in the experiments is provided in Table 1 below.

Table 1. Contaminants and Substrates Examined Using Fluorescence Imaging

	Substrate			
Contaminant	6061 Al	D6AC Steel	NBR*	Quartz
Conoco HD-2	X	X	X	X
Mineral oil	X			
DC 93-500 adhesive	X	X	X	X
Halocarbon wax	X			

*Neoprene-butadiene rubber

Samples of the HD-2 grease were provided by Conoco. The mineral oil was spectroscopic grade and was purchased from Fisher Scientific. The DC93-500 adhesive is a special space-qualified, low outgassing RTV compound manufactured by Dow-Corning and specified by NASA and DOD for spacecraft use to reduce contamination effects. The halocarbon wax was purchased commercially from Halocarbon Products Inc. The composition of the wax was not specified by the vendor.

Precise contaminant dosing of the substrates was accomplished using modified techniques developed at the NASA Marshall Space Flight Center. Contaminants were diluted in a volatile solvent and applied to 2 x 2 $in.^2$ coupons of the substrate material using a Paasche #5 airbrush. The coupons were placed between a quartz crystal thin film monitor (QTFM) (Sycon Instruments Model STM-100) and two aluminum foil witness plates for determination of the dosing level. The contaminants were applied to the surfaces manually. Experiments were conducted to determine the spatial uniformity of the application technique and the fidelity of the QTFM in determining the dosing level. Less than 10%

non-uniformity was observed in the dosing of a 6 x 6 in^2 surface which enclosed the substrate coupon, QTFM, and aluminum foil witness plates.

The fidelity of the QTFM was verified by simultaneously dosing the QTFM and the two Al foil witness plates. The plates were weighted and compared with the mass gain inferred from the change in crystal oscillation frequency. These experiments could be performed without complication up to dosing levels of approximately 50 $\mu g/cm^2$. At this level the QTFM behaved erratically, indicating that there was poor coupling between the thick contaminant film and the crystal. Calibrations at higher dosing levels were performed by removing and cleaning the crystal prior to reaching the 50 $\mu g/cm^2$ limit. Additional dosings were then performed with the clean crystal. The dosing level was obtained from the sum of the readings prior to each cleaning cycle. The correlation between the mass gain inferred from the QTFM and the Al foil witness plates is better than 95%.

Absorption and Emission of Spectra of Contaminants

Contaminant absorption spectra were recorded using a standard laboratory spectrophotometer (Shimadzu UV-3100). The contaminants were applied to S1-UV quartz substrates (160 to 2200 nm transmission) using the spray station at dosings ranging from 100 to 150 $\mu g/cm^2$. The absorption spectra are presented over the relevant wavelength regions in Figure 1. The contaminants are observed to have absorption features primarily in the wavelength regions below approximately 250 nm, which is consistent with our expectation for aliphatic species. The spectra were analyzed using a Beer-Lambert Law type expression:

$$\ln(I_0/I_t) = \alpha\ T \qquad (1)$$

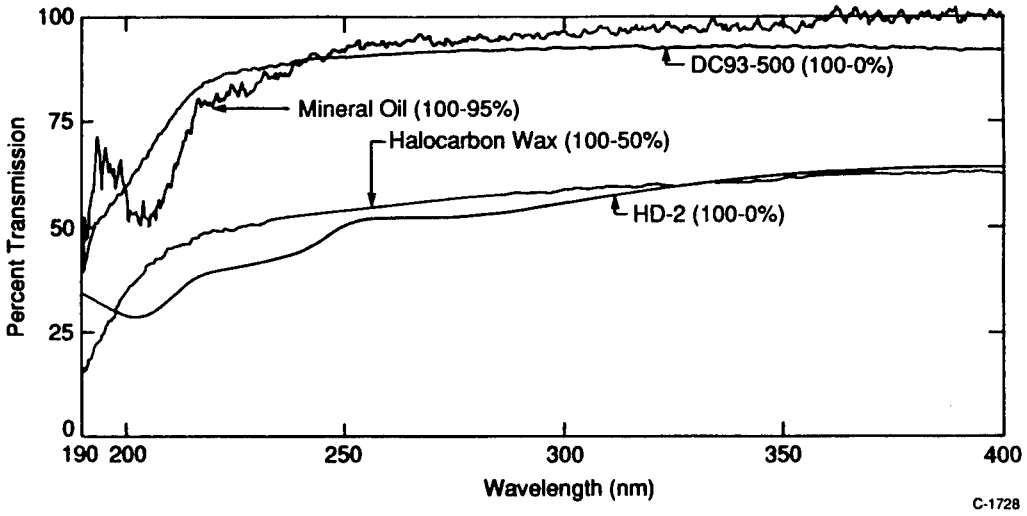

Fig. 1. Absorption spectra of HD-2 Grease, DC93-500, mineral oil, and halocarbon wax.

where α is the extinction coefficient in $cm^2/\mu g$, T is the film thickness in $\mu g/cm^2$ and I_0 and I_t are the incident and transmitted light intensities. The extinction coefficient is comprised of two components, absorption of the light by the contaminant and scattering and reflection of the light by the layer. To first order, only absorption leads to fluorescence, although multiple scattering and further absorption within the medium will enhance absorption. Thus, the measured extinction coefficient represents an upper bound on the absorption by the film.

The optimum wavelength for the excitation and detection of these contaminants falls in the 190 to 240 nm region. Two high energy excitation sources produce light in this wavelength region: an

excimer laser operating on the ArF line at 193 nm and a UV flashlamp, which has emission throughout the UV and visible region of the spectrum. The ArF laser was used as source for excitation of the contaminants due to the close overlap between their absorption and emission bands.

The absorption spectra and the extinction coefficients indicate that a small fraction of the incident light is absorbed by the film, even for thicknesses as great at 150 $\mu g/cm^2$. Hence, the films are "optically thin" and attenuation of the excitation source through the layer is not an issue in the detection of the contaminants. The light absorbed by the film is simply:

$$I_a = I_0 - I_t \tag{2}$$

and by combining Expressions 1 and 2 we obtain

$$I_a = I_0[1 - \exp(-\alpha T)] \ . \tag{3}$$

In the optically thin limit ($\alpha T << 1$) Expression 3 reduces to

$$I_a = I_o \ \alpha \ T \ . \tag{4}$$

Hence, the absorbed intensity is linearly related to both the incident intensity and the contaminant film thickness in this regime. This is a primary feature of the fluorescence imaging technique.

Emission spectra were recorded by irradiating an S1-UV quartz plate coated with the contaminants at an angle of 45 degrees with respect to the surface normal using the 193 nm output from the excimer laser. Fluorescence from the coated substrate was viewed at 45 degrees from surface normal and 90 degrees with respect to the laser axis with a 0.3 meter scanning monochromator equipped with a photomultiplier tube (PMT). The fluorescence was collected with an f/4 UV lens and passed through a KBr disk to block scattered light from the laser while passing the fluorescence at wavelengths longer than 200 nm.

Emission spectra were recorded from 200 to 650 nm in two segments. A color filter was used to isolate the spectral orders of the monochromator. Spectra were recorded with coated and uncoated substrates and subtracted to eliminate substrate fluorescence effects, which were minor over most of the spectral region. The relative response of the spectrometer was calibrated using NBS- traceable deuterium and quartz-halogen emission standards. The emission spectra of the films are presented in Figure 2. The emission features are broad and all start from the short wavelength cutoff of the spectrometer and extend to approximately 400 nm. The relative intensities are qualitative, but show that the HD-2 and mineral oil samples are the strongest, followed by the DC93-500 and the halocarbon wax. The emission spectra of the contaminants indicated that a broadband UV filter which blocks the 193 nm laser light is optimum for detection of the contaminants. A Corning 7-54 color glass filter was chosen based on these considerations for use in these measurements.

The wavelength resolved emission spectra revealed that the primary regions of emission occur where the films do not strongly absorb radiation. Hence, there will be no "trapping" of the fluorescence by the film. The combination of "optical thinness" for both the excitation and emission wavelengths leads to a contaminant detection system which should have a linear response over a broad range of contaminant levels. To first order, the observed fluorescence intensity can be related to the absorbed intensity via the expression

$$S_F = I_0 \ \alpha \ T \ \Phi_f \ A_o \ \Omega_o \ \tau_o \ Q_e \ / N_p \tag{5}$$

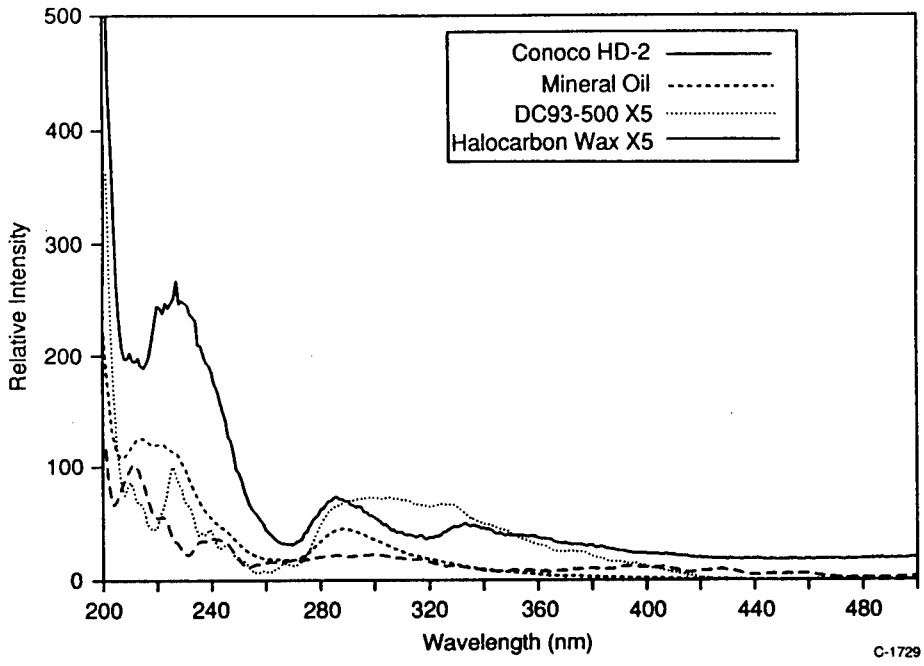

Fig. 2. Emission spectra of HD-2, mineral oil, DC93-500, and halocarbon wax excited at 193 nm.

where

Φ_f is the fluorescence efficiency for the contaminant,
A_o is the aperture of the fluorescence collection optics,
Ω_o is the steradiancy (field of view) of the detection system,
τ_o is the transmission of the optics and filters,
Q_e is the quantum efficiency of the detection system,
N_p is the number of pixels in the detector for imaging,

and where these quantities have been averaged across the bandwidth of the detection system, as appropriate. The reduction in S_F by N_p assumes that the detection system is viewing a spatially homogenous field. Of course, this is not a requirement of the system but it does place a lower bound on the signal levels.

The fluorescence efficiency, Φ_f, is given by the ratio of the fluorescence emission rate to the total rate of decay of the fluorescing state. The primary influence on the fluorescence efficiency is the rate at which the excited state is quenched by the surrounding molecules. Except for those molecules which are quite close to the surface of the substrate or the air interface, the environment around the excited state is constant, and hence so is Φ_f. Only for extremely thin layers should the efficiency deviate from a constant value. The thickness at which this effect becomes important can not be predicted, a priori, but would be observed in the measurements as a curvature in the response of the system at low contaminant levels.

Optical Detection of Contaminants

Experiments were conducted to determine the energy and concentration dependence of the fluorescence signal from the contaminants on the substrates previously described. The experimental apparatus is shown schematically in Figure 3. The apparatus can be described in terms of an excitation system, a fluorescence detection system, and a diagnostics system.

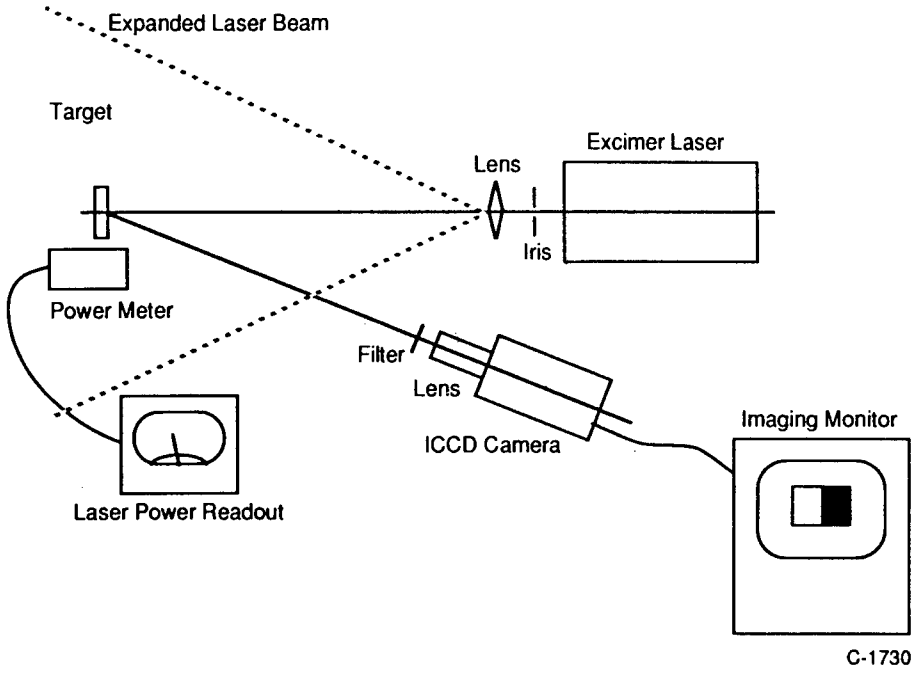

Fig. 3. Experimental fluorescence imaging apparatus using an ArF excimer laser and gated, image-intensified CCD camera.

The excitation system consisted of a rare gas halide excimer laser (Questek Model 2820) operated on the ArF line at 193 nm. The laser output energy was 200 mJ/pulse at a repetition rate of 10 pulses per second. The pulse duration was approximately 20 ns. The laser beam was rectangular (5 x 20 mm) and moderately divergent. A lens was placed at the beam exit port of the laser, causing the beam to come to a focus and then diverge as it illuminated the target substrate, which was located approximately 150 cm from the lens.

The substrate was typically a 2 x 2 $in.^2$ coupon mounted on an optical post in the beam path. The laser beam fully illuminated the target substrate. A surface absorbing power meter (Scientech 36-0001) could be substituted in place of the target to measure the laser energy incident at the illumination plane. For these measurements the laser fluence was typically 100 $\mu J/cm^2$/pulse. The 2 x 2 $in.^2$ coupons were dosed using the system described previously. A mask was applied to one half of the coupon during application of the contaminant in order to provide a clean surface reference for each measurement. The sample coupon was dosed sequentially, with increasing amounts of the contaminants, when constructing a calibration curve. Repeated exposure to the UV light had no observable effect on the behavior of the films, with the exception of the DC93-500 silicone dosed substrates, which will be discussed later.

Contaminant fluorescence was observed using an intensified and cooled CCD camera (Princeton Instruments). The pixel resolution of the camera was 526 x 384. The intensifier was gated to match the duration of the fluorescence signal, which was typically 1 to 2 μs. Gating of the detection system was also a key factor in excluding background illumination from the image. A 105 mm f/4.5 UV imaging lens (Nikon) interfaced to the camera, was used to capture the fluorescence from the films. The Corning 7-54 color filter was mounted at the entrance to the lens. In some experiments, a 35-105 mm standard zoom lens (Nikon) was used to widen the field of view of the detection system in order to observe

contamination levels on larger objects. This capability was achieved at the expense of approximately a factor of 7 in sensitivity due to the reduced UV transmission of the glass optics in the lens.

The camera was interfaced to a computerized data acquisition system consisting of a PC type computer (Gateway 2000 486/33) operating on software furnished with the camera by Princeton Instruments. The software allowed for the acquisition of fluorescence images from single pulses of the laser. For weaker signals multiple pulses could be averaged on the camera chip or in computer memory. In most cases, single shot fluorescence intensities provided sufficient signal levels to meet the detection goals. Fluorescence intensities for the dosed and clean sides of the coupon were processed by the camera system to obtain signal levels (counts) per pixel. A simple subtraction of the two signals yielded the fluorescence intensity due to the contaminant alone as a function of position on the coupon. A false color scale could be applied to the image to indicate the absolute level of contamination, given the proper calibration factors. Images could be stored in memory for further processing, photographed for presentation, or used to produce contour plots of the contamination levels.

The detection of HD-2 grease was the primary focus of the effort. Figure 4 shows the fluorescence intensity per pixel as a function of contaminant level for HD-2 on the aluminum, D6AC steel, quartz, and NBR substrates. Signal levels range from a high of 10,000 counts/pixel, where the camera saturates, to less than 100 counts/pixel over a concentration range from 0.1 to 100 $\mu g/cm^2$. A least-squares fit to the data on these log-log plots indicate that the signal is linearly proportional to the contaminant level, within experimental accuracy, over nearly three orders of magnitude. Furthermore, the linearity is independent of the identity of the substrate, i.e., the technique is equally applicable to insulating materials. The contrast between the dosed and clean sides of the substrate is excellent, and greater than 5 even at the lowest dosing levels considered.

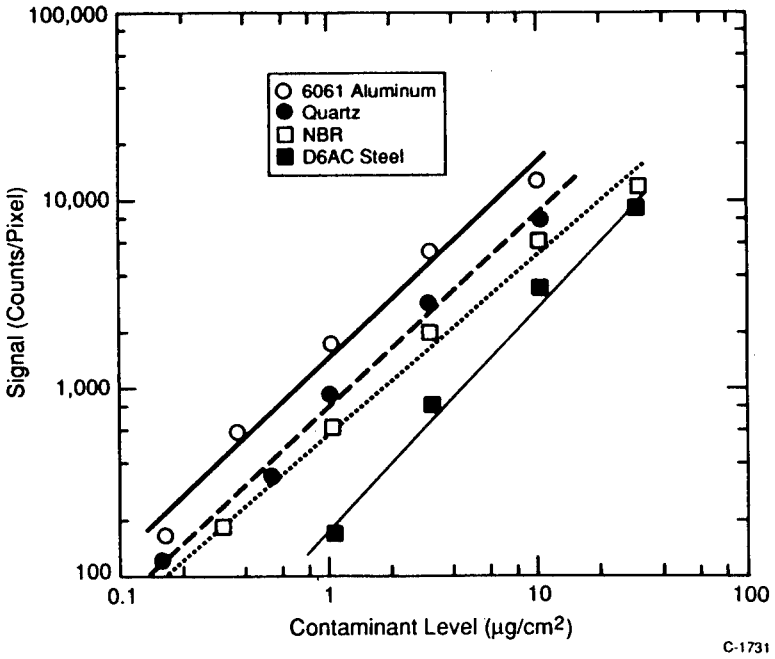

Fig. 4. Fluorescence signal as a function of HD-2 contaminant level for various substrates.

The behavior of the fluorescence as a function of laser illumination level is provided in Figure 5 for the Al substrate. The intensity is observed to be a linear function of the laser intensity for aluminum as well as all of the substrates considered.

A lesser set of data was recorded for the detection of mineral oil, since it appeared to behave similarly to HD-2. As with the HD-2, the response of the fluorescence detection system is linear, within experimental error, as a function of both contaminant level and laser intensity.

Unanticipated problems arose in the detection of DC93-500 silicone adhesive. The fluorescence signal was strong but behaved erratically. Further investigation revealed that photochemical processing of the adhesive by the UV light was altering the composition of the film. This effect is most likely due to photochemical polymerization of the unreacted monomers in the contaminant layer. The effect was most pronounced for the D6AC steel, where a chemical interaction with the substrate produced a black layer which did not fluoresce. We believe this anomalous behavior is an artifact of the contaminant preparation method rather than an indication of the true response of the system to the silicone impurities. Our preparation technique allowed a high level of unpolymerized compound to be deposited on the surface. Normal polymerization of the RTV adhesive is via a radical catalyst. The photochemical production of these radicals by the laser promotes the further catalysis of the polymer, which was arrested by the dilution of the reacting mixture in the solvent at the time the sample was prepared.

Detection of fluorocarbon wax by this technique proved quite difficult. Both the absorption and emission spectra indicated a weak response to light at 193 nm. The indications were confirmed when little or no signal was observed with the fluorocarbon wax. Our previous experience in imaging a fluorocarbon based vacuum grease had shown some promise. Hence, further examination of these compounds is warranted before excluding their detection by this technique.

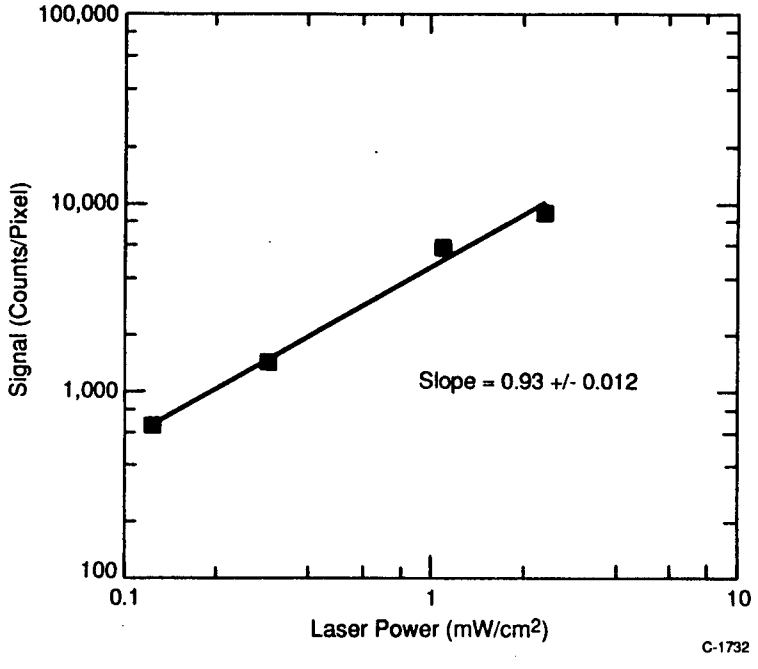

Fig. 5. Dependence of the fluorescence signal on laser intensity for a 6061 aluminum substrate.

DISCUSSION

The fluorescence imaging results presented in this report verify the physical model of contaminant fluorescence based on simple absorption and emission of radiation in the optically thin limit. The model predicts a linear dependence of the contaminant fluorescence signal on contaminant level and illumination intensity. Our assumption that the technique was equally applicable on insulating and conducting surfaces was also verified. The influence of surface structure on the fluorescence signal

was clearly evident in the data. As demonstrated in Figure 4, HD-2 grease fluorescence on 6061 aluminum is much stronger than on D6AC steel for comparable dosing and illumination intensities.

Two rather simple explanations might be offered to account for the differences. The first explanation considers the surface reflectance of aluminum compared to D6AC steel. The aluminum appears visually to be highly reflective. In contrast, the D6AC steel is black and has a grit blasted surface which acts as a good light trap. A highly reflective surface can effectively double the apparent light path through the contaminant. In the optically thin limit of contaminant absorption, this effect would increase the fluorescence signal on the aluminum by a factor of two compared to the steel for normal incidence by the light source. While this explanation is plausible, it is not consistent with the fluorescence data recorded on the quartz (smooth and transmissive) and NBR (smooth and absorbing) substrates. The absolute sensitivity for HD-2 grease on both these smooth surfaces is virtually identical to the absolute sensitivity measured for HD-2 on the aluminum substrate. Hence, we must conclude that the aluminum is not highly reflective at 193 nm and that the fluorescence signal is due completely to the first transit of the contaminant film by the excitation light.

The second explanation for the apparent decreased sensitivity on D6AC steel is due to the increased surface roughness of the sample. Since the surface is highly roughened (approx. 100 μin. scale size), the effective surface area is much higher for a 2 x 2 $in.^2$ coupon of the steel compared to the Al. The contaminant dosing assumes a smooth surface, hence the effective dosing level per unit surface area is reduced due to the surface roughness. Similarly, the intensity of the light incident on the surface is reduced by this same roughness factor. However, the projection of a camera pixel onto the roughened surface will incorporate the total mass and the total energy deposited into the area. Hence, the effects of surface roughness should cancel in the optical detection system.

A second influence of the surface roughness may be in the coupling of the electronic energy in the contaminant molecules to the underlying substrate. For the roughened surface the effective thickness of the contaminant layer is reduced and the contaminant may interact with the surface to a much greater extent. The coupling of the molecular electronic energy to the surface acts to reduce the fluorescence quantum efficiency. The reduced fluorescence efficiency translates into a reduced detection sensitivity for the film. One impact of this phenomenon would be a non-linear dependence of the fluorescence signal on film thickness, since the range to the underlying substrate increases and its influence should decrease. The correlation of the fluorescence signal with the film dosing level for HD-2 on D6AC steel is somewhat greater than linear. However, the uncertainty in the correlation is with the limits of a linear response. Further data would be required to definitively establish the correlation. Data on the dependence of the signals on surface roughness and fluorescence excitation and viewing angles are also desirable to understand the response on D6AC steel. The acquisition of this data was beyond the scope of the current effort.

The focus of our initial efforts was in the detection of specific isolated contaminants on a range of substrates. A key issue in the implementation of the diagnostic will be the ability to detect multiple contaminants, perhaps with different detection efficiencies. The data indicate that differentiation of contaminants will be extremely difficult in most cases. The absorption and emission bands for the contaminants examined in this effort had few features which might enable differentiation between compound types. Specific identification of compounds would not be possible except in well defined scenarios. We also did not examine any synergism between mixed contaminants on a surface. This synergism can influence the fluorescence signal as an enhancing factor, in which energy is transferred from an absorbing molecule to one which fluoresces with greater efficiency. A similar energy transfer mechanism could reduce the signal if energy was transferred to a compound which did not fluoresce or emitted light in a spectral region outside the detection system bandpass. In general, the diagnostic is best suited for situations in which the range of contaminants which might be present on the bonding surface is reasonably well defined. This condition is present in a large number of bonding and manufacturing tasks.

CONCLUSIONS

The use of UV fluorescence imaging of contaminants on bonding surfaces has a high degree of sensitivity, a linear response with contaminant level and light intensity, and is independent of substrate material. Large and irregularly shaped objects can be imaged with the technique, often without any rastering of the detection system or object required. Calibrated false color-encoded images of the surfaces can be provided with existing software. The system has been demonstrated to detect Conoco HD-2 grease on grit-blasted D6AC steel, 6061 aluminum, and NBR with sensitivity as low as 0.1 $\mu g/cm^2$ (0.11 mg/ft^2) with a spatial resolution of 1 mm^2. This capability has direct application to quality control in the maintenance of Shuttle solid rocket motors.

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CLEANING VERIFICATION—INSTRUMENTATION AND TECHNIQUES 2

SURFACE INSPECTION USING FTIR SPECTROSCOPY

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ABSTRACT

The use of reflectance Fourier transform infrared (FTIR) spectroscopy as a tool for surface inspection is described. Laboratory instruments and portable instruments can support remote sensing probes that can map chemical contaminants on surfaces with detection limits under the best of conditions in the sub-nanometer range, i.e.. near absolute cleanliness, excellent performance in the sub-micrometer range, and useful performance for films tens of microns thick. Examples of discovering and quantifying contamination such as mineral oils and greases, vegetable oils, and silicone oils on aluminum foil, galvanized sheet steel, smooth aluminum tubing, and sandblasted 7075 aluminum alloy and D6AC steel. The ability to map in time and space the distribution of oil stains on metals is demonstrated. Techniques associated with quantitatively applying oils to metals, subsequently verifying the application, and non-linear relationships between reflectance and the quantity oil are described.

INTRODUCTION

Reflectance Fourier transform infrared (FTIR) spectroscopes are powerful techniques for materials characterization and surface analysis provided the spectrometer can address the appropriate location on a specimen under conditions for which the resulting measurement is meaningful(1). The spectra obtained over the energy range of 400 to 5000 cm^{-1} (wavelength range of 2 to 25 μm) contains information that directly correlates qualitatively and quantitatively to chemical functional groups, and that can be read like a book by most chemist. Reflectance techniques include external or specular, internal, and diffuse reflection. In collaboration with Harrick Scientific, Inc., a system of remote sampling terminals individually dedicated to each of these reflectance techniques, along with the means for multiplexing these terminals, was developed for use with FTIR spectrometers to obtain spectra from the surfaces of large flat or convex objects in ambient air or in environmental chambers with sufficient ease that meaningful statistical comparisons of spectra obtained from many locations on an object or from many objects can be made (2). Capabilities for gas analysis and emission analysis were also integrated into the system. External reflectance is done at 75° with an externally operated KRS-5 wire-grid polarizer. Internal reflectance uses a 45° single-reflection ZnSe element with p-polarized light, and diffuse reflection uses a barrel ellipse. The system, attached to a BIO-RAD FTS-60 FTIR spectrometer, also includes the capability to perform the above functions in controlled environments, i.e., cells and glove boxes, facilities for mapping surfaces, i.e., obtaining spectra from measured coordinates on a specimen, a 1-m path high-throughput gas-cell, and a spare port. The key design features of these sensors are maximum light recovery from the specimen, maximum signal-to-noise (sensitivity) for a given spectrum, no limitation on specimen size, high specimen throughput rate, and convenience. A portable surface inspection

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instrument, consisting of a barrel ellipse diffuse reflectance sampling terminal attached to a MIDAC Illuminator FTIR spectrometer configured for 12-Vdc operation and minimum size (200 mm by 200 mm by 600 mm) and weight (13 kg) has also been developed. Internal reflectance spectroscopy is being heavily exploited by the chemical industry for process monitoring of organic liquids, requires intimate contact with the specimen, and has a strong potential for bulk and surface analysis of soft, organic materials. External and diffuse reflectance are methods for analyzing the surfaces of solids and their potential in process monitoring and inspection is just beginning to be recognized. This paper describes the application of external and diffuse reflectance optics to practical inspection processes on metals of practical importance. Qualitative and quantitative determination of surface contamination is demonstrated and discussed. Criteria are presented that are consistent with current state-of-the-art FTIR spectrometry for a practical, hand-held FTIR surface inspection machine and the technical support necessary for its implementation.

EXTERNAL REFLECTANCE

External reflectance is simply the reflection of light by a mirror in which light passes through films on the mirror surface. Grazing angle 75° reflectance from relatively flat metal objects is the most sensitive method of surface analysis, with p-polarized light (light oscillating normal to the sample surface) being absorbed by surface species and s-polarized light (light oscillating in the plane of the surface) not being absorbed by surface species. Specular reflectance is normally considered to be a method for analyzing mirror finishes, but in the mid-infrared region (λ = ~10 μm), quite a number of very practical surfaces pass for mirrors. High-quality, front-surface, gold mirrors are used as the reference spectra, requiring a separate reference for each polarization. These mirrors are prepared by degreasing with a household spray cleaners containing detergents and 2-butoxyethanol grease cutters followed by a deionized water rinse, a 1-ks soak in concentrated sulfuric acid, another thorough deionized water rinse, and a rapid drying in a nitrogen stream. Calibration is done using aluminum foil, which is weighed, wiped uniformly with an oil, thoroughly wiped with dry tissue to remove all excess oil, and reweighed. Such treatment leaves behind typically 150 mg m^{-2} (~ 150 nm film, 14 mg ft^{-2}) of residue, which is easily weighed on foil specimens of 0.1 m^2 area and yields spectra of good quality. Many spectra (typically 12) can be obtained from one calibration specimen to give reasonable statistics to the calibration measurement. Calibrations were performed using DC-200 (5 cps) silicone (dimethoxy silane), corn oil, (polyunsaturated triglyceride) and a commercial light mineral oil (aliphatic hydrocarbon). Table 1 shows the results of these calibrations.

Table 1. Calibration values for oil stains on aluminum foil.

Oil	Band	Calibration Factors	Standard Deviation
DC-200 5 cps	2965 cm^{-1}	2.694 g m^{-2} $(a.u.)^{-1}$	2960 nm $(a.u.)^{-1}$ 13%
DC-200 5 cps	1265 cm^{-1}	1.536 g m^{-2} $(a.u.)^{-1}$	1688 nm $(a.u.)^{-1}$ 17%
Mineral Oil	2925 cm^{-1}	1.491 g m^{-2} $(a.u.)^{-1}$	1373 nm $(a.u.)^{-1}$ 13%
Corn Oil	2925 cm^{-1}	1.324 g m^{-2} $(a.u.)^{-1}$	1218 nm $(a.u.)^{-1}$ 19%
Corn Oil	1750 cm^{-1}	1.490 g m^{-2} $(a.u.)^{-1}$	1371 nm $(a.u.)^{-1}$ 27%

The noise level of the system is typically 0.0002 a.u. near 2900 cm^{-1}, so that the presence of hydrocarbons at the nanometer film thickness level (1 mg m^{-2}) can be detected with certainty. Aluminum foil, as taken from the roll, shows no detectable hydrocarbon bands at the 0.0002 a.u. level. At this noise level, the sulfuric acid cleaning process appears to be equivalent to sputter cleaning of the gold mirrors immediately before obtaining the reference spectra. Angle-resolved electron spectroscopy for chemical analysis (ESCA) generally supports the observations that the 1-nm hydrocarbon film, as determined by the preceding calibration, left behind by the cleaning described above is equivalent to 1 nm of carbon residue

supporting the general assumption that the calibration can be linearly extrapolated to lower concentrations.

Galvanized sheet steel specimens (0.3 m by 0.3 m) were exposed to a variety of greases, paints, and oils, was hammered, and then a 0.1 m region near the center of each specimen was cleaned using a carbon dioxide pellet blaster. They were evaluated for residual contamination using 75° specular reflectance mid-infrared spectroscopy. Figure 1 shows the p-, s-, and p- minus s-polarization spectra for this galvanized sheet metal in new condition, degreased with a spray cleaner, and thoroughly rinsed with water. The absorption bands for zinc oxide (1100 cm^{-1}) and sorbed water (1600 cm^{-1} and 3400 cm^{-1}) are obvious. A trace of water vapor (near 1600 cm^{-1} and 3800 cm^{-1}) can be seen in the p- and s-polarization spectra. Since this water vapor is in the spectrometer and not on the specimen surface, it occurs equally in both spectra and disappears in the difference spectra.

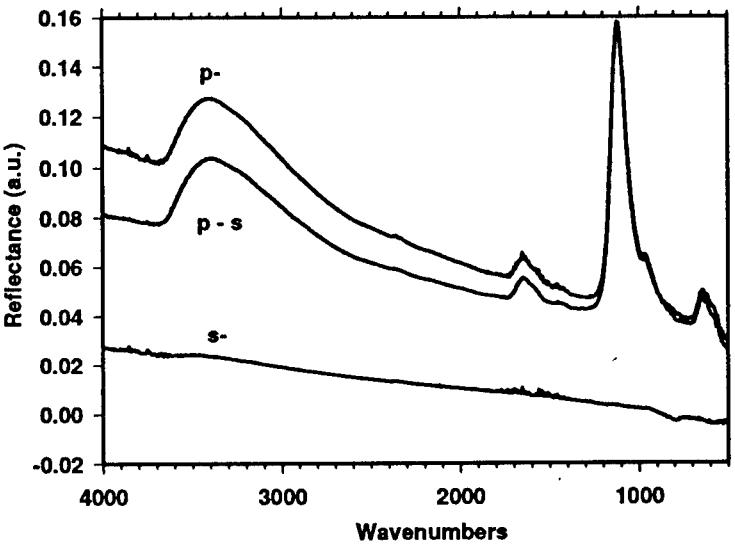


Figure 1. The polarization dependent, 75° specular reflectance spectra for galvanized steel sheet referenced to a gold mirror.

Figure 2 shows typical p-polarization spectra of galvanized sheet metal having ink, silicone, and corn oil stains with the as-cleaned metal. The carbon dioxide pellet blasting cleaned these specimens to an effective hydrocarbon film of 3 to 5 mg m^{-2}, with the exception of two specimens that had a silicone-based, high-temperature lubricant that indicated 8 and 18 mg m^{-2} as silicone. On the peripheral region of these specimens, where the carbon dioxide blaster did not clean, silicone levels as high 118 mg m^{-2} were detected. The hammered surfaces were not as reflective as the original metal and resulted in a decrease in the signal to noise that translated into a lower level of detection of 1 mg m^{-2}.

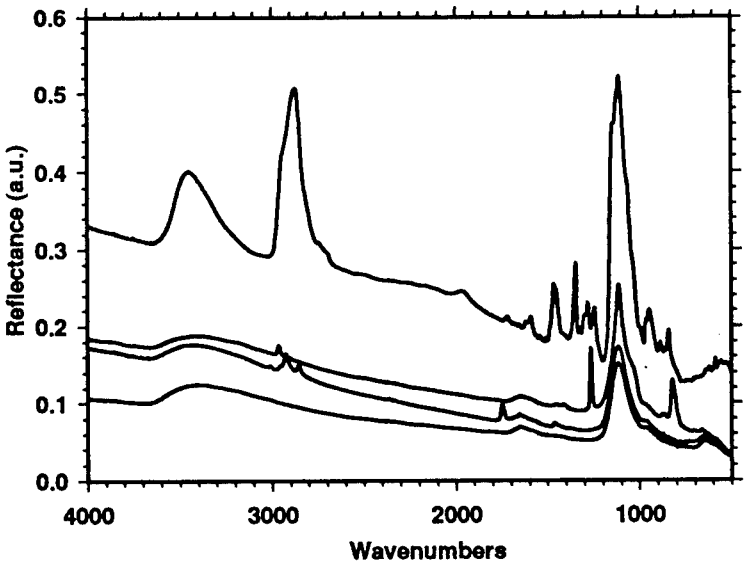


Figure 2. Typical p-polarized 75° specular reflectance spectra for contamination on galvanized steel sheet referenced a cleaned gold mirror. Bottom-to-top: cleaned, corn oil stain, silicone grease, orange felt-tip pen mark.

Another study involved the analysis of a 25-mm-diam by 1.45-m-long aluminum tube that was suspected of being contaminated with some unknown film. The axis of the rod was aligned with the direction of the infrared beam, and the resulting spectra identified the contaminant

as a silicone oil. The rod was then repositioned such that many spectra were taken along the surface of the rod to map the contamination along the rod. Figure 3 compares a spectrum from the rod to spectra of Dow-Corning silicone vacuum grease (high-viscosity), DC-200 silicone temperature bath fluid (low-viscosity), and fused silica (solid, spectra determined by internal reflectance). Figure 3 demonstrates the simple relationship between chemical functional groups and the infrared absorption spectra. The infrared spectra of the silicone oils are very similar to fused silica (O-Si-O polymer) with additional bands corresponding to CH_3 (2965 cm^{-1}) and to Si-C bonds (1265 cm^{-1}). Subtle differences around the 800 cm^{-1} distinguish the grease from the light oil. Based on 19 measurements along the rod, the absorbance from the 2965 cm^{-1} band was 0.0182 a.u. (49 mg m^{-2}, σ=0.0048 a.u.) and the 1265 cm^{-1} band was 0.0499 a.u. (77 mg m^{-2}, σ=0.0184 a.u.) with no values observed to be less than 29 mg m^{-2}. Ratios of the methyl band (2965 cm^{-1}) to the Si-C band (1265 cm^{-1}) indicates that the silicone is not DC-200 (5 cps) and this is supported by the lack of structure near 850 cm^{-1}. Thus, the conclusion that the silicone is similar to Dow Corning high vacuum grease. Others studies have been carried out on aluminum and aluminum alloys with good results. For these systems, the reflectance spectra indicate not only the presence of contaminants, but also bands from surface oxides and other reflective losses, perhaps from surface texture, that seem to be strongly dependent on the cleaning agent.

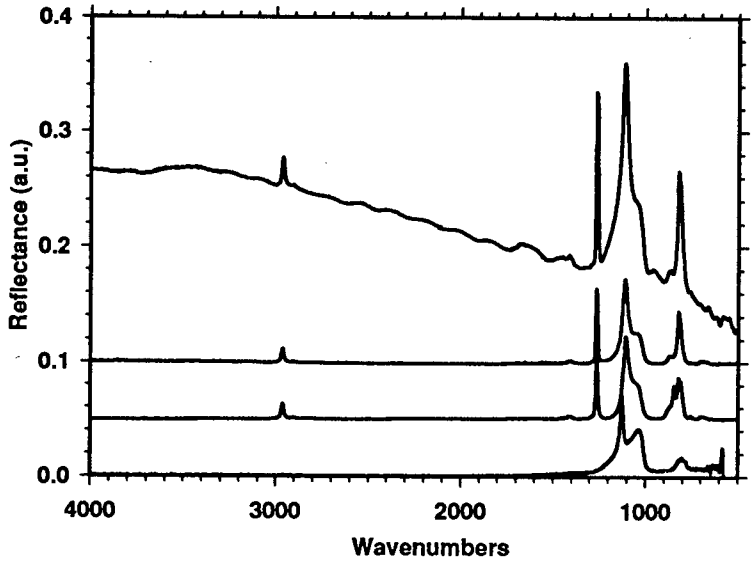


Figure 3. A comparison of external reflectance spectra from an aluminum rod with silicone greases on gold mirrors. Bottom-to-top: fused silica (by internal reflectance), DC-200 (5 cs), vacuum grease, aluminum tube.

DIFFUSE REFLECTANCE

In the strictest sense, diffuse reflectance refers to light which is simultaneously absorbed and scattered in a generally transparent medium. Paper is an example of a diffuse scatterer. The absorbance relationship used for external reflectance of thin films discussed above is simply first-order absorption of light in a film as a function of concentration and thickness of the film leading to a logarithmic relationship between light lost and concentration/film thickness. For a true diffuse reflector, differential equations for first order light scattering and first order adsorption are solved simultaneously to yield the Kubelka-Munk relationship. The optics required for diffuse reflectance is such that only light diffusely scattered is directed to the detector and specularly reflected light is rejected from the detector, a process that is optimized by the barrel ellipse. For the analysis of textured metal surfaces, for which sandblasted metal surfaces and graphite cloth are two common examples, diffuse reflectance optics are used to collect light that is specularly reflected in random directions. For the examples to follow, the light scattering process will be specular reflectance from randomly oriented micromirrors for which diffuse reflectance optics works very well. This approach has a significant loss of sensitivity relative to grazing angle external reflectance because the effective light path, determined by the angle of incidence and of reflection, through the film is shorter by a factor of 3 or 4, and because p- and s-polarizations cannot be separated. The s-polarized light contributes to the total light intensity, but not to reflective losses, lowering the sensitivity by a factor of 2. For cleanliness, more sensitivity is always desirable, however,

the 10,000:1 or greater signal-to-noise is retained and losses in the high sensitivity, low detection limit are converted to good performance for thick films. For example the resin (tens of microns thick) on the outer surface of most graphite-resin composites (graphite cloth) is ideally suited for cure and heat damage inspection using diffuse reflectance optics. The barrel ellipse remote sensor is an imminently practical way to passively look down on a host of surfaces, without demanding too much knowledge of either the surface or the light scattering processes, to reveal a rich world of chemistry. As with most aspects of analytical chemistry, there remains the task of providing standards of known composition with which to calibrate the method.

Marshal Space Flight Center provided several 6 by 6-in. plates of sandblasted 7075 aluminum alloy and D6AC steel specimens that had been sprayed with grease contaminants (Conoco HD-2 grease, Kaydol oil, and CRC silicone grease) dissolved in a volatile solvent. Aluminum foil masks were used to form 1-in. wide concentration steps on these plates and the masks were subsequently weighed to determine the quantity of grease deposited. Contamination levels varied from a clean first step to levels as high as ~35 mg ft^{-2}. These plates were analyzed using a barrel ellipse mapping station supported by a BIO-RAD FTS-60 FTIR spectrometer by obtaining spectra at 0.1-in. intervals along a line normal to the steps near the center of the plate. Spectra were taken using sandblasted gold as a reference, and once verified to be as clean as the gold the reference was changed to the clean step on the plate. Each spectrum consisted of 256 coadded scans at 16 cm^{-1} resolution and 4 times zero-filling.

The results for the 7075 aluminum alloy in terms of the most sensitive peak heights for these contaminates are shown in Figure 4. The HD-2 grease was present on the plate as steps, but the lighter Kaydol oil at all but the lowest concentrations migrated to erase the steps. For Kaydol, the 5 to 6 in. step was not the maximum contamination level because this oil migrated off the edge of the plate. The higher

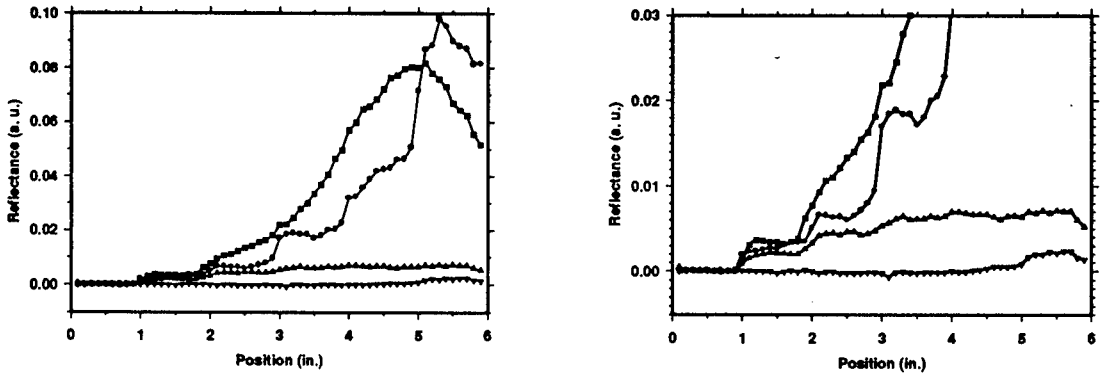


Figure 4. Absorbance measurements on 7075 aluminum alloy based on the 2925 cm^{-1} band for HD-2 and Kaydol and 1265 cm^{-1} for the silicone. Squares - Kaydol, Circles - HD-2, Up-triangles - silicone, Down triangles - 3010 cm^{-1} baseline.

dose silicone levels appear to be in distinguishable. The D6AC steel plates responded similarly, but with less sensitivity. Figure 5 gives the average step level and standard deviations for the data for both types of plates using the log-linear format because the sensitivity appears to decrease superlinearly with decreasing dose. Spectral manipulation techniques in FTIR spectroscopy are very powerful tools that allow one to average all the spectra taken in a region to improve the signal-to-noise and thus the sensitivity for detecting surface contamination. Figure 6 shows the average of spectrum for each step for the 7075 aluminum alloy plate and similar data for silicone on D6AC steel, the plate with the lowest detectability limits on the basis of both dose and substrate. For the six plates, the only step on which the presence of the contaminant could not be detected and distinguished from the other two contaminants was the lowest step (1.5 mg ft^{-2} CRC silicone) on the D6AC steel plate. The spectra of HD-2 grease and the Kaydol are very similar, i.e., both are aliphatic hydrocarbons with the dominant C-H stretching band at 2925 cm^{-1} and bending modes near 1400 cm^{-1}, with the exception that HD-2 grease contains a carbonate additive to

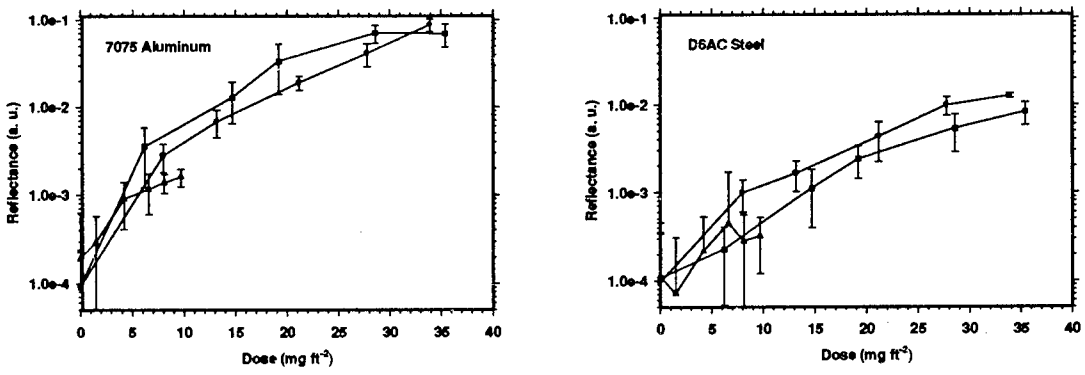


Figure 5. Average absorbance measurements as a function of dose on 7075 aluminum alloy (left) and D6AC steel (right) based on the 2925 cm^{-1} band for HD-2 and Kaydol and 1265 cm^{-1} band for the silicone. Squares - Kaydol, Circles - HD-2, Up-triangles - silicone.

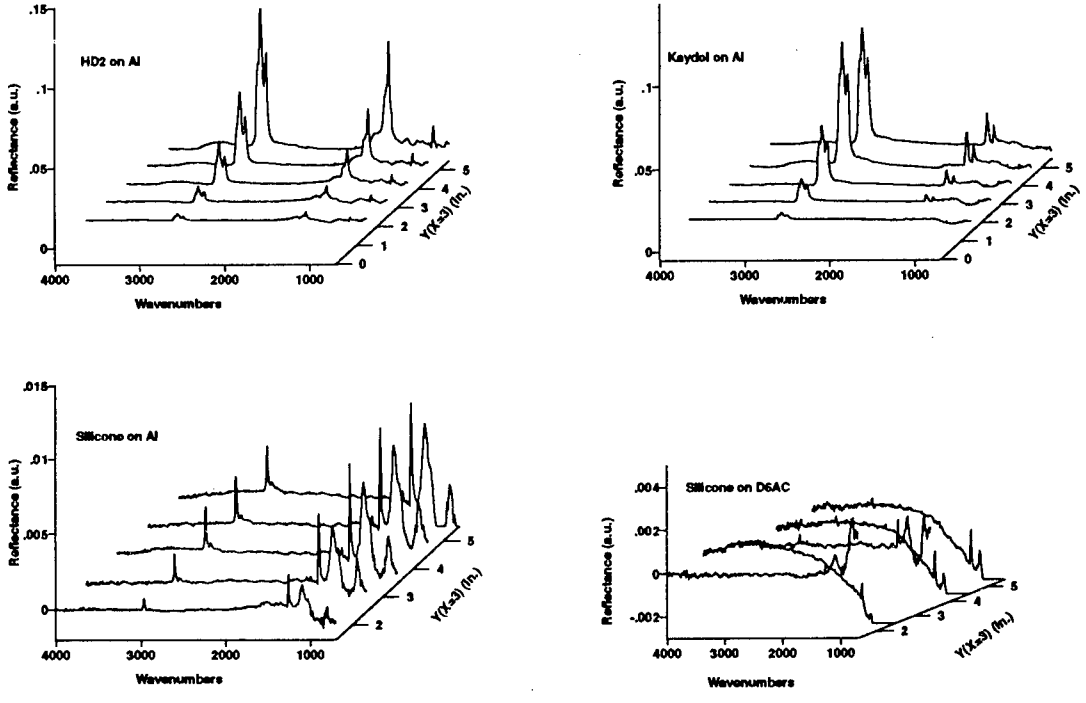


Figure 6. Reflectance spectra from 7075 aluminum alloy and D6AC steel. Each spectrum is located at its average step position and each spectrum is the average ten spectra taken on that step.

control pH that obscures the C-H bending modes and makes for a clear distinction between the two contaminants. The silicone spectra were described in the previous section of this paper.

The behavior of various common contaminants on sandblasted aluminum plates (3-in. by 3-in. by 0.04-in.) have been further explored using a mechanically rastered air brush to apply the contaminant as a dilute solution in acetone through a mask that allows a 0.3-in. diam. spot to be contaminated to relatively high levels of ~1 g ft^{-2}. The dose was controlled by the composition and quantity of the acetone solution being sprayed. Mapping techniques were then applied to measure a contamination profile across the specimen. These profiles were repeated at time intervals to monitor the spread of the oil across the plate. Once the spread of the oil had stabilized, the spot could be mapped in

two dimensions. One major difficulty was moisture sorption on the plate that produced a weight gain comparable to the applied oil. Another difficulty was that many oils spread very fast. The early time profiles were measured using the Harrick/MIDAC Inspector located near the hood where the spraying was carried out because of its superior data collection speed. Once the stain stabilized, the operation was transferred to the barrel ellipse mapping station supported by a BIO-RAD FTS-60 FTIR spectrometer because of better sensitivity near 3000 cm^{-1}. Figure 7 shows the short term response of the 2925 cm^{-1} band for the mineral oil as it spread over the aluminum plate and diminished in intensity. Weight gain measurements indicated that a maximum of 1.5 mg of oil had been deposited on the plate. As shown in Figure 8, this spread continued at a diminishing rate for several weeks forming a stain with an abrupt

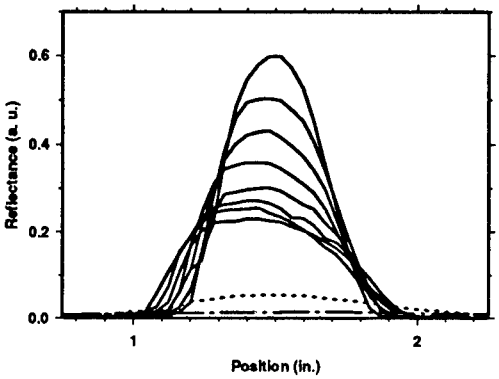


Figure 7. The short term spread of light mineral oil over sandblasted aluminum alloy based on the reflectance response of the 2925 cm^{-1} band. Solid curves taken at 0.04-in. steps at 30-min. intervals starting 10-min. after spraying. Dotted curve - 24 hr. after spraying. Dot - dash curve - 8 d. after spraying.

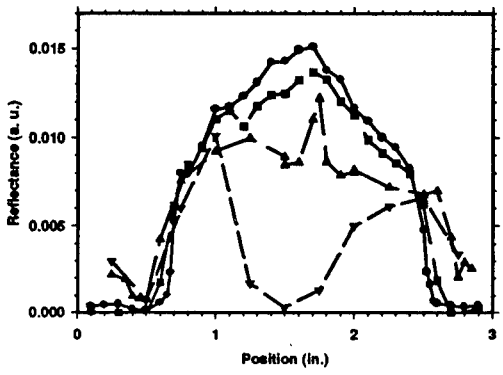
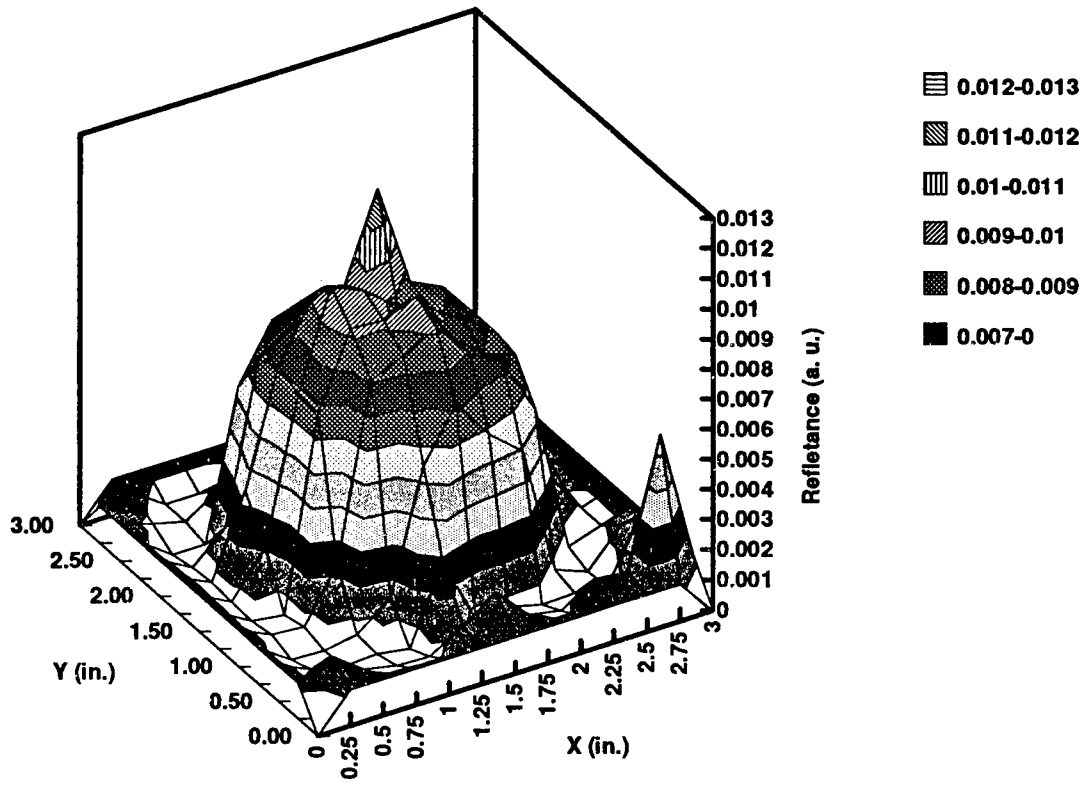


Figure 8. The long term spread of light mineral oil over sandblasted aluminum alloy based on the reflectance response of the 2925 cm^{-1} band. Circles - 8 d. after spraying, Squares - 15 d. after spraying, up-triangles - 6 wk. after spraying, down triangle - 7 wk. after spraying and spot extraction of the oil with freon.

edge. After 6 weeks, the stain was mapped in both dimensions of the surface and the resulting definition of the stain is given in Figure 9. In a further effort to quantify the amount of stain on the aluminum plate, an extraction method was devised to remove the oil from a well defined area of the plate. A mini-conflat straight union, consisting of a 3-in. long by 0.75-in. diam. tube, was closed at one end with a blank flange and copper gasket. The opposite end was clamped to the oil stained plate with a viton O-ring sealing the assembly that was filled with freon. The system was shaken and the freon was recovered. The plate was remapped yielding the lower curve in Figure 8 and the entire process was repeated. The freon from the second extraction was analyzed by transmission infrared absorption spectroscopy against a calibration curve developed from the original mineral oil and indicated that 50 μg of oil had been extracted. This corresponded to a net change of 0.00226 a.u. in^2 or a calibration factor of 22 mg $a.u.^{-1}$ in^{-2}. The stain described in Figure 9 has a total volume of 0.0245 a.u. in^2 that indicates a mineral oil content of 0.54 mg spread over 0.02 $ft.^2$ indicating a contamination level in the stained region of 26 mg ft^{-2} giving this aluminum plate sample a calibration factor similar to that observed for the D6AC steel. This is approximately one-third of the weight gain during the original spraying operation that may have overestimated the oil quantity by as much as a factor of two due to moisture absorption. There is also the possibility that some of the oil may have evaporated. Spray experiments with docosene-1 ($CH_3(CH_2)_{18}CH_3$) indicates that this hydrocarbon does not spread from where it is deposited, octadecene-1 ($CH_3(CH_2)_{16}CH_3$) spreads in a manner similar to the light mineral oil used for this study, and hexadecene-1 ($CH_3(CH_2)_{14}CH_3$) evaporates. The large decrease in the reflectance values during the spreading of the oil is generally consistent with the increase in area of the stain, i.e., and increase by approximately a factor of 40.



DISCUSSION

Reflectance mid-infrared Fourier transform spectroscopy is a very powerful tool for determining the surface cleanliness of metals, particularly when remote sensing hardware is used so that there is minimum perturbation of the materials being analyzed and large numbers of analyses can be made. The large sample capability is critical both for mapping capability and for the passive nature of the analysis. Obtaining a cleanliness determination from metal parts is demanding, but not as demanding having the parts unaffected by the experience. External reflection at grazing incidence with p-polarized light on smooth metal surfaces yields the best detection limits. Diffuse reflectance optics offers an extremely practical approach to a host of real surfaces that are neither smooth or well understood. Computerized data processing of FTIR spectroscopic data has been around for a quarter century. Much progress has been made in the last two years in developing software to match the great and growing potential of microcomputers, particularly in the areas of speed and decreasing size and cost. A practical portable FTIR surface analyzer has been fielded. Smaller, more rugged, and more sensitive instruments operating at near real time speeds will soon be available. The potential for imparting intelligence to these inspection machines is tremendous.

The surfaces to be analyzed, however, are infinitely variable and diverse with complex processes related to the fundamental manner with which particular contaminants interact with particular surfaces in relation to how light interacts with a particular surface and a particular contaminant. Apparent nonlinear calibration curves, and migration and fractionation of the contaminant over time are possible explanations

for some of the above observations. Experimental technique is very demanding for the preparation of calibration standards, reference materials, and corroboration of calibration standards. But these techniques are no more demanding than the handling of very clean materials before, during, and after the analysis. Though these machines may be trained to recognize contaminants, mixtures of contaminants, and give forth a quantitative number, at the 10 mg ft^{-2} contamination level the distinction between the spectra of an aliphatic hydrocarbon, a triglyceride, and a silicone is as plain as the nose on your face.

ACKNOWLEDGMENTS

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REFERENCES

1. Griffiths, P. R., and DeHaseth, J. A., Chemical Infrared Fourier Transform Spectroscopy, (Wiley, New York, 1986)

2. Powell, G. L., Milosevic, M., Lucania, J., and Harrick, N. J., "The Spectropus System, Remote Sampling Accessories for Reflectance, Emission, and Transmission Analysis using Fourier Transform Infrared Spectroscopy," *Appl. Spectrosc. 46*, 111 - 125 (1992).

3. Powell, G. L., Smyrl, N. R., Janke, C. J., Wachter, E. A., Fisher, W. G., Lucania, J., Milosevic, M., and Auth, G., "Nondestructive Inspection of Graphite-Epoxie Laminates for Heat Damage using DRIFT and LPF Spectroscopies," in *The Proceedings of the Conference on Characterization and NDE of Heat Damage in Graphite Epoxy Composites, NTIAC*, Austin, Texas, 97 - 111 (1993).

Cleanliness Evaluation of Rough Surfaces with Diffuse IR Reflectance

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Abstract

Contamination on bonding surfaces has been determined to be a primary cause for degraded bond strength in certain solid rocket motor bondlines. Hydrocarbon and silicone based organic contaminants that are airborne or directly introduced to a surface are a significant source of contamination. Diffuse infrared (IR) reflectance has historically been used as an effective technique for detection of organic contaminants, however, common laboratory methods involving the use of a Fourier transform IR spectrometer (FTIR) are impractical for inspecting the large bonding surface areas found on solid rocket motors. Optical methods involving the use of acousto-optic tunable filters and fixed bandpass optical filters are recommended for increased data acquisition speed. Testing and signal analysis methods are presented which provide for simultaneous measurement of contamination concentration and roughness level on rough metal surfaces contaminated with hydrocarbons.

Introduction

IR reflection spectroscopy is an analytical methodology that has been applied previously to the problem of surface and thin film characterization (1-3). More specifically, diffuse reflectance IR spectroscopy has been evaluated for detection of organic contaminants on bonding surfaces (4-6) and has been found to be effective for detection of contaminants with sufficiently strong IR absorption bands. The use of IR spectroscopy allows both the detection and identification of contaminant types since each has a characteristic absorption spectrum (fingerprint). However, the use of laboratory analytical FTIR instrumentation is not practical for on-line inspection or mapping of large bonding surface areas such as those found on solid rocket motor components the size of the Shuttle and large strategic defense motors. In addition to the rapid data acquisition requirements imposed by their large size, surfaces on solid rocket motors tend to be rough, such as grit blasted metal surfaces, or machined surfaces of fiber filled polymeric materials. Roughness has a tendency to lower signal to noise ratios and thus may impose additional constraints on optical design.

Contaminants most commonly found on solid rocket motor bonding surfaces are either hydrocarbon or silicone based and are introduced by direct contact with tooling or personnel, or environmentally introduced via airborne particulates that are deposited on the surface. When these contaminants are found on rough metal surfaces, diffuse IR reflectance methods must be able to find the contaminant in the presence of roughness and further, must be able to distinguish contaminant concentration variations from roughness variations. Optical methods and data acquisition and reduction methods for providing speed and reliable detection of hydrocarbon contamination on rough (grit blasted) metal surfaces are specifically addressed in this paper.

Methodology

Hydrocarbons can be readily detected on a surface by looking for the presence of their characteristic carbon-hydrogen (C-H) stretch band at about 3.4 micrometers (μm). Previous work (4) has indicated that backscattered IR methods provide greater sensitivity to small concentrations of contaminants on rough metal surfaces than do specular methods. Backscatter optics must be coupled with a means for rapid detection of scattered light intensity over a continuous band of wavelengths or at several discrete narrow wavelength bands that include the 3.4 μm absorption band and at least two reference wavelength bands (side-bands). This is accomplished by using an acousto-optic tunable filter (AOTF) for continuous or discrete wavelength band detection, or by using fixed band-pass filters for discrete wavelength band detection. Figures 1 and 2 show schematic diagrams for these two optical methods. Both the AOTF and the discrete optical filter methods shown in the figures provide sufficiently rapid data acquisition capability so that an instrument based on either method can collect data on-the-fly when scanned over a surface at speeds up to a few inches per second. Hence, measurement rates on the order of 10's to 100's of complete spectral measurements (described below) per second are achievable. The AOTF optical method is described in detail in reference (4) and will not be further described in this paper. The discrete optical filter method, shown in Figure 2, splits the scattered beam into three beams by using spectral beam splitters and band-pass filters. Each beam has its own detector, hence, parallel data collection is made possible for each wavelength band, significantly increasing data collection speed. A more complete description of this optical setup is found in reference (7). All data presented in this paper was obtained with the discrete optical filter design implemented in a packaged instrument cooperatively developed by TMA Technologies and Thiokol Corporation and given the trade name of SurfMap-II™.

The objective of the optics is to rapidly obtain measurements from which the peak height of the C-H stretch absorption band is determined. The required measurements are the absorbance at two side-band wavelengths, with one on each side of the band peak, and the absorbance at the wavelength of the band peak. Figure 3 shows the spectrum of the C-H stretch absorption band for a typical hydrocarbon contaminant with the wavelength bands of the three measurements indicated. In order to determine the peak absorbance, a line is fit to the two side-band measurements to approximate the baseline of the spectrum. The interpolated value of the baseline at the wavelength of the peak is subtracted from the measured peak absorbance. The resultant value, ΔA, is indicated in Figure 3 and has been found to be directly related to contamination concentration (4-6). The process is mathematically described below.

The linear approximation of the absorption spectrum baseline is calculated from

1) $$A_b(\lambda) = a + b\,\lambda$$

where a and b are constants determined from the side-band measurements, 1 and 2, shown in Figure 3, and λ is the wavelength. Constants a and b are given by

2) $$b = (A_2 - A_1) / (3.7\text{-}3.2) = (A_2 - A_1) / 0.5$$

3) $$a = A_1 - b\,(3.2)$$

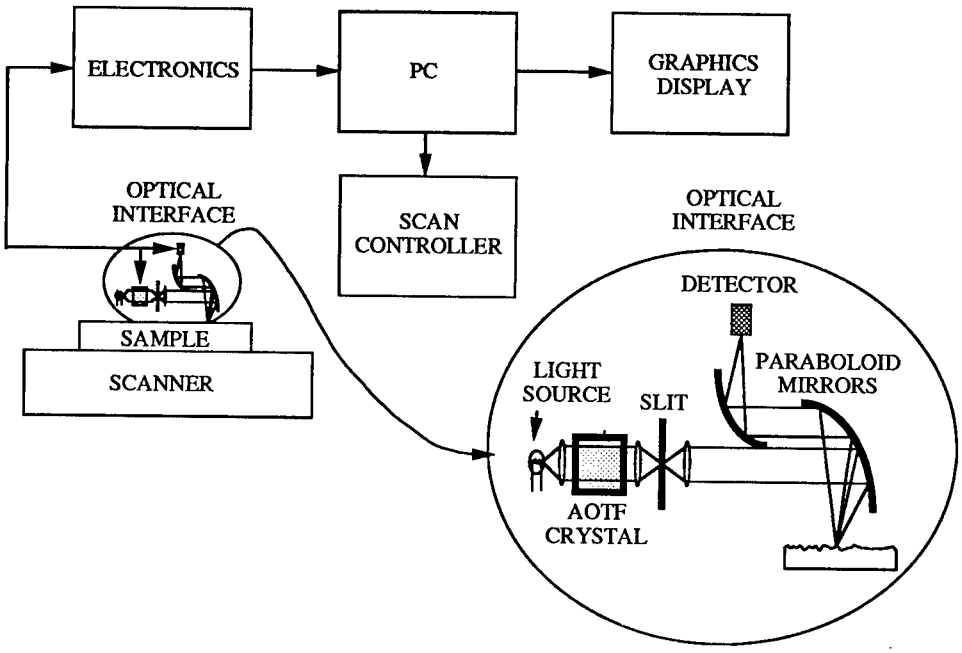

Figure 1. Schematic diagram for AOTF based optical setup.

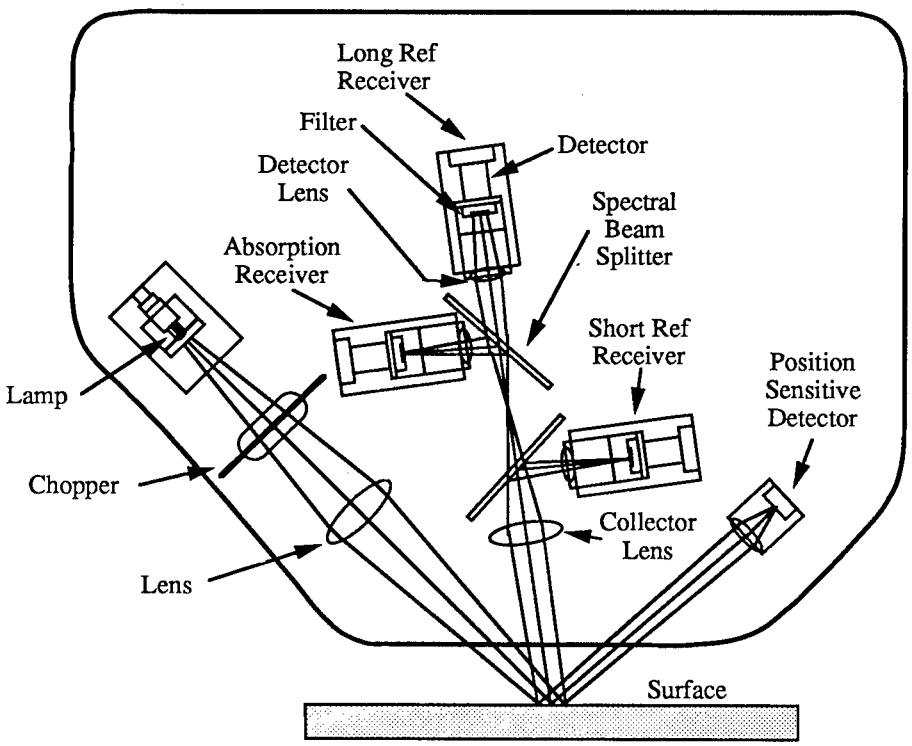

Figure 2. Schematic diagram for discrete band-pass filter based optical setup.

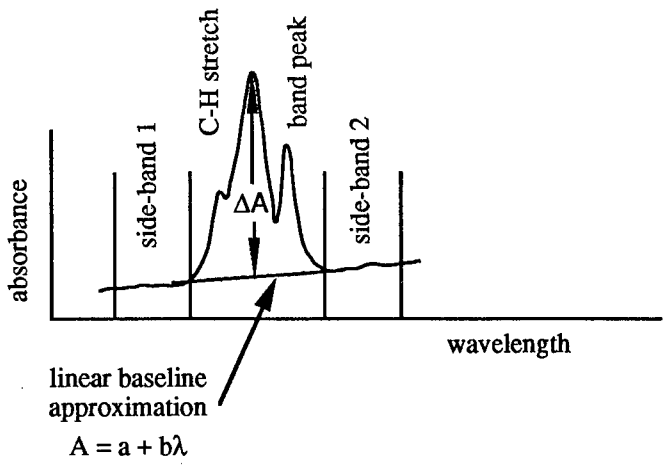

Figure 3. Typical C-H stretch absorption band with filter band locations indicated.

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where A_1 and A_2 are the measured absorbances for the two side-band wavelengths. For the C-H stretch absorption band, side-band 1 wavelength is assumed to be 3.2 μm, side-band 2 wavelength is assumed to be 3.7 μm, and the peak wavelength is assumed to be 3.4 μm for the specific optical filters used in the SurfMap-II™. Using equation 1, ΔA is calculated from

4) $$\Delta A = A_p - A_b(\lambda=3.4)$$

where A_p is the measured absorbance at the C-H stretch band peak.

The absorbance measurements A_p, A_1, and A_2 are determined from the backscattered IR light power measured from the surface and from corresponding measurements taken from a clean reference plate with a known average root mean square roughness (RA). That is,

5) $$A_1 = - \log_{10}(P_{1s}/P_{1ref})$$

6) $$A_2 = - \log_{10}(P_{2s}/P_{2ref})$$

7) $$A_p = - \log_{10}(P_{ps}/P_{pref})$$

The quantities P_{1s}, P_{2s}, and P_{ps} are the measured backscattered power levels from the sample surface at the respective wavelengths, 3.2, 3.7, and 3.4 μm. Likewise, P_{1ref}, P_{2ref}, and P_{pref} are the corresponding power measurements for the clean reference plate.

Subtracting the baseline from the peak absorbance measurement is important as it has been determined experimentally that this procedure significantly reduces the effect of roughness variations on the measurement as will be further discussed in the next section. The SurfMap-II™ performs the calculations listed above and outputs a, b, and ΔA in the form of a computer image file which is constructed while raster scanning the instrument over a surface.

Since The effect of roughness on absorbance measurements is reduced by applying

equation 4, it is plausible that one or both of the constants a and b in equation 1 relate to roughness. In the following section, it is shown that the baseline slope, b, can be correlated with RA.

Results

A series of grit blasted steel (D6AC) plates with clean surfaces and known RA roughness were mapped with the SurfMap-II™. The average ΔA, a, and b were determined from scan data for each plate. Reference measurements were taken from a clean plate with known RA. These tests were repeated several times using reference plates with different RA values. The average ΔA, a, and b values were plotted with respect to average RA for each plate and it was found that b was proportional to the difference between the RA of the sample and the RA of the reference plate. That is,

8) $$RA - RA_{ref} = S_b\, b$$

where S_b is a proportionality constant determined by linear regression.

The samples were then prepared with known concentrations (approximately 5, 10, and 15 mg/ft^2) of a hydrocarbon grease (CONOCO HD-2). Measurements of average ΔA, a, and b were repeated and it was further found that b was insensitive to the presence of contamination at these low concentrations. Hence, b provides an independent measurement of surface RA if RA_{ref} is known and S_b has been determined. Figure 4 shows a plot of RA-RA_{ref} verses b for all measurements from both clean and contaminated samples.

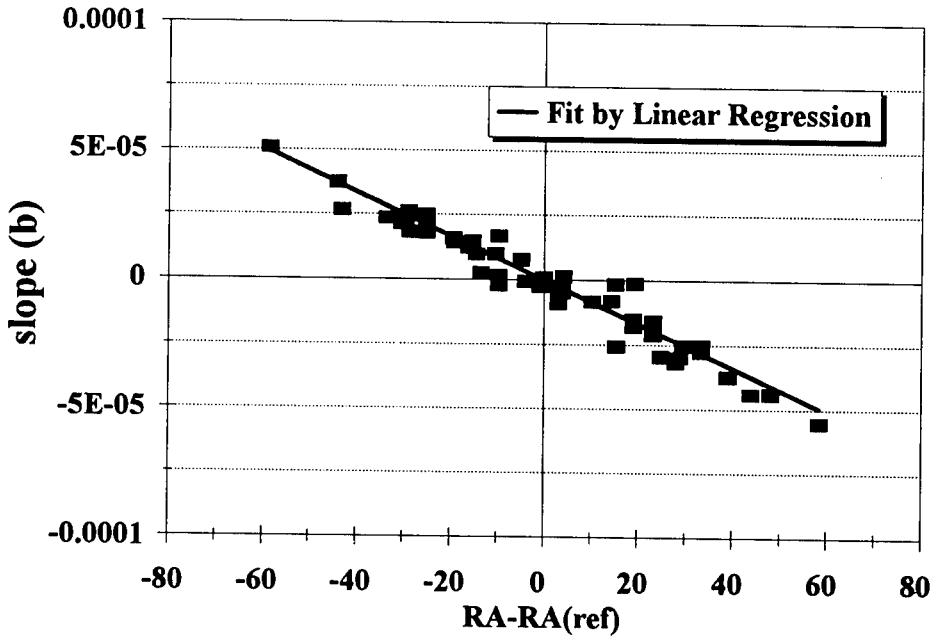

Figure 4. Dependence of approximated spectrum baseline slope, b, on RA.

When correlating ΔA with RA and with contamination concentrations it was found that ΔA is strongly dependent upon contamination concentration as expected since ΔA is a measure of the C-H band peak height, but it is also weakly dependent on roughness, that is, upon $RA-RA_{ref}$. The dependence on $RA-RA_{ref}$ was found to be linear, but the slope of the line was empirically determined to be quadratically related to contamination concentration (see Figure 5) and the intercept was found to be proportional to contamination concentration (see Figure 6). That is,

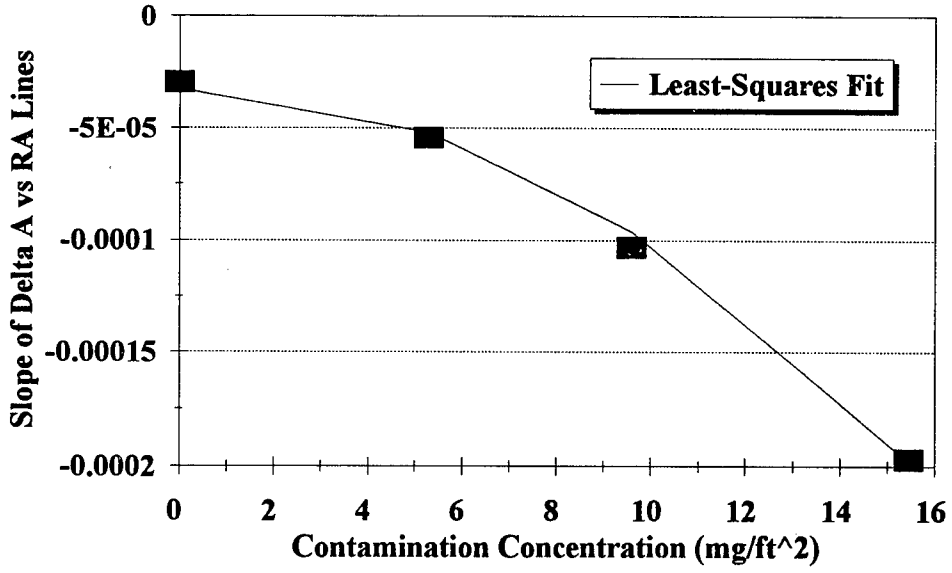

Figure 5. Dependence of slope ($S_{\Delta A}$) of ΔA verses RA curves on contamination concentration.

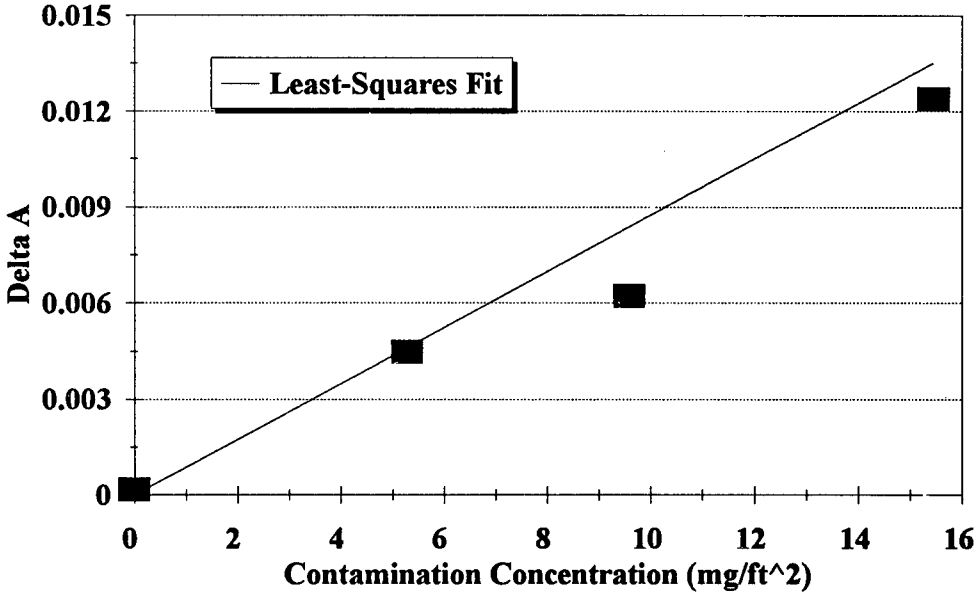

Figure 6. Dependence of ΔA on contamination concentration.

9) $\Delta A = \Delta A_{ref} + S_{\Delta A} (RA - RA_{ref})$

where

10) $\Delta A_{ref} = S_c h$

11) $S_{\Delta A} = y_s + S_s h^2$

Substituting equations 10 and 11 into equation 9 gives

12) $\Delta A = S_c h + [y_s + S_s h^2] S_b b$

The known hydrocarbon contamination concentration is h, and S_c, y_s, and S_s are constants determined by a least-squares fit of measured ΔA, b, and known h to equation 12.

When $RA = RA_{ref}$, it is found that $b = 0$ and equation 12 becomes

13) $\Delta A = S_c h$

It is observed that the second term in equation 12 is the correction for RA when RA_{ref} is different than RA for the sample (when $b \neq 0$). When the constants, S_c, y_s, S_s, and S_b have been determined, it is possible to estimate the roughness corrected contamination concentration from

14) $$h = \frac{-S_c + [S_c^2 - 2 S_s S_b b (y_s S_b b - \Delta A)]^{1/2}}{2 S_s S_b b}$$

which is obtained by solving equation 12 for h. If roughness is ignored, then contamination concentration is estimated from equation 10 by solving for h to give

15) $h = \Delta A / S_c$

Figure 7 shows the correlation of estimated h with known h when using equation 15 and Figure 8 shows the correlation using equation 14. Note that when correcting for RA (using equation 14), the data spread is reduced measurably so that at low contamination concentrations (h near zero), the accuracy is improved by about a factor of 2 from about $\pm$ 2 mg/ft^2 to about $\pm$1 mg/ft^2.

Conclusions

Optical methods have been recommended for providing rapid acquisition of absorbance data needed for detecting hydrocarbon contaminants on rough metal bonding surfaces. Signal processing methods have been developed for allowing simultaneous determination of contamination concentration and RA roughness. These optical and signal analysis tools provide a practical system for on-line inspection of large area bonding surfaces such as is found on solid rocket motors.

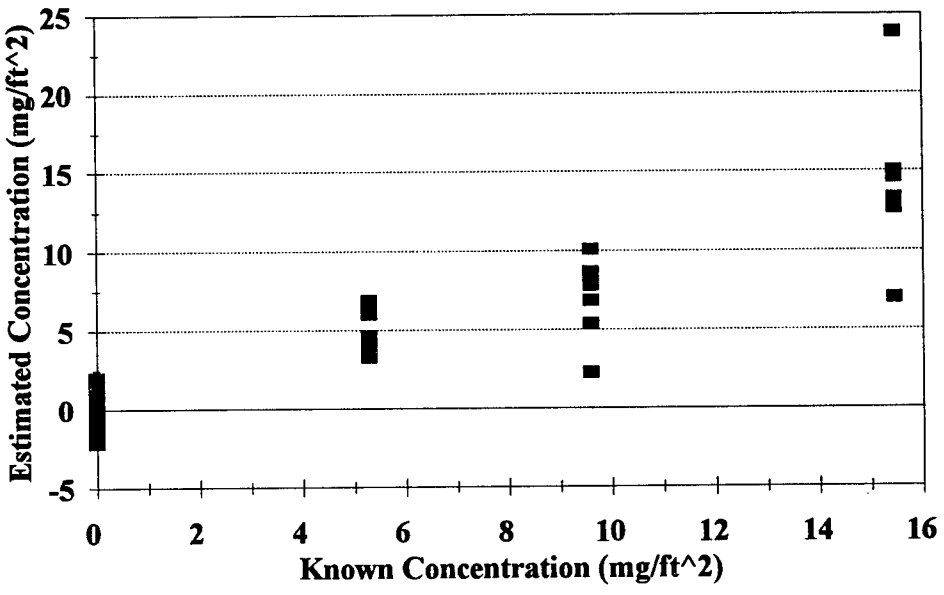

Figure 7. Contamination concentration estimate from ΔA measurement compared with known concentration without correction for RA (equation 15).

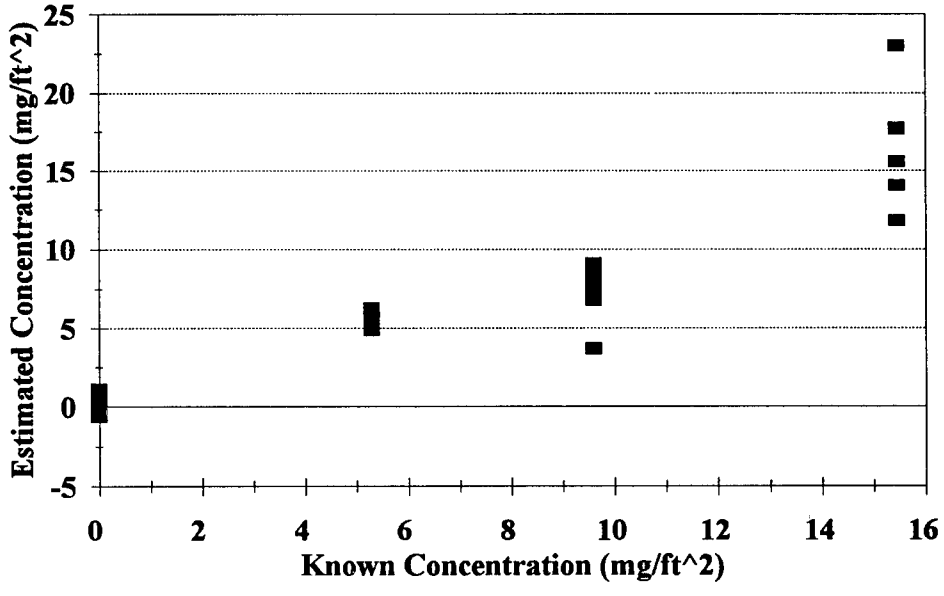

Figure 8. Contamination concentration estimate from ΔA measurements compared with known concentration using RA corrected equation 14.

References

1. Hansen, W. N., "Reflection Spectroscopy of Adsorbed Layers," Symposium of the Faraday Society, 1970, No. 4, pp. 27-35.

2. Hansen, W. N., "Reflection Spectroscopy of Optical Coatings," J. Opt. Soc. Am., Vol. 69, No. 2, 1979, pp. 264-272.

3. Hansen, W. N., Pearson, L. H., and Hansen, G., "Characterization of Small Absorptions in Optical Coatings," Laser Induced Damage in Optical Materials, NBS Spec. Publ. 568, 1979, pp. 247-251.

4. 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, pp. 1619-1623.

5. 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, pp. 581-588.

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, pp. 2017-2024.

7. Swimley, B. D., Knighton, M. W., Khurdal, V. C., Pearson, L. H., Stover, J. C., "Design review of an Instrument to Map Low-Level Hydrocarbon Contamination," Proc. SPIE, 1995-10, July 1993, pp 92-100.

CLEANING VERIFICATION BY AIR/WATER IMPINGEMENT

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ABSTRACT

This paper will discuss how the Kennedy Space Center intends to perform precision cleaning verification by Air/Water Impingement in lieu of chlorofluorocarbon-113 gravimetric nonvolatile residue analysis (NVR). Test results will be given that demonstrate the effectiveness of the Air/Water system. A brief discussion of the Total Carbon method via the use of a high temperature combustion analyzer will also be given. The necessary equipment for impingement will be shown along with other possible applications of this technology.

INTRODUCTION

Recent links between chlorofluorocarbon 113 (CFC-113) and upper atmospheric ozone depletion have caused the John F. Kennedy Space Center (KSC) to plan the phase out of all CFC's by 1995. CFC-113 is currently in use at the Kennedy Space Center as a precision cleaning and verification solvent. A CFC-113 rinse is routinely used to verify that small fittings, valves and regulators, large valves, pipes, flex hoses, and tubing meet non-volatile residue (NVR) requirement of less than 11.1 milligram (mg) per square meter (m^2) (1 mg/ft^2) of surface area.

Small parts NVR verification has successfully been met by the use of deionized water and ultrasonic baths (Allen, pp 37-48). Currently, CFC-113 is being phased out and water/ultrasonics is being phased in for small parts only. However, a technique for the verification of large components needed to be identified. Based on the success of small parts with water, and for environmental reasons, it was desirable to attempt large component verification with water.

Presently, KSC processes close to 250,000 piece parts through the component cleaning facility per year. Only 1000 of these parts fall under the heading of large components. These are components too large for the cleaning and verification processes conducted in the cleanroom. Consequently, these parts are cleaned and verified in an area known as Field Cleaning. Current CFC-113 cleaning and verification techniques accounted for the purchase of about 60,000 pounds of solvent during the 1993 calendar year. While 1000 is not a large number of components, the quantity of CFC-113 used for verification is quite large due to their size and configuration.

Items found under the heading of large components are fluid system components: valves, regulators, and relief valves. KSC has a large number of oxidizer systems. These systems, both cryogenic and hypergolic, require a cleanliness level of 11.1 mg/m^2 (1 mg/ft^2) to eliminate any possible fuel to support combustion in a highly oxidizing environment. The variety of large components entering Field Cleaning eliminates the possibility of an automated system due to a lack of similarity among parts. A manual system of cleaning verification by a properly trained technician is required. The system needs to be as insensitive to the variation in the technician-related procedure as possible.

Large components are routinely received in the Field Cleaning Facility that may be contaminated with several families of substances. These families can be summarized as hydrocarbons, silicones, fluorosilicones, and fluorocarbons. Therefore, any test to evaluate a new cleaning and/or verification method must address these contaminants.

IMPINGEMENT VERIFICATION SYSTEM

KSC's answer to this problem is cleaning verification by air/water impingement. Over the last several years development has been progressing on this new verification technique (Dearing, pp 66-77; Melton, pp 642-650; Melton, pp 97-107). The evolution of the design and development process has produced the air/water system shown in Figure 1. The system consists of a regulated gas supply, a pressurized water tank, a water metering and injection device, a flex hose, a nozzle assembly, a catchpan, and associated valves, fittings, and hardware.

The gas supply pressure is used to pressurize the water tank via the water injector. The water injector utilizes two orifices to control the gas and water flowrate. The first orifice provides a pressure differential between the gas stream upstream and downstream of the orifice. This, in turn, pressurizes the water tank. The pressurized deionized water is then injected through a liquid metering orifice just downstream of the gas metering orifice at the point of lowest pressure. The flex hose allows the nozzle to be manipulated freely for work on various components or surfaces. The nozzle assembly consists of one or more supersonic, converging-diverging nozzles.

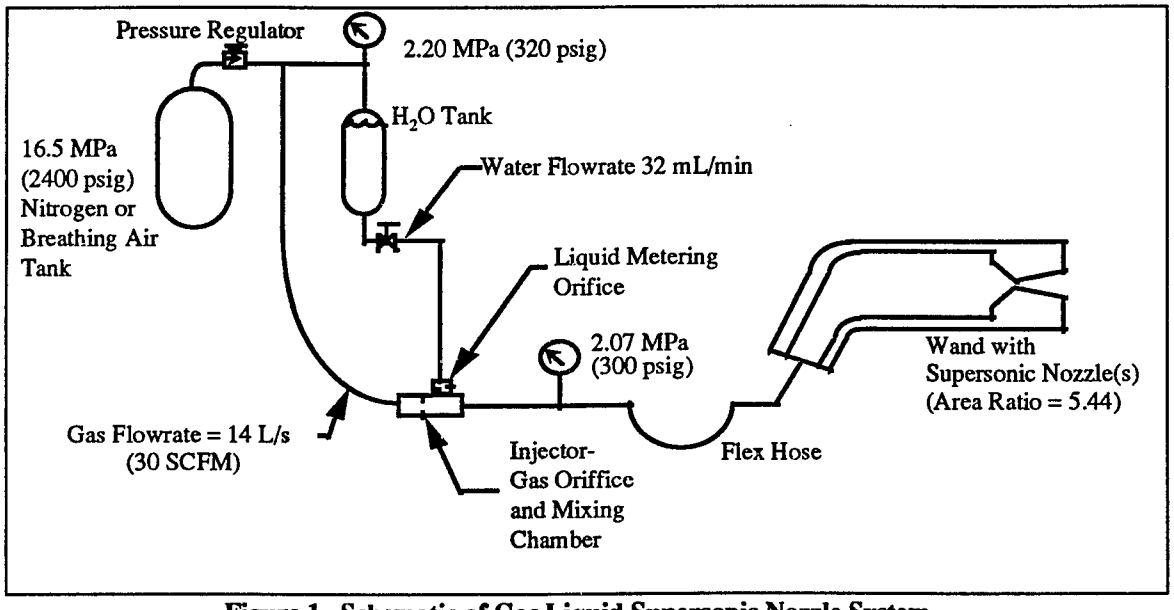

Figure 1 Schematic of Gas Liquid Supersonic Nozzle System

Theory

The nozzles were designed for two-phase flow using the assumption that the nozzle would expand the mixture isentropically. The area ratio was optimized to create the highest velocity with the shortest nozzle geometry, having a ratio of the throat area to the exit area of 5.44. It was found that, if the diverging section was too long, friction would cause a normal shock to form inside the nozzle, reducing the nozzle effectiveness. The exit mach number of the nozzle as designed is 3.2. The water flowrate and gas pressure required were determined empirically. The quantity of water used is small compared with other impingement methods; thus, the concentration of contaminant in the water is high and relatively easy to evaluate.

The solubility of most contaminants is very low in room temperature water. Because a homogeneous suspension is required for Total Carbon (TC) analysis (the technique used to verify NVR level), a technique capable of putting the contaminant into suspension is required. In the small parts verification process, ultrasonic energy is used to place the contaminant into suspension. In this impingement process, the velocity of the water droplets, which are accelerated by the air, provides the energy required to remove the contaminants and place them into a water emulsion. After impingement, the collected water is subjected to TC analysis, which determines the parts per million (ppm) of carbon in the sample.

The Dohrmann DC-190 High Temperature (880 °C) Combustion TC Analyzer was used. In the TC analysis technique, a sample of water/contaminant rinse is introduced into the combustion chamber, converted to carbon dioxide, and measured by a nondispersive infrared detector. The concentration of carbon is measured in parts per million (ppm). This is a simple technique and easily adaptable to a production environment. The major disadvantage is low response to silicone class compounds, where carbon content is dependent on functional groups.. With TC analysis, the concentrations of inorganic and organic carbon can be determined. It is known that the majority of contribution from contaminants entails organic carbon. Therefore, TC is a good representation of the amount of contaminant in a sample.

Procedure

The objective of testing was to obtain both water impingement samples and CFC-113 samples in parallel tests from each of four similarly sized valve bodies. This was accomplished by subjecting each valve body to an initial cleaning process, followed by either an impingement cleanliness verification or a CFC-113 gravimetric NVR cleanliness verification. In both set-ups, the valve body was suspended over a catchpan, which caught the effluent from the process and directed it into a beaker located beneath the pan.

Before testing began, both catchpans were thoroughly cleaned for approximately 15 minutes using the impingement nozzle. Water and CFC-113 blanks were then captured in order to determine a baseline cleanliness of each pan. All valve bodies were immersed in a 60°C (140°F) bath of Brulin 815GD for 30 minutes and then rinsed with 82°C (180°F) water. The valves were then immersed in an ultrasonic bath rinse tank for 15 minutes with a submerged water jet, cooled with an ambient water rinse, and dried with air. Impingement samples were taken after the initial cleaning of each valve to establish a baseline cleanliness level.

Each valve body was evenly contaminated with one of four contaminants at one of three contaminant levels. The four contaminants used were:

Amoco-Rykon II (petroleum grease)
Chevron Molykote (molybdenum disulfide grease)
Dow-Corning DC-55M (silicone grease)
Dupont Krytox 240 AC (fluorinated polyether grease)

Each contaminant was tested at three contamination levels: 11.1, 22.2, 111 mg/m^2 (1, 2, and 10 mg/ft^2). After contamination, the next step was impingement for two minutes followed by a CFC-113 rinse, which removed any contaminant that may have remained on the body. In the case of the equivalent CFC-113 test, the valve body was rinsed with approximately 100 ml of CFC-113 after the contamination occurred.

In summary, the valve bodies were processed through a complete cleaning and each of the two cleanliness verification cycles. One process involved cleaning, contamination, and verification by

impingement; the other involved cleaning, contamination, and verification by CFC-113 rinsing. This procedure allowed for direct comparison of the results.

Analysis

After each series of tests, TC analysis and two NVR analyses were performed (one each for the CFC-113 rinse following impingement and the CFC-113 rinse verification tests). In the TC analysis, a 200 microliter (µL) sample was injected into the combustion chamber for processing. A TC reading, in ppm, was obtained. Typically, an average of three to five injection samples was required to obtain a consistent value. The remaining effluent volume was then measured for use in the equivalent NVR (ENVR) calculation. ENVR is the value of a NVR analysis that would have been obtained using conventional CFC-113 rinse methods. The equation was as follows:

$$ENVR = \frac{Va * (TC_S - TC_B)}{Vav * S * A} \qquad \text{(Equation 1)}$$

where

Va = volume, actual collected (mL)
TC_S = total carbon, sample (ppm)
TC_B = total carbon, blank (ppm)
Vav = average volume of effluent collected, 45 mL (based on impingement duration, nozzle flowrate)
S = sensitivity, (ppm/mg)
A = area of impinged surface (m^2)

A gravimetric NVR was performed on the CFC-113 rinse that followed impingement to determine if any contaminant remained after the process. This was another check on the removal efficiency of the impingement method.

Results

The sensitivity factor is a measure of the level of responsiveness of the process. Sensitivity values were determined from the following equation:

$$S = \frac{Va * (TC_S - TC_B)}{Vav * C_{act} * A} \qquad \text{(Equation 2)}$$

where: C_{act} = actual contamination level of valve body (mg/m^2)

Table 1 contains the calculated sensitivities for the contaminants at each of the three contamination levels. From these data, an overall sensitivity (used in Equation 1) was determined. An average value of sensitivity for each contaminant at each level was first calculated and weighed, based on the likelihood of finding it on the actual component. Since the area of primary concern was in the 11.1 mg/m^2 (1 mg/ft^2) range, the overall sensitivity factor for the process was chosen at the 11.1 mg/m^2 (1 mg/ft^2) level. While this will give lower ENVR's for higher contamination levels, it should fail any component having an initial contamination greater that 11.1 mg/m^2 (1 mg/ft^2).

Table -1 Sensitivity vs. Contaminant and Contamination Level

Contaminant	Level (mg/m^2)	Sensitivity (ppm/mg)
Amoco Rykon II	111	0.93
	22.2	1.22
	11.1	2.97
Chevron Molykote	111	1.11
	22.2	1.75
	11.1	3.03
Dow Corning DC-55M	111	1.16
	22.2	2.13
	11.1	4.20
Krytox 240 AC	111	0.12
	22.2	1.18
	11.1	1.21

Table 2 contains a comparison of average ENVR's calculated from the impingement results and NVR values obtained directly from the CFC-113 testing. The ENVR for each contaminant at the three contamination levels was plotted and may be seen in Figures 2 - 6. Three of the four contaminants were readily detected; Krytox 240 AC, which has very low levels of carbon, was not detectable by TC analysis. However, the NVR analyses of the CFC-113 rinse that followed the valve impingement showed that the impingement method effectively removed Krytox 240 AC from the valve body surface.

Table 2 - Average ENVR vs. NVR ($mg/0.09m^2$)

Contaminant\Level ($mg/0.09m^2$)	1.0		2.0		10.0	
	ENVR	NVR	ENVR	NVR	ENVR	NVR
Amoco Rykon	0.9	0.7	0.7	1.7	2.7	7.1
Chevron Molykote	0.9	0.7	1.0	1.3	3.3	6.7
DC-55M	1.2	1.0	1.3	1.4	3.4	6.4
Krytox 240 AC	0.4	0.7	0.7	1.4	0.4	7.9

On viewing these data, some scatter will be seen. This is due to the sensitivity of the system to the operator's procedure and environmental conditions. The data presented in this paper were gathered in less than ideal environmental conditions, but are felt to generally be representative of the capabilities of the system. Presently, operations have been moved to a clean room facility where testing is being conducted using the same baths and rinses as the production cleaning operations are using.

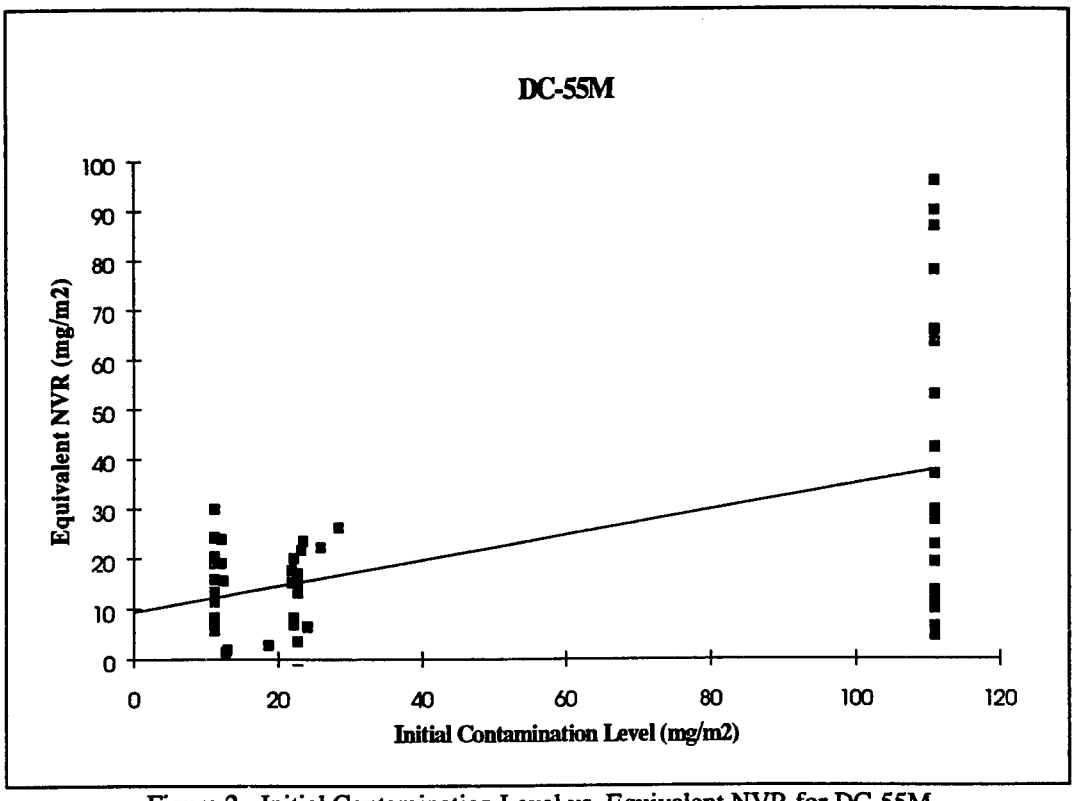

Figure 2 - Initial Contamination Level vs. Equivalent NVR for DC-55M

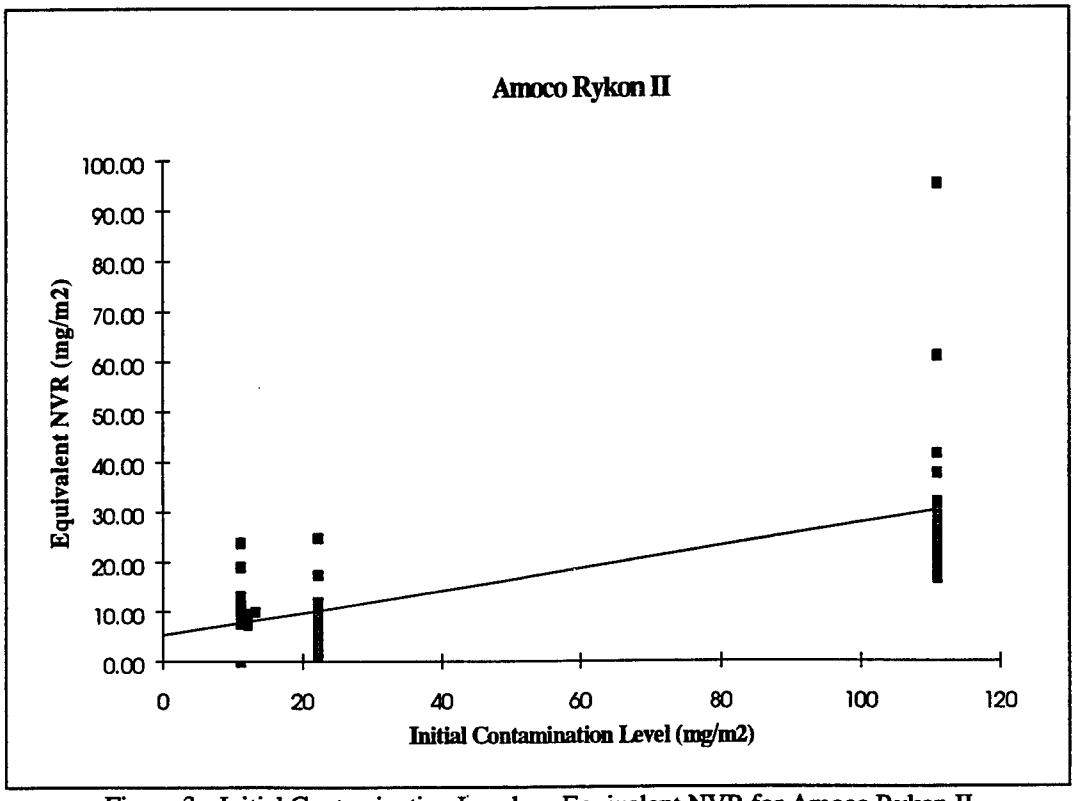

Figure 3 - Initial Contamination Level vs. Equivalent NVR for Amoco Rykon II

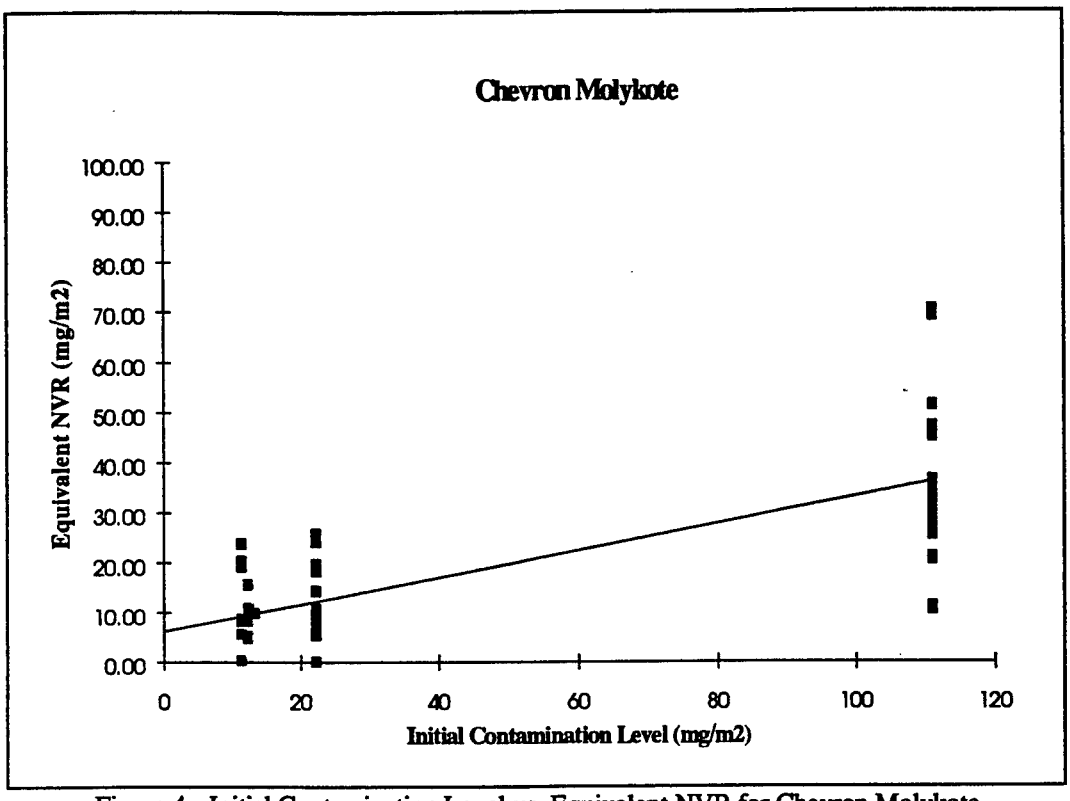

Figure 4 - Initial Contamination Level vs. Equivalent NVR for Chevron Molykote

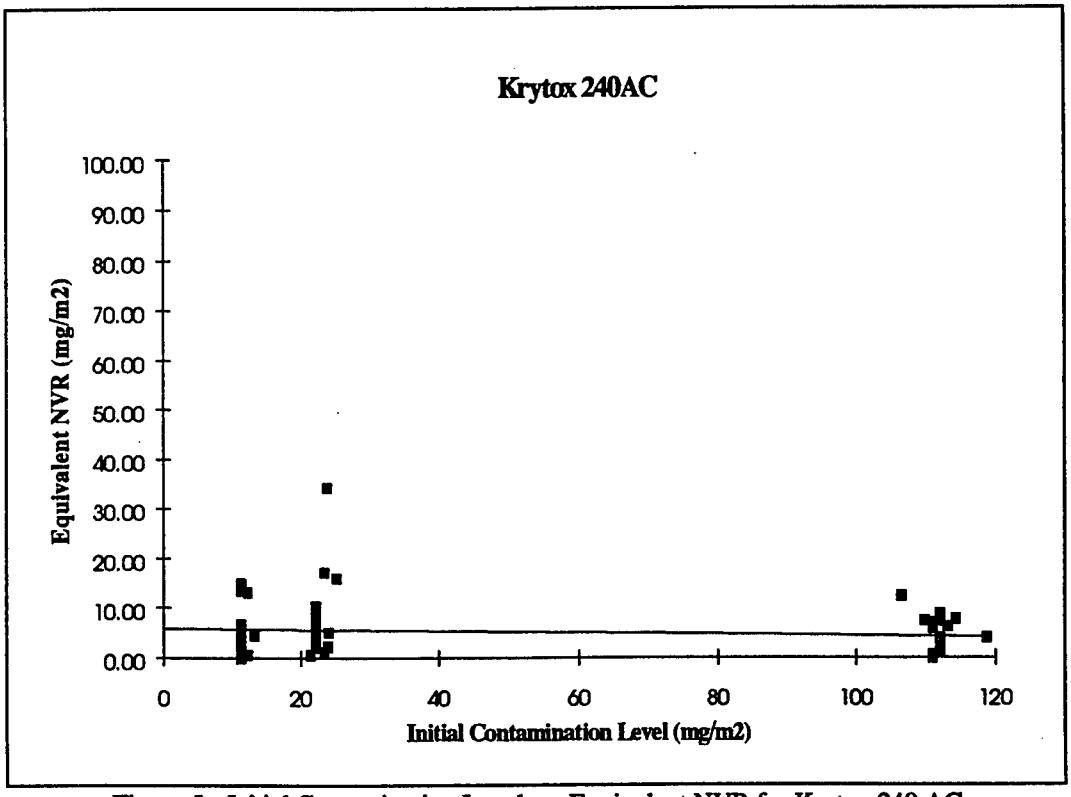

Figure 5 - Initial Contamination Level vs. Equivalent NVR for Krytox 240 AC

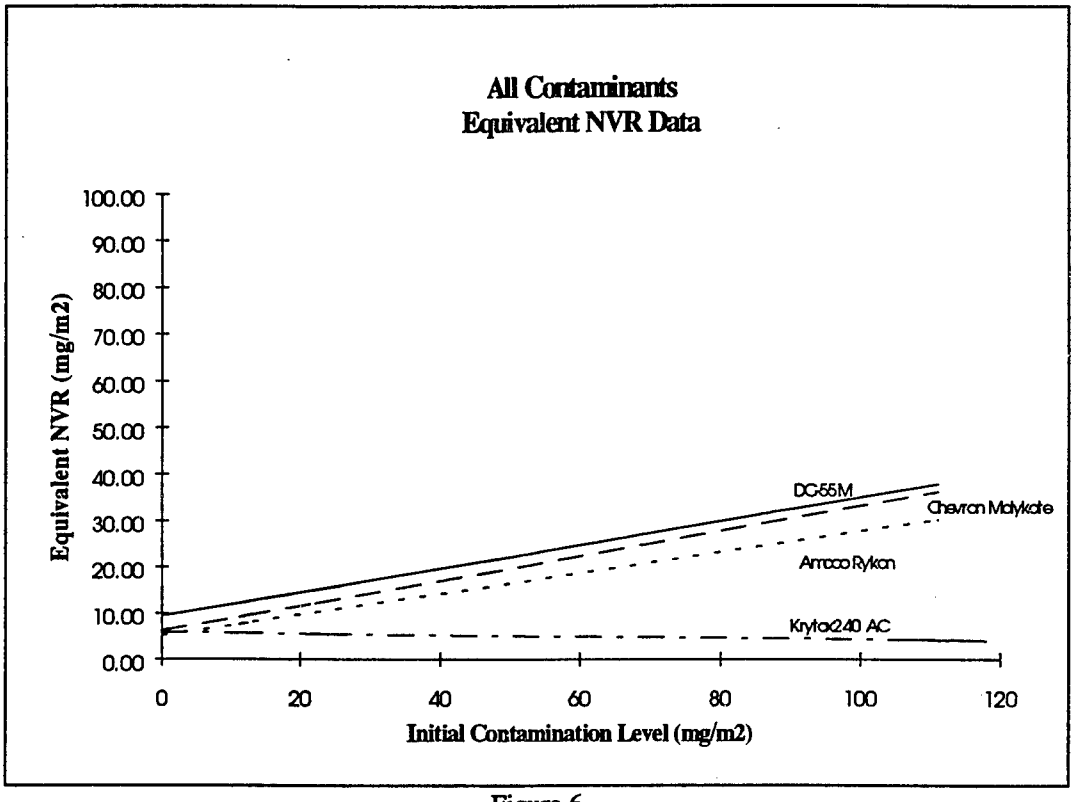

Figure 6

The curves in Figure 6 indicate that, if extrapolated to an initial contamination level of zero, all of the curves intersect the ENVR axis at values above zero. Since it is not possible to completely clean a component to the zero level, and the exact level and content of initial contaminant is unknown, there will be a baseline "noise" level of ENVR.

Table 3 containing ENVR values for the tested valve size has been generated from the data shown in Figure 6 and Equation 1. Using this table, a technician will be able to read an ENVR value based on the component size, TC reading, and actual volume of effluent collected. The technician will then compare the ENVR to the 11.1 mg/m^2 (1 mg/ft^2) pass/fail criterion. A series of tables for different component surface areas will be generated for field usage after future tests are completed.

Table 3 - Example ENVR Calculation Worksheet
Equivalent NVR (mg/0.09m^2)

S = 3.4 A = 0.9 ft2

Vol (ml)\TC (ppm)	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0
30	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
32	0.4	0.6	0.8	1.0	1.3	1.5	1.7	1.9	2.1	2.3
34	0.4	0.7	0.9	1.1	1.3	1.6	1.8	2.0	2.2	2.4
36	0.5	0.7	0.9	1.2	1.4	1.6	1.9	2.1	2.4	2.6
38	0.5	0.7	1.0	1.2	1.5	1.7	2.0	2.2	2.5	2.7
40	0.5	0.8	1.0	1.3	1.6	1.8	2.1	2.4	2.6	2.9
•	•									•
•	•									•
50	0.7	1.0	1.3	1.6	2.0	2.3	2.6	2.9	3.3	3.6

Differing methods of applying this impingement technique are being developed. Rather than use a wand with a single nozzle, devices that automatically rotate and contain multiple nozzles are under development. These new tools should reduce the errors induced by differences in operators or procedures. Such new tools have the potential for greatly reducing the amount of time that is required to sample a component while greatly increasing the sensitivity to contamination on the component being verified.

CONCLUSIONS

The results of the testing performed to date have shown that the Impingement Verification System (IVS) will be a successful replacement for the traditional CFC-113 rinse method for cleanliness verification for large components. Three of the four contaminants tested were able to be detected using IVS and TC analysis. Krytox 240 AC was not detectable, however, it is oxidizer-compatible and could not support combustion, and, therefore, not of concern.

It must be emphasized that although this method is successful for the particular application at KSC for which it was developed, it must be appropriately tailored in order to be used in other applications. The system in which it would be applied, the types of contaminants, and the contamination level all play an important role in the determination of the sensitivity factor.

ACKNOWLEDGMENTS

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REFERENCES

[1] Allen, G. J., Hoppesch, C. W., Johnson, R. S., Buckley, M., "Aqueous Non-Volatile Residue Validation of Precision Cleaned Hardware," Alternatives to Chloroflurocarbon Fluids in the Cleaning of Oxygen and Aerospace Systems and Components, STP 1181, July 1993, pp 37-48.

[2] Dearing, W. L., Bales, L. D., Bassett, C. W., Caimi, R. E., Lafferty, G. M., Melton, G. S., Sorrell, D. L., Thaxton, E. T., "Methods for Using Water Impingement in Lieu of Chlorofluorocarbon 113 for Determining the Non-Volatile Residue Level on Precision Cleaned Hardware," Alternatives to Chloroflurocarbon Fluids in the Cleaning of Oxygen and Aerospace Systems and Components, STP 1181, July 1993, pp 66-77.

[3] Melton, G. S., Caimi, R. E., Thaxton, E. T., "Determination of Non-Volatile Residue on Precision Cleaned Oxygen and Aerospace Systems and Components by Means of Water Impingement and Total Organic Carbon Analysis," The 1993 International CFC and Halon Alternative Conference, Washington DC., October 1993, pp 642-650.

[4] Melton, G. S., Caimi, R. E., Littlefield, M. D., Thaxton, E. T., "Cleaning Verification by Air/Water Impingement," Precision Cleaning '94, May 1994, pp 97-107.

Investigation of Cleanliness Verification Techniques for Rocket Engine Hardware

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Abstract

Oxidizer propellant systems for liquid-fueled rocket engines must meet stringent cleanliness requirements for particulate and nonvolatile residue. These requirements were established to limit residual contaminants which could block small orifices or ignite in the oxidizer system during engine operation. Limiting organic residues in high pressure oxygen systems is particularly important. The current method of cleanliness verification used by Rocketdyne requires an organic solvent flush of the critical hardware surfaces. The solvent is filtered and analyzed for particulate matter, followed by gravimetric determination of the nonvolatile residue (NVR) content of the filtered solvent. The organic solvents currently specified for use (1,1,1-trichloroethane and CFC-113) are ozone-depleting chemicals slated for elimination by December 1995.

A test program is in progress to evaluate alternative methods for cleanliness verification that do not require the use of ozone-depleting chemicals and that minimize or eliminate the use of solvents regulated as hazardous air pollutants or smog precursors. Initial results from the laboratory test program to evaluate aqueous-based methods and organic solvent flush methods for NVR verification are provided and compared with results obtained using the current method. Evaluation of the alternative methods was conducted using a range of contaminants encountered in the manufacture of rocket engine hardware.

Introduction

Background

Stringent particulate and nonvolatile residue (NVR) cleanliness requirements for liquid rocket engine hardware, including fuel, oxidizer and pneumatic systems, are imposed by customer specifications. The current method for cleanliness verification involves a final flush of the hardware surfaces immediately following the vapor degrease or solvent flush precision cleaning operation. A sample of the final flush solvent is collected, filtered for particulate matter analysis and tested for nonvolatile residue by a gravimetric technique. The specified cleanliness requirement is less than 1 mg of NVR per square foot of significant surface area. Significant surfaces are defined as those hardware surfaces that may contact the propellants or pneumatic gases during engine operation.

A variety of hardware configurations, material substrates and contaminants are encountered during the final cleaning and verification process. The hardware includes simple detail parts such as seals, bearings, nuts and bolts; complex detail parts such as lines, pump and valve housings, and pump volutes and impellers; moderate size subassemblies such as valves, flex joints and turbopumps; and large complex subassemblies such as flexible propellant ducts, powerheads, nozzles and main combustion chambers. Material substrates include nickel, iron and cobalt-base superalloys; stainless and low alloy steels; aluminum alloys; copper alloys; nickel, silver, gold and copper plating; polychlorotrifluoroethylene, polytetrafluoroethylene, polyimide and polyethylene terephthalate plastics; various elastomers; carbon; and dry film lubricants. Typical contaminants include machine coolants; machining, cutting and tapping fluids; hydraulic fluids; inks; dye penetrants and other fluids to support NDT operations; hydrocarbon, fluorinated and silicone greases; paraffin waxes; detergent residues; tape adhesive residues; and fingerprints.

The solvent predominantly utilized by Rocketdyne for precision cleaning and cleanliness verification is 1,1,1-trichloroethane (TCA). TCA is an ozone-depleting substance and will be banned from

manufacture as of December 1995. Rocketdyne has an environmental task to evaluate and implement alternative methods of cleanliness verification that do not require the use of ozone-depleting chemicals and that minimize or eliminate the use of other regulated solvents. In general, the alternative technique(s) must be capable of detecting a variety of contaminants, be suitable for use on a variety of surface finishes, be capable of sampling internal cavities where the residue is most likely to be entrapped, not recontaminate the hardware, yield quantitative results that can be correlated to the current technique, be compatible with hardware materials, be applicable in a production environment and at the same time meet environmental and safety constraints.

Approach

The overall task proceeds from laboratory evaluation of the candidate techniques to hardware-scale demonstration to final production implementation. The status of the laboratory-scale evaluation of the aqueous and the organic solvent techniques will be discussed.

NASA-KSC has developed an aqueous verification technique in which the cleaned part is ultrasonically agitated in heated deionized (DI) water to remove any residual organic contaminants from the surfaces.(1) The contaminant concentration in the water is then determined by total organic carbon (TOC) analysis. Based upon the promising results obtained by NASA-KSC, the technique is under evaluation using the contaminants, substrates and configurations specific to Rocketdyne. However, as the technique is applicable to hardware of a limited size and some items (i.e., dry film lubricated parts and fragile instrumentation) are damaged by the ultrasonics, additional techniques will also be required. Organic solvents, other than the ozone-depleting chemicals, are under evaluation for these applications.

To evaluate the aqueous technique developed by KSC, the effectiveness of ultrasonic agitation for removing contaminants from surfaces was determined and the method of TOC analysis for determining the contaminant concentration in an aqueous medium was investigated. The effectiveness of ultrasonics was initially determined on small, flat coupons. Investigation of the TOC technique included determination of sample preparation techniques, construction of correlation curves and determination of the limits of detection. Finally, the entire verification process, ultrasonic removal and TOC analysis, was performed on coupons with a known level of contamination and the results verified gravimetrically. Additional testing will be conducted using complex test samples and small hardware.

The evaluation of alternative organic solvents will proceed along the same path as the investigation of the aqueous method except greater emphasis will be placed on solubility characteristics rather than on mechanical agitation techniques to remove the contaminant from a surface. The candidate fluids were identified, physical and chemical properties tabulated, and a review performed by Rocketdyne's Health, Safety & Fire Engineering and Environmental Protection departments. Downselected candidates were tested for residue and contaminant removal effectiveness. Once the final candidates have been identified, they will be tested for rinsability and material compatiblity. Removal testing on complex coupons and small hardware will then proceed as with the aqueous method.

Procedure

Ultrasonic Contaminant Removal Tests

Initial testing to determine the effectiveness of ultrasonic agitation with heated water to remove contaminants from flat coupons was evaluated. Small (1" x 1") flat Alloy 718 coupons were initially prepared by ultrasonic cleaning in tetrachloroethylene, drying, ultrasonic cleaning in heated DI water and drying. The coupon weights were monitored after each drying step to verify cleanliness. The cleaning cycle was repeated until no weight change was noted. Upon verification of cleanliness, each coupon was contaminated by spreading approximately 2 mg of the contaminant over one surface. The coupons were then heated for 1 hour at 95°C, allowed to cool and reweighed to determine the amount of contaminant remaining. The heating step eliminated any highly volatile species and more closely simulated the nature of a contaminant residue as it is present on actual hardware. Each coupon was then immersed in 100 mL of deionized water heated to 52°C and ultrasonically agitated for 10 minutes. The coupons were dried for 0.5 hour at 95°C, allowed to cool and reweighed to determine the residual contaminant remaining on the coupon. The percentage contaminant removed from each coupon was calculated from the weight data.

Testing was conducted using a 0.75-gallon, 47-kHz ultrasonic tank with a 150-watt power level and a 5-gallon, 25-kHz ultrasonic tank with a 600-watt power level. All tests were performed in triplicate using the contaminants listed in Table 1.

Test Contaminant	Description
Cool Tool, Monroe Fluid Tech.	Hand-applied cutting and tapping fluid containing paraffinic oil
MIL-H-83282 Micronic 882, Bray Oil Co.	Synthetic hydrocarbon hydraulic fluid containing triphenyl phosphate
MIL-H-5606	Hydraulic fluid containing naphthenic distillate with polymer additives and triphenyl phosphate
Rust Foil L-492 Preservative Oil, Franklin Oil Co.	Solvent-dispersed corrosion preventive compound containing aliphatic hydrocarbons and mineral oil
Krytox 240 AC, DuPont	Perfluoroalkylether grease with TFE filler used as a lubricant for oxygen systems and for pressure testing
CIMSTAR 3700, Cincinnati Milacron	Semi-synthetic water-soluble metal working fluid containing mineral oil, di- and tri-ethanolamines, aminomethylpropanol and a synthetic lubricant
DTE 24, Mobil Oil	Petroleum distillate oil
Lapping Compound 38-1200, USP	Ultra fine grit lapping compound containing aluminum oxide
CRC 3-36, CRC Ind.	Petroleum distillate and paraffinic oil containing lubricant and rust inhibitor
Centerpoint Lube, Chicago Manuf. & Dist.	High viscosity, grease-like extreme pressure machining lubricant containing petroleum oil, wax, and rosin ester
Bio-Pen P6R, Ardrox Inc.	Detergent-based visible, solvent-removable dye penetrant
Bio-Pen P6F-4, Ardrox, Inc.	Fluorescent, water-washable dye penetrant
Bio-Pen NQ-1 Developer, Ardrox Inc.	IPA and silica containing spray developer for penetrant inspection
Turco 3878 LF-NC, Turco Products	Aqueous emulsion cleaner containing sodium tripolyphosphate, glycol ether, and proprietary salts of anionic surfactants
Braycote 236, Castrol Inc.	Petrolatum used to lubricate o-rings during pressure test
Paraffin Wax	Low-melting-point, 107°F, wax used as machining maskant
Vacuum Grease, Dow Corning	Silicone vacuum grease used during pressure test
China Marker 165-T, Empire Berol Corp.	Red water-resistant marking pencil
Hydro Marker 665-T, Empire Berol Corp.	Red water-soluble marking pencil

Table 1. Test Contaminants

TOC / Contaminant Concentration Correlation Curves

To relate the TOC value of a sample to the actual contaminant concentration, a series of correlation curves were generated using prepared standards. Standard solutions of 20.5 ppm, 50.5 ppm and 80.3 ppm of Cool Tool; 19.5 ppm, 50.8 ppm and 93.3 ppm of MIL-H-5606 hydraulic fluid; 24.0 ppm, 52.3 ppm and 81.0 ppm of CRC 3-36; and 20.3 ppm, 59.3 ppm and 88.0 ppm of Centerpoint Lube each in 400 mL of DI water were prepared. To emulsify the contaminant, each solution was agitated by manual shaking for 30 seconds and then immersed in a 25-kHz ultrasonic bath at 52°C and agitated for 10 minutes after thermal equilibrium had been obtained. Each solution was then analyzed in triplicate for TOC content using a Rosemount Analytical Model DC-190 High Temperature TOC Analyzer. A sample of DI water was also analyzed to obtain a blank value.

TOC Analysis of Water from Coupon Tests

A quick assessment of the feasibility of the ultrasonic agitation/TOC analysis for cleanliness verification was performed using the small Alloy 718 coupons. The coupons were cleaned, verified and contaminated as in the ultrasonic removal tests, except varying levels of initial contaminant were applied. The target contamination levels were 1 mg, 2 mg and 5 mg. Two contaminants were tested, Cool Tool and Centerpoint Lube. Each sample was ultrasonically agitated in 100 mL of heated DI water as described previously. The water sample was then analyzed for TOC content. From the correlation curves, the contaminant concentration in the water was calculated and the total amount of contaminant removed from the coupon was calculated using Equation 1.

$$\text{Contaminant Removed (mg)} = \frac{TOC - B}{M} \times V \qquad (1)$$

TOC	=	TOC value in ppm or mg/liter
B	=	the y-intercept of the correlation curve, i.e., the TOC of the DI water blank in ppm or mg/liter
M	=	slope of line of correlation curve in ppm TOC / ppm contaminant concentration or (mg/liter) / (mg/liter)
V	=	volume of water used for ultrasonic extraction in liters

For comparison, the amount of contaminant removed was also calculated by the change in coupon weight after ultrasonic immersion.

Complex Coupon Tests

Test coupons with configurational complexities (Figure 1) were utilized to further test the aqueous verification technique. The coupons were precleaned by ultrasonic agitation in TCA for 10 minutes. Cleanliness was then verified by ultrasonically agitating each coupon in 500 mL of TCA and performing a gravimetric NVR on the TCA. Each sample was immersed in 500 mL of 52°C DI water and ultrasonically agitated for 10 minutes. The water sample was analyzed for TOC to provide a "blank" value. The samples were dried and 5 to 10 mg of Cool Tool applied to each coupon. Each sample was then immersed in 500 mL of 52°C deionized water and ultrasonically agitated for 10 minutes. The water sample was subsequently analyzed for TOC. Each coupon was reverified clean by ultrasonic agitation in TCA followed by gravimetric NVR. A sample that had been contaminated, but not aqueously verified, was solvent verified as a control.

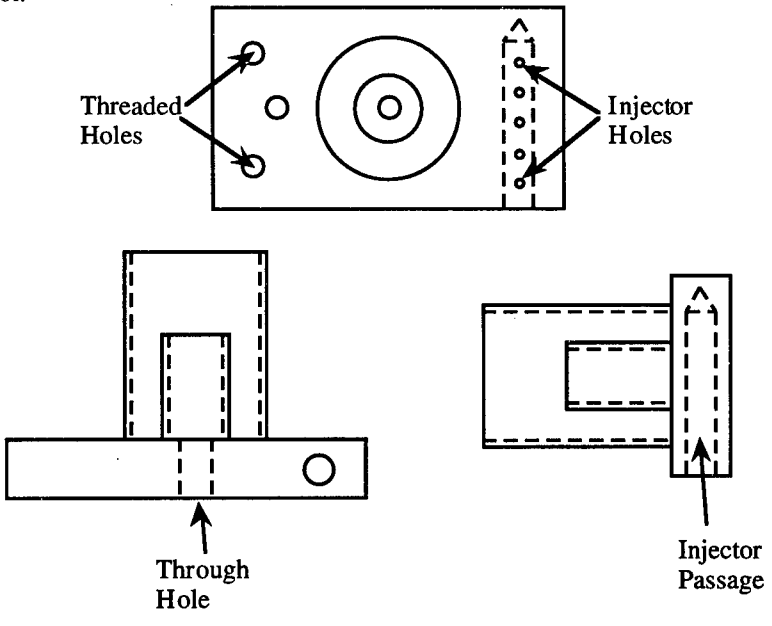

Figure 1. Alloy 718 Complex Test Coupon Configuration

Organic Solvent Evaluation

A list of candidate alternative solvents was compiled from a literature search, published data bases and supplier information. The categories of solvents considered included chlorinated solvents, hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), fluoroiodocarbons (FICs), alcohols, terpenes, ketones, aliphatic and alicyclic hydrocarbons, ethers, glycol ethers, esters, amines, aromatic hydrocarbons, methyl siloxanes and parachlorobenzotrifluoride. An abbreviated list of candidates was compiled using the following criteria:

Essential characteristics:

- Moderate to high volatility to promote evaporation from complex hardware and ease of performing a gravimetric NVR
- Comparable solubility to trichloroethane for a range of contaminants used at Rocketdyne
- Available in high purity and leaves little or no residue upon evaporation
- Existing or near-term availability
- Non-ozone depleting

Desirable characteristics:

- Not currently listed nor proposed to be listed on California Proposition 65, AB2588 or classified as a HAP (hazardous air pollutant)
- Does not contribute to global warming
- Not classified as a VOC (volatile organic compound)
- Permissible exposure level greater than 100 ppm
- Nonflammable
- Inoffensive odor

Contaminant removal tests were then performed to assess the effectiveness of the candidate solvents relative to TCA. Approximately 10 to 30 mg of contaminant were applied to the bottom of a clean, tared aluminum weighing pan. The contaminated pan was heated for 1 hour at 95°C, allowed to cool to room temperature and reweighed to determine the amount of contaminant remaining. The dish was then sequentially filled and drained with the filtered test solvent until a total of 100 mL had been used. The pan was dried for 1 hour at 108°C to evaporate any residual solvent, allowed to cool to room temperature and reweighed. The percentage of the initial contaminant removed was calculated using the weight data. A gravimetric NVR was also performed on each solvent sample and a percentage of contaminant removed was calculated. Tests were performed in triplicate with the contaminants listed in Table 1.

Results and Discussion

Ultrasonic Contaminant Removal Tests

The results from the removal tests for the seventeen contaminants tested using both the 47-kHz ultrasonic bath and the 25-kHz bath are shown graphically in Figure 2. In general, the 25-kHz bath was slightly more effective than the 47-kHz bath. The average removal of all of the contaminants was 83% for the 47-kHz bath and 85% for the 25-kHz bath. For the majority of the contaminants, ultrasonic agitation in water was greater than 90% effective in removing the contaminant residues. The Krytox grease, silicone vacuum grease, paraffin wax and China marker were the most difficult contaminants to remove as shown by their 10 to 80% removal. Not surprisingly, these contaminants are also the most difficult to remove using organic solvents.

Because of the simple configuration of the test coupons used, the removal efficiencies may not translate directly to more complex geometries. The coupons were selected so the contaminant removed could be determined by simple gravimetric means with relatively little error. For example, the accuracy of the percentage removal data is approximately $\pm$ 5% with the error derived from the limitations of the balance. To fully evaluate the effectiveness of the ultrasonics, more complex test coupons and hardware will be tested and an organic solvent verification method used to assess the results.

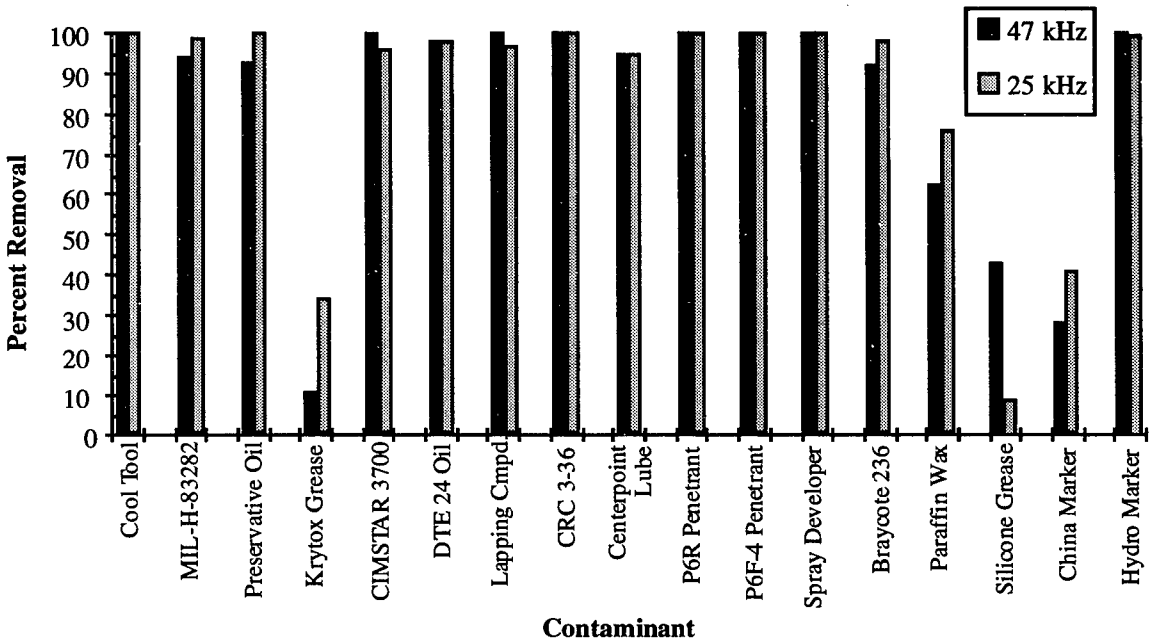

Figure 2. Contaminant Removal Effectiveness by 10-Minute Immersion in 52°C DI Water with Ultrasonic Agitation

TOC / Contaminant Concentration Correlation Curves

In order to relate the measured TOC value to the actual concentration of the contaminant in water, correlation curves were generated. The curves for four contaminants, Cool Tool, Centerpoint Lube, CRC 3-36 and MIL-H-5606 hydraulic fluid are shown in Figure 3. The average measured TOC value for each of the standard solutions prepared was plotted and a best fit line determined by the method of least squares. As shown, for the concentration ranges tested, the linear fit of the data is excellent. Testing is continuing to generate correlation curves for the other contaminants of interest.

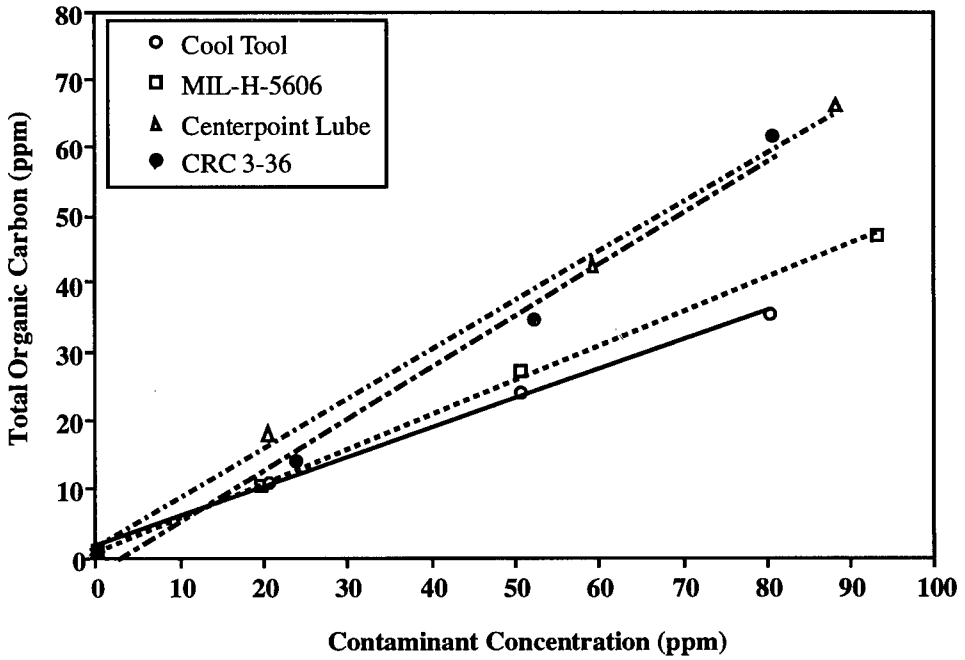

Figure 3. Correlation of Contaminant Concentration with TOC

TOC Analysis of Water from Coupon Tests

Testing was performed using the small coupons to verify the ability of the TOC analysis to accurately measure the amount of contaminant removed after ultrasonic agitation. The contaminant removed was calculated both gravimetrically and by TOC analysis. These coupons were used because cleanliness assessment could be made gravimetrically rather than by the more time consuming solvent verification method. As shown in Figures 4 and 5, contaminant removal results determined by the TOC method compare favorably to those obtained by the gravimetric method. The favorable results indicate that the aqueous verification technique is viable, at least for simple geometries and the contaminants tested to date. Based upon these successful results, testing was initiated with more complex geometries.

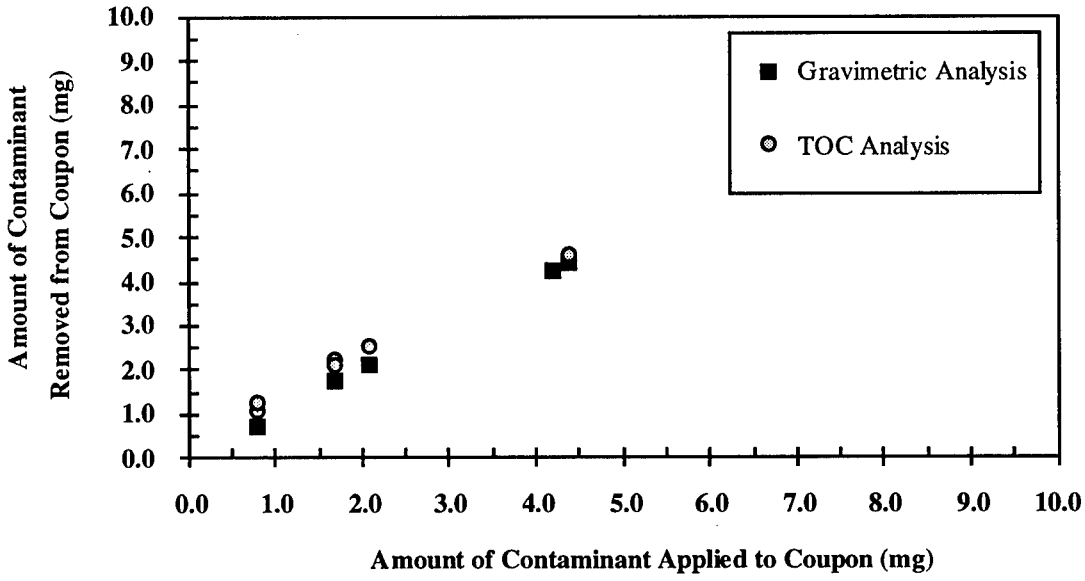

Figure 4. Comparison of Aqueous Verification with Gravimetric Results for Determining Cool Tool Residue on Alloy 718 Coupons

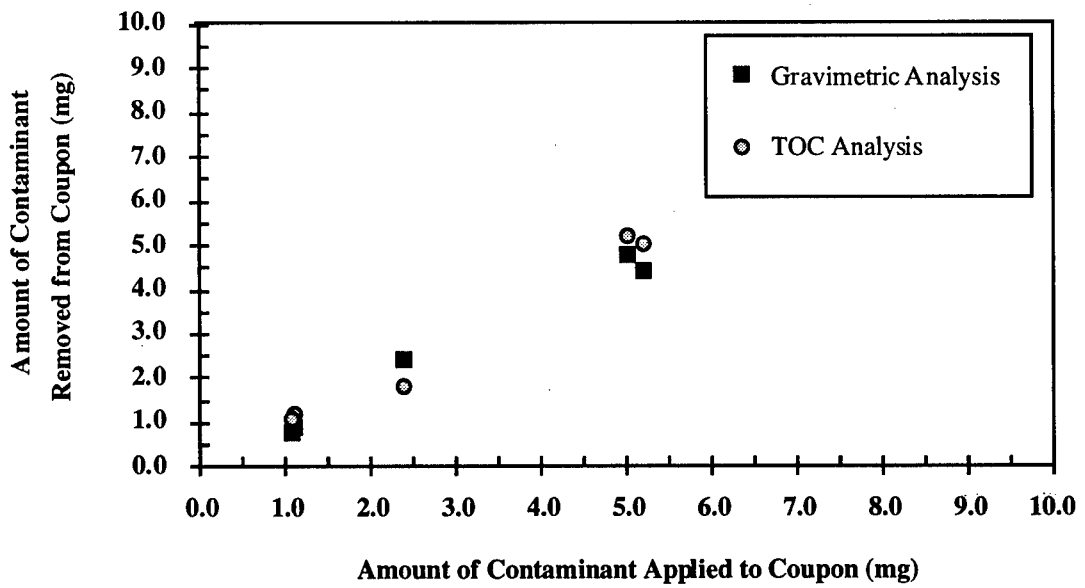

Figure 5. Comparison of Aqueous Verification with Gravimetric Results for Determining Centerpoint Lube Residue on Alloy 718 Coupons

Complex Coupon Tests

The first series of tests performed with the more complex test coupons involved placing a controlled amount of contamination on a relatively exposed surface of the Alloy 718 coupon and performing the aqueous verification technique. The TOC results were converted to amount of contaminant removed from the test piece by use of the correlation curve and the results are shown in Table 2 along with the results from the subsequent NVR analysis. As shown by the TOC results and by the low NVR results, the aqueous technique was successful in detecting the contaminant on the test pieces. The control coupon which was contaminated and then verified with TCA shows that not even the standard solvent verification method is precise in determining the entire amount of contaminant on a surface. This may be due either to incomplete removal by the solvent or to slight evaporation of the Cool Tool during the gravimetric analysis. Testing is now being extended to include additional contaminants and to contaminate more inaccessible regions on the test sample, such as the threaded holes and the through holes. If required, the process parameters will be adjusted to maximize the contaminant removal.

Contaminant	Amt. Applied (mg)	Verification Results	
		By TOC (mg)	By TCA NVR (mg)
Cool Tool	10.98	8.40	0.1
	13.70	13.87	0
	5.18	Not Performed	4.4

Table 2. Aqueous Verification Results on Complex Test Coupons

Organic Solvent Alternatives

Candidate organic solvents under initial consideration as alternatives to TCA include isopropyl alcohol (IPA), acetone, cyclohexane, ethyl acetate, a 33% IPA - 67% cyclohexane azeotrope, HCFC 225 and an HFC. Of these, IPA, acetone, cyclohexane, ethyl acetate, and the azeotrope have been subjected to solubility testing. These solvents were selected for initial evaluation based upon promising results obtained by other companies that require alternative verification methods. Testing was also conducted using TCA for comparison.

A comparision of the percentage of contaminant removed as determined by coupon weight data and by solvent NVR was conducted to assess the accuracy of the current gravimetric technique. Testing was performed for all of the contaminants using TCA, IPA, cyclohexane and ethyl acetate; however, only the TCA results are shown. From Figure 6, it can be seen that for those contaminants readily removed by the solvent, the NVR results are typically 85 to 100% of the results obtained gravimetrically, except for the MIL-H-5606 and the DTE 24. The difference between the NVR and the gravimetric results is primarily attributed to the volatility of the contaminant, i.e., some of the contaminant is evaporated along with the solvent during the evaporation phase of the NVR procedure. This is particularly apparent with the light hydrocarbon contaminants, such as the MIL-H-5606 hydraulic fluid and the DTE 24. Previous testing in which the contaminant was not initially dried resulted in an even greater difference betweeen the NVR and weight data. Drying the contaminant prior to testing aids in reducing the difference but does not entirely eliminate the effect.

The effectiveness of each solvent for removing the selected contaminants is presented as a percentage removal in Figures 7 and 8. The results are based upon the gravimetric data rather than the NVR values and are shown with the TCA results for comparision. As shown, isopropyl alcohol and acetone are less effective than TCA for the contaminants tested, whereas cyclohexane, ethyl acetate and IPA/cyclohexane are nearly as effective as TCA for the majority of the contaminants. As shown, even the TCA only partially removed the lapping compound, the Centerpoint Lube and the Turco 3878. Furthermore, the TCA is relatively ineffective in removing the Krytox grease, the silicone vacuum grease, and the markers. For these contaminants, it was noted that any removal at all was primarily the result of

mechanical action rather than dissolution in any of the solvents. Of the solvents tested to date, cyclohexane showed the most promise as an alternative to TCA. However, testing is still in progress with some of the other candidates.

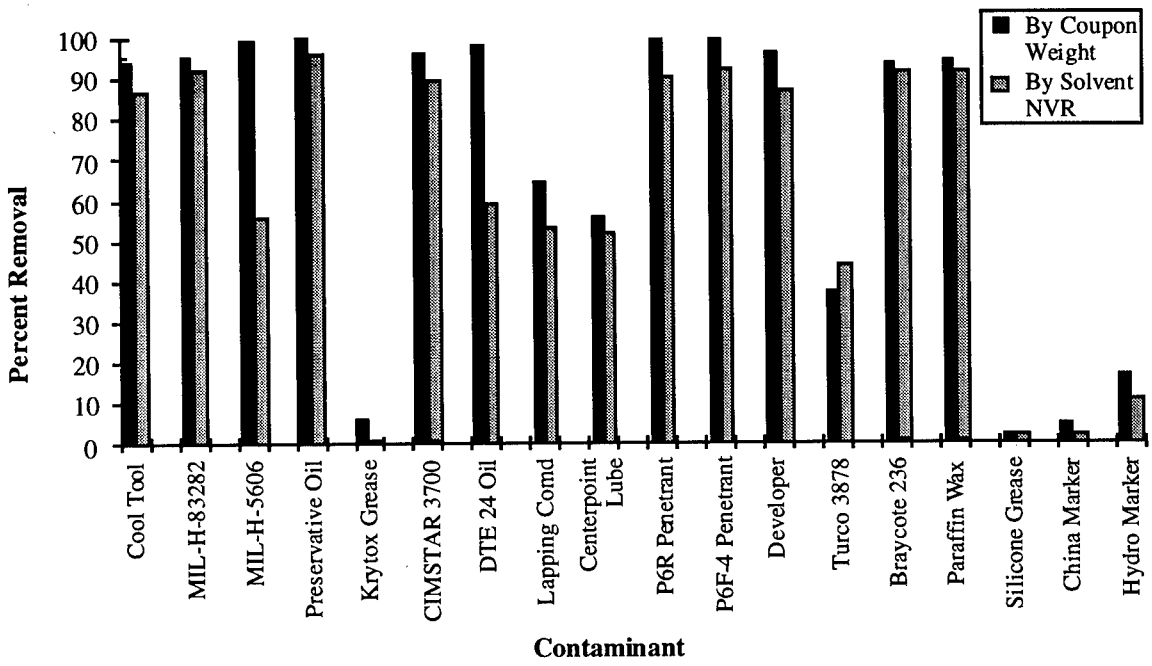

Figure 6. Contaminant Removal Tests with Ambient Temperature TCA

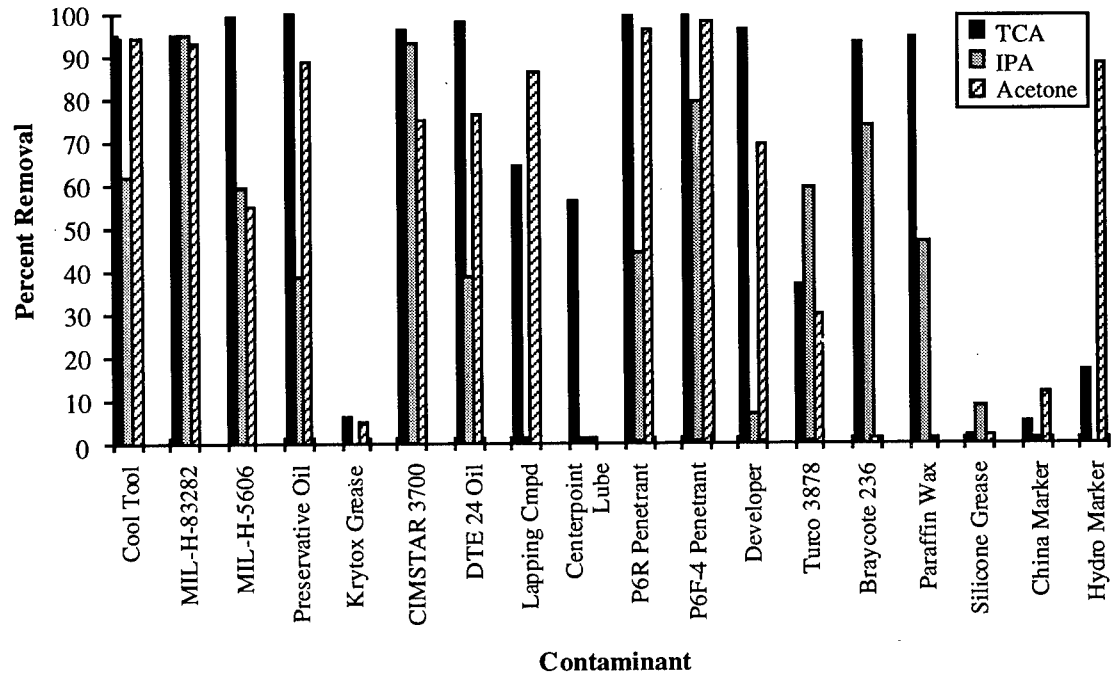

Figure 7. Contaminant Removal Tests with Ambient Temperature 1,1,1 Trichloroethane, Isopropyl Alcohol and Acetone

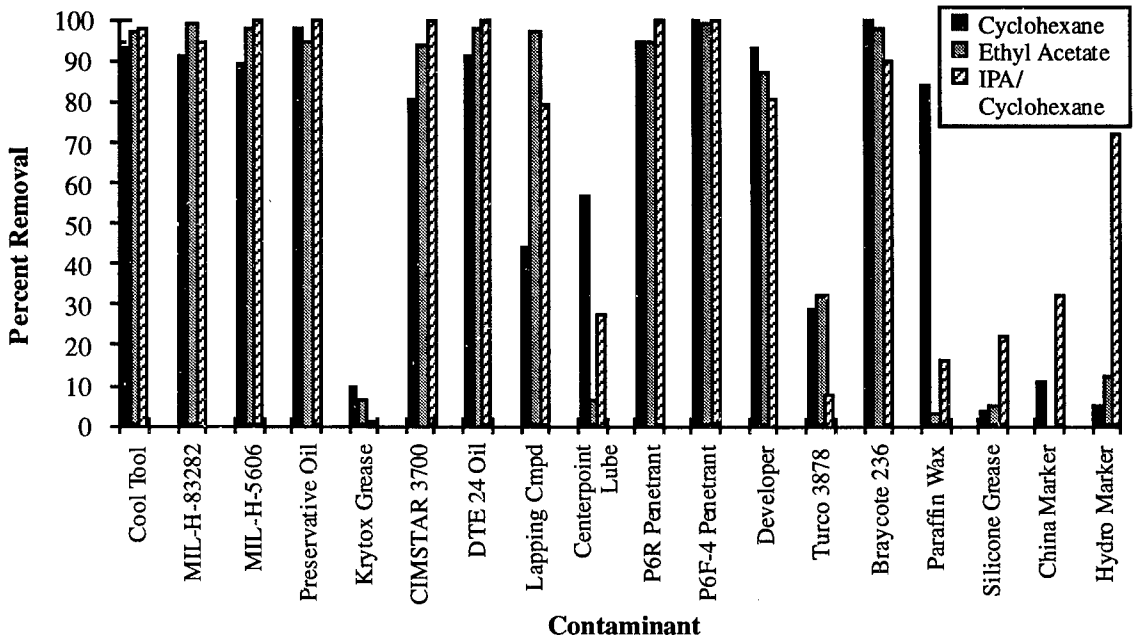

Figure 8. Contaminant Removal Tests with Ambient Temperature Cyclohexane, Ethyl Acetate and IPA/Cyclohexane

Conclusions

Based upon limited laboratory testing, the aqueous verification technique developed by NASA-KSC has been shown to be feasible for some Rocketdyne applications. Use of 25-kHz ultrasonic agitation is slightly more effective than 47-kHz ultrasonic agitation for removing the majority of the test contaminants with heated DI water. Through the use of correlation curves, TOC analysis of the water used during the ultrasonic cleaning is accurate in determining the amount of contaminant removed from the surface. Testing, however, was very limited and must be extended to the more difficult to remove contaminants and more complex geometries.

The majority of the organic solvents that can be considered as alternatives to TCA have disadvantages such as toxicity, flammability, or classification as VOCs (volatile organic compounds) or HAPs (hazardous air pollutants). From the limited testing performed to date, cyclohexane is nearly equivalent to TCA in contaminant removal. However, cyclohexane is a VOC and has a low flash point. Furthermore, as with the majority of the solvents, cyclohexane is not compatible with oxygen and must be completely removed from any oxidizer hardware. Testing will continue to evaluate other alternatives with final technique validation performed on full-scale hardware.

Acknowledgement

The assistance of M. Price for technical and editorial advice, and of S. Klee, N. Cimarusti, M. Maseda, and M. Sylvia for developing test techniques and performing testing in support of this project is greatly appreciated.

Reference

(1) Allen, G. J., Hoppesch, C. W., Johnson, R. S., Buckley, M. D., "Aqueous Nonvolatile Residue Validation of Precision Cleaned Hardware", Alternatives to Chlorofluorocarbon Fluids in the Cleaning of Oxygen and Aerospace Systems and Components, ASTM STP 1181, 1993, pp. 37 - 48.

Verification of Surface Preparation for Adhesive Bonding

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Abstract

A survey of solid rocket booster (SRB) production operations identified potential contaminants which might adversely affect bonding operations. Lap shear tests quantified these contaminants' effects on adhesive strength. The most potent contaminants were selected for additional studies on SRB thermal protection system (TPS) bonding processes. Test panels were prepared with predetermined levels of contamination, visually inspected using white and black light, then bonded with three different TPS materials over the unremoved contamination. Bond test data showed that white and black light inspections are adequate inspection methods for TPS bonding operations. Extreme levels of contamination (higher than expected on flight hardware) had an insignificant effect on TPS bond strengths because of the apparent insensitivity of the adhesive system to contamination effects, and the comparatively weak cohesive strength of the TPS materials.

INTRODUCTION

Contamination control is one of the most crucial elements of a bonding system or process. Contamination is the presence of a foreign material on a bonding surface or in an adhesive and can prevent a bond from holding two materials together at full strength. Good, reliable bonds are important in aerospace applications, such as applying TPS to launch vehicles.

The accuracies of current surface inspection methods have been questioned due to variability among operators and a lack of specific data for defining surface conditions. Examination of these criticisms indicated that inspection operations may benefit greatly with automated methods. New inspection techniques, which yield a quantitative surface description, might provide a measurable standard for process improvement and bond reliability.

Critical evaluation of current inspection methods is necessary before evaluating a new inspection system. The objective of this program was to characterize the existing contamination controls for USBI bonding processes by identifying potential contaminants, determining their effects on bonds, and assessing the accuracy of current inspection techniques to detect these contaminants which jeopardize good adhesive bonding.

APPROACH

The program was carried out in three major steps: (a) identify specific contaminants that could be introduced into a bonding process, (b) establish the contamination level of these contaminants that will degrade adhesion, and (c) assess capability of current inspection methods to reject potential unsatisfactory levels of contaminants.

USBI uses bonding processes that may be placed in four distinct groups: thick film spray, thin film spray, trowelled, and fayed (closely fitted) surfaces. Generic methods for identifying potential contaminants and to study process sensitivity were based on three of these processes. Painting (a thin-film spray) was omitted from the test plan, because (for the SRB) hardware processed in this manner does not sit around unprotected. It is a continuous process. Examples of the other three processes include: MSA-2 (thick film), BTA (trowelled), and cork bonding (fayed). Experience gained from problem reports showed that it was necessary to identify contamination caused by the process itself and its assigned work area, and to track down *opportunistic* contamination (i.e., contamination that comes from random exposure to uncontrolled events).

Once potential contaminants were identified, a laboratory study was performed to quantify the effects of bondline contamination using lap shear coupons in a controlled environment. This identified the critical contaminants which actually have a significant effect on bonding using the adhesive from the processes under study.

Next, test panels with controlled amounts of contamination were produced for processing with selected TPS application techniques. The panels were inspected by two commonly used techniques—visual with white light and visual with black light. Inspections were performed by Quality personnel (inspectors). Each contaminant was applied at several levels so that the associated effects may be assessed. Normal bonding operations were performed and the contamination effects on bond adhesion in the process environment were evaluated. Water break-free testing was omitted from the test plan because (for the SRB) this inspection is typically done prior to Alodine treatment and prior to painting, which was not evaluated.

RESULTS AND DISCUSSION

Contaminant Identification

As many potential contaminants as possible were identified in an audit of the USBI SRB processing facility in the operating areas where bonding processes are being executed. Thirty-one contaminants identified in the audit were categorized into three groups: facility, process, and opportunity. Facility contaminants are those generated from installed or permanent fixtures in the processing area. Process contaminants are those from the materials in the process itself. The final group of materials are contaminants of opportunity, materials which reach the process area through auxiliary tasks, or the personnel working in or passing through an area. This last group is often the hardest to track when processing problems occur as they tend to occur intermittently. A broad range of credible contaminants, which are typical of any aerospace hardware processing facility, were identified (e.g., oils and greases, cosmetics, cleaners, insect repellents, etc.) A listing of the 31 materials identified by the survey is presented in table 1.

Facility contaminants were monitored using practices common to the aerospace industry. Standard nonvolatile residue (NVR) plates were deployed as *witness* panels in the major processing areas in Florida. These panels were exposed for 48 days at two different times. The residue from each plate was analyzed to determine a deposition rate and chemical composition. The deposition rates ranged from a low of 0.088 mg/ft^2/month, to a high of 0.239 mg/ft^2/month. This compares favorably with a maximum deposition rate of 1.0 mg/ft^2/month which is the limit for the most tightly controlled payload processing clean rooms. Chemical analysis was performed by gas chromatography and Fourier transform infrared spectroscopy. Two significant peaks were found in the residue. The largest was methyl isobutyl ketone (MIBK), a component of an SRB paint system. The second was ethylene glycol. Even though the deposition rate for these two compounds did not indicate cause for concern, they were added to the potential contaminant list for testing. That they made up an overwhelming majority of the residue, suggested that we should evaluate the effects of large localized deposits which could be a plausible occurrence through facility or process upsets.

Residues which can pass from one processing step to the next were the next major group to be identified. Tape and vacuum bag sealant residue from masking, bonding, and other operations have proved difficult to locate and remove. Residue from incomplete removal of corrosion preventive grease, an ultrasonic coupling agent, and a specialty aluminum detergent were targeted because the ability to detect their presence in follow-up inspections is undocumented. Incorrect use of conversion coatings may leave a powdery surface with poor adhesion characteristics, so that material was added to the list.

Contaminants of opportunity are materials which do not have a documented presence during the normal operation of the facility and process. These materials may come from maintenance activities, leaks or system failures, or personnel working in the area. Four different oils and greases were identified which are normally used in routine equipment maintenance and which could drip or otherwise be transferred to hardware in process. Gloves are not required in all of the processing areas, making fingerprints, hand cream, uncontrolled water, and insect repellent all potential contaminants from personnel. Aerosol sprays (e.g., insecticide, insect repellent, and various cleaners) are suspect contaminants due to a lack of control of their use around hardware. The best method found for identifying these types of items was an informal survey of the personnel tool chests and storage in the processing areas. A second survey of the logistics areas, to determine what materials were available to personnel on an unrestricted basis, also proved beneficial.

Table 1 Contaminants

Contaminant Source	Identified Potential Contaminants
Facility	Ethylene glycol Diesel exhaust MIBK
Process	Perchloroethylene Vinyl tape GS-37 sealant Distilled water Masking tape Rymple cloth Airtec 23 cleaner Conoco grease Paper tape Echo ultragel II 1,1,1 Trichloroethane Alodine 1201
Opportunity	Fingerprints Anchorlube 6-771 Siloo glass cleaner Wasp Killer Bard skin care cream Vacuum pump oil Spray Nine cleaner Sea water Insect repellent Pennzoil EP grease 302 Breathing mask towellette Tapwater Drop dead insecticide Skin So Soft Perspiration Chain and cable fluid

Contaminant Dispersions Method

Contaminant sensitivity testing required a methodology for controlled contaminant application. With an accurate deposition technique, the level or coating weight (mg/ft^2) at which contamination begins to affect bonding may be determined. Acceptable application requires the ability to apply a uniform layer of the contaminant to the test coupons and panels. Through a review of literature, it was determined that an air brush technique using serial dilutions of the contaminants would produce the best results. With this technique, predictable, repeatable levels of contamination were produced. Contaminant levels were determined gravimetrically using clean aluminum foil as a witness surface. Some items such as tapes, sealants, solvents, fingerprints, and different types of water were applied at 100 percent by weight to simulate process conditions. Other contaminants were diluted in solvents and air brushed.

Lap Shear Sample Preparation

A bonding test method had to be selected from which to determine contamination effects. The method would test bonds containing controlled levels of contamination. It was necessary to screen the contaminants in the lab because of the large number, various levels of interest, convenience, and cost. The failure mode of greatest concern for the processes under study is in the shear direction. For this reason lap shear bond testing (per American Society for Testing and Materials (ASTM) D 1002) was chosen as our evaluation method. The adhesive used was EC 2216 two-part epoxy from 3M Corporation. Dedicated control coupons, as well as control specimens adjacent to the contaminated specimens used on each contaminated coupon, provided confidence in the lap shear data.

Theoretically, there are two threshold contaminant weights [mg/ft^2] of interest for each contaminant: (a) the minimum contaminant weight (cw_{min}) (not detected by current inspection techniques) to affect lap shear strength, and (b) the maximum contaminant weight (cw_{max}) (not detected by current inspection techniques) to affect lap shear strengths. A given contaminant may exhibit both, one or none of these defined weights for a given bonding process. In practice, these defined coating weights were not well defined points.

Lap Shear Results (Laboratory)

Each potential contaminant in table 1 was tested in the lap shear study, except 1,1,1 trichloroethane, which was found clean from the gas chromatograph results, and perspiration, for which a consistent supply had not been located.

The 31 contaminants were sorted into three groups defined by sensitivity (i.e., strength loss per coating weight). The three groups are presented in table 2.

Not all potential contaminants could be used in the process testing phase, since the program would have become unwieldy. Thus, based on the lap shear results, seven contaminants with the largest effects were chosen to be used.

Preliminary black light and white light inspections were used to determine detectable levels of coating weights to be used in the process testing. The preliminary inspections were carried out by M&P technicians. Yes and no ratings were used if the contaminant was either observed or not in the lab on white test panels, a preliminary pass or reject rating.

Preliminary inspections performed in M&P labs were similar to Quality inspection of hardware (i.e. panels were not handled and viewing angles were not lighted in optimum conditions).

Hardware Process Sensitivity Study

At USBI, bonding processes may be placed into four distinct groups: thick film spray, thin film spray, trowelled, and fayed (closely fitted) surfaces. Several TPS bonding processes were selected to evaluate contamination effects: the bonding of MSA-2, BTA, and cork. MSA-2 is a two-part epoxy, EC-2216, loaded with solvents and fillers, and is a thick film spray. BTA is filled EC-2216 epoxy and trowellable. Cork is bonded with EC-2216, applied to both surfaces and vacuum bagged, and is a faying surface application. Paint application was omitted from the test plan.

The seven most deleterious contaminants were chosen for testing on the selected TPS application processes. They were masking tape, vinyl tape, ethylene glycol, Conoco grease, Spray Nine cleaner, vacuum pump oil, and Skin So Soft. These materials were selected because of their effect on lap shear strength loss (most deleterious).

The levels of contamination used for the TPS bonding study were determined by the lap shear testing. Based on the threshold criteria (when available) for the lap shear results, levels were chosen to span and enter this contamination range. For example, if a particular contaminant caused a loss in lap shear strength at a given coating weight and was not visible under black or white light, then coating weights lighter and heavier and at that weight were applied on the large test panels for analysis.

Table 2 Contaminant Sensitivity

Material	Reason for Omission in Process Testing
Very Sensitive (Loss per weight range 0.3-21 %/mg/ft²)	
GS-37	Not applied directly to substrate in production
Vinyl tape	(Tested)
Masking tape	(Tested)
Paper tape	Similar to vinyl tape
Perchloroethylene	Perc had broken down, full strength
HD Conoco grease	(Tested)
Pennzoil EP grease	Similar to Conoco
Breathing mask towelette	Not realistic[1]
Echo Ultra Gel II	Not used after painting
Exhaust, Diesel	Small effect at full strength
Sensitive (Loss per weight range 0.008-0.2 %/mg/ft²)	
Skin care cream	Difficult to atomize
Vacuum pump oil	(Tested)
Skin So Soft	(Tested)
Spray Nine cleaner	(Tested)
Drop Dead	Small effect at full strength
Ethylene glycol	(Tested)
Seawater	Not realistic[2]
Wasp Killer	Similar to Drop Dead
Deep Woods Off	No longer used at FL Ops
Chain & cable lube	Low loss/weight
Not Very Sensitive (Strength loss negligible)	
Airtec 23 cleaner	
Alodine 1201	
Anchorlube	
Distilled water	
Fingerprints	
MIBK	
Rymple cloth extract	
Siloo glass cleaner	
Tapwater—FL	

1—Breathing mask towelette residue would not come in direct contact with flight hardware.
2—Seawater would not come in contact with flight hardware after refurbishment.

Note: Throughout this paper, strength losses are designated by negative numbers.

Several differences exist between the lap shear and TPS process bonds. Surface finishes are different: bare etched aluminum for the lap shear coupons and sanded epoxy paint for the process test panels. Mechanical testing was lap shear versus flatwise tensile for the process TPS materials. Lap shear testing was aluminum bonded to aluminum, and process panels were TPS bonded to epoxy paint. Methods of adhesive application and cure schedules differed between the two studies. Epoxy adhesive EC-2216 was common to both lab and process studies.

Sixty 2-by-2-foot painted aluminum panels were contaminated and then bonded with MSA-2, BTA, and cork, i.e., 20 panels of each TPS material. Each panel that was contaminated received only one contaminant coating weight. Standard technical procedures (STPs) were followed during fabrication, with the exception of adding a contaminant to the painted aluminum panel surface that was to be bonded. The process consisted of sanding the panel,

applying the contaminant in a predetermined pattern (allowing for uncontaminated control areas), inspection of the panels by Quality inspectors using black light and white light, applying TPS materials, curing, then sectioning and surfacing specimens for flatwise tensile testing.

Contaminants were sprayed in one of nine patterns on each contaminated panel. Areas had to be left uncontaminated on the panels for control purposes. These control areas were masked by aluminum foil, which were used as witness foils to calculate actual panel coating weights. Some panels did not receive any contamination and were also used as controls. Different contaminant patterns were selected, so that Quality inspectors would not catch on to any one pattern when looking for contamination, thereby giving inspectors a significant advantage of finding any contamination. Contaminants were feathered in each case, thus not giving inspectors other visual advantages. Contamination is much easier to spot when there is a definite line of demarcation.

Each panel was inspected by two groups of two Quality inspectors, using both black light and white light. One group would inspect a panel with white light and black light at different times, then the other inspectors would do the same. Each inspector would not know the outcome of any previous inspections since the order of inspecting the 60 panels was changed for each inspection. Inspection results were quantified. During the inspection, each inspector was asked to map out the contamination (on Quality evaluation sheets) that could be seen. Thus, for each panel there existed four maps, two with black light results and two with white light results. These inspection results were compared to the actual contamination pattern. If the inspector found all the contamination, the inspection map received a rating of 10. If the inspector did not see any of the contamination, the inspection map received a rating of 0. Results in between were judged by percent of contamination found and received integer ratings of 1 through 9. Inspectors were not allowed to handle the panels, and used lighting identical to that used when inspecting flight hardware. The inspectors were requested to not clean off the contamination found.

Presented in figures 1 and 2 are the detectability of the contaminants on the TPS test panels using white and black light, respectively, as a function of contamination weight. Tape residue contamination is not included in these figures. From figure 1, white light effectiveness begins in the 30 to 60 mg/ft^2 range regardless of contaminant type, excluding ethylene glycol. This range is identified by the two vertical lines. From figure 2, black light was effective at lower coating weights (approximately 15 mg/ft^2) in some cases, but not fully reliable until higher weights are applied (approximately 95 mg/ft^2), denoted by the vertical line. The scatter in this figure is due to the fact that black light effectiveness is dependent on the fluorescent properties of the contaminant.

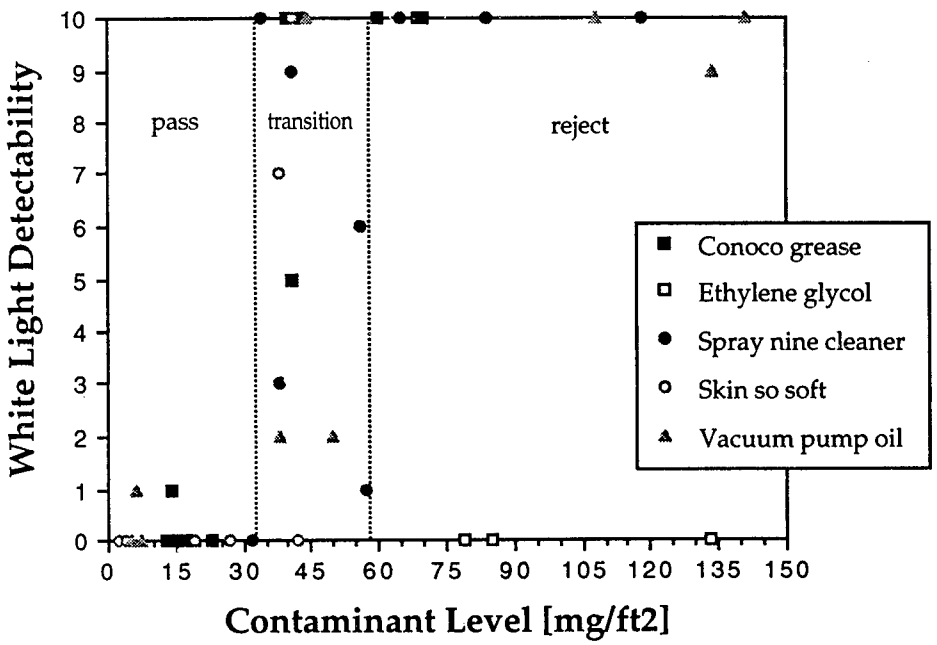

Figure 1 White Light Inspection Results

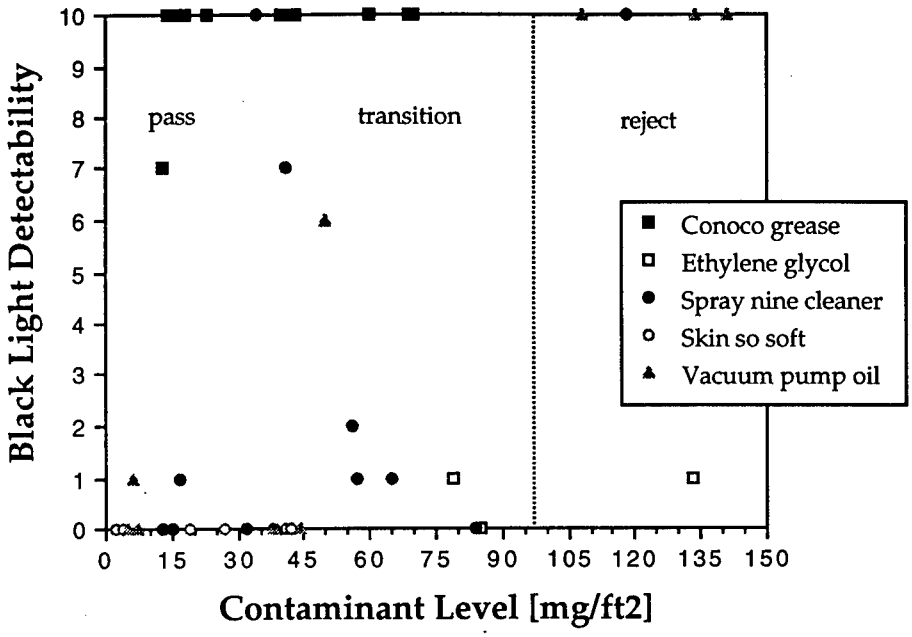

Figure 2 Black Light Inspection Results

Strength Testing

Upon completion of the inspection of the sixty panels, TPS materials were applied to the contaminated panels then bonded and/or cured. The panels were then cut into 2-by-2-inch squares or coupons for flatwise tensile testing (FWT) to evaluate any contamination effects.

To eliminate unnecessary mechanical testing, the highest level of contamination for each contaminant and each TPS material was pulled first. It was hypothesized that if no contamination effects were observed at the highest levels of contamination for all the contaminants, then further testing at lower levels of contamination would not be necessary.

From each contaminated test panel there were four control and six contaminated test specimens cut out and FWT tested. From each control panel there were 10 control test specimens cut out and FWT tested.

MSA-2

The FWT strength data generated on MSA-2 does not support any significant contamination effect. Little or no effect was observed by the contaminants on MSA-2 bonding. Three panels may have exhibited small effects: ethylene glycol (-5.3 ±3.3 percent), vacuum pump oil (-8.0 ±3.6 percent), and Skin So Soft at 19 mg (-4.1 ±7.4 percent). However, Skin So Soft did not show an effect on the one panel at higher contamination (i.e., 38 mg). All failures were substantially above design requirements, 75 psi individual minimum, and 85 psi average. Another way to analyze the data is to compare the average contamination data for each panel (since the contaminated data is more widely distributed spatially than the control areas on the contaminated panel), to the control averages on the two control panels, 143 psi and 150 psi or 147 psi average. Here four contaminated panels pulled less than 147 psi: Skin So Soft (38 mg) at 136 psi, ethylene glycol at 143 psi, Spray Nine cleaner at 145 psi, and Conoco grease at 139 psi. Only one of these panels, when compared to its own control areas, showed a strength loss: ethylene glycol (-5.3 ± 3.3 percent).

BTA

Four panels may have produced small loss effects: Skin So Soft (-5.7 ± 3.6 percent), Conoco grease (-6.1± 7.8 percent), masking tape (-4.0 ± 1.5 percent), and vinyl tape (-4.5 ± 1.5 percent). BTA FWT strengths tended to be

randomly distributed over the panels, probably mostly due to material inhomogeniety, and varying combined failure modes. All failures were substantially above design requirements (i.e., less than 100 psi).

Comparison of the average contamination data for each panel to the control averages on the two control panels, 1,475 psi and 1, 140 psi or 1,308 psi average, showed no effect. Only one contaminated panel pulled less than 1,308 psi: Conoco grease at 1,283 psi. Six out of the seven contaminated panels produced small losses in strength when compared to the smaller control areas.

Sheet Cork Bonded with EC-2216 Epoxy

Four out of the seven contaminated panels produced small losses in strength when compared to the control areas, three of these four are ethylene glycol (-7.3 ± 4.2 percent), masking tape (-4.5 ± 6.4 percent), and vacuum pump oil (-3.2 ±3.7 percent). Standard deviation for the masking tape control specimens was 6.4 percent, greater than the 4.5 percent loss. Ethylene glycol and vacuum pump oil controls were the strongest pulled, thus making any loss comparison extra sensitive. These small decreases are believed to be due to cohesive strength variations in the cork sheet and not contaminant effects, because of the cohesive failure modes. All failures were substantially above design requirements (i.e., greater than 50 psi). Comparison of the average contamination data for each panel to the control averages on the two control panels, 161 psi and 167 psi or 164 psi average, showed little effect. Only two contaminated panels pulled less than 164 psi: masking tape at 150 psi and Skin So Soft at 160 psi. Since the cork pulled cohesively, it is believed that the strength variations are in the cork sheet.

Comparison of Inspection Results and TPS Panel FWT Results

Presented in table 3 is a summary of the inspection results and associated strength losses for each contaminant at the highest applied coating weights. The reported percent contamination detected indicates the amount of contaminant coverage detected of that actually present. It was anticipated, from lab testing, that each of these coating weights would have been 100 percent detected by either black light, or white light, or both. This did not occur and cw_{max} was not reached for ethylene glycol and Skin So Soft. Theoretically, higher coating weights may cause significant strength losses where detectability is unknown for these particular contaminants.

Vinyl tape residue (tape dwell—48 hours) was detected by black light and not by white light. Black light inspectors found 87 percent of the tape residue coverage. Operator variability was observed here. Only one of the six black light inspections failed to find 100 percent of the residue. On this panel, one inspector found 100 percent of the residue and the other inspector found 60 percent of the residue. This particular panel had a strength loss of 1.7 percent.

Vacuum pump oil was detected by black light and white light. On the three panels with coating weights of 108 mg/ft^2 and greater, 100 percent of the oil was detected with black light and 97 percent with white light. Strength losses for the panels with coating weights of 108 mg/ft^2 and greater were, -8 percent, and -3.2 percent. Only one of the six white light inspections failed to find 100 percent of the oil residue. On this panel, one inspector found 100 percent of the residue and the other inspector found 70 percent of the residue. This particular panel had a strength loss of -8 percent.

Spray Nine cleaner was detected by white light and not black light. White light inspectors found 100 percent of the cleaner residue on panels with coating weights 65 mg/ft^2 and greater. Strength loss for the panel with a coating weight of 84 mg/ft^2 was -1.9 percent.

Skin So Soft was partially detected by white light and not by black light. White light inspectors found 57 percent of the Skin So Soft residue on panels with coating weights of approximately 40 mg/ft^2. One panel had 100 percent detection by two inspectors, the second panel had 0 percent detection by both inspectors, and the final panel had 100 percent and 30 percent detection by the two inspectors. Strength loss for the one panel was -5.7 percent. Significant operator variability was observed here.

Masking tape (natural rubber on paper) residue, if present, (tape dwell 48 hours) was not detected by either white light or black light. Panel strength losses were small (i.e., -4 percent and -4.5 percent).

Table 3 Inspection and FWT Results for Highest Contamination

Contaminant	Coating Weight	TPS	% Contamination Detected BL	% Contamination Detected WL	Strength Loss
Conoco Grease	60	MSA-2	100	100	NSD
	69	Cork	100	100	NSD
	70	BTA	100	100	-6.1%±7.8%
Vinyl Tape	NA	MSA-2	60	10	-1.7%±3.9%
	NA	BTA	100	0	-4.5%±1.5%
	NA	Cork	100	0	NSD
Vacuum Pump Oil	108	BTA	100	100	NSD
	134	MSA-2	100	90	-8%±3.6%
	141	Cork	100	100	-3.2%±3.7%
Spray Nine Cleaner	57	Cork	10	10	-1.8%±4.8%
	65	MSA-2	10	100	NSD
	84	BTA	0	100	-1.9%±6.3%
Masking Tape	NA	MSA-2	10	10	NSD
	NA	BTA	0	0	-4%±1.5%
	NA	Cork	0	0	-4.5%±6.4%
Ethylene Glycol	79	BTA	10	0	-0.4%±5.4%
	85	MSA-2	0	0	-5.3%±3.3%
	133	Cork	10	0	-7.3%±4.2%
Skin So Soft	38	MSA-2	0	70	NSD
	41	Cork	0	100	NSD
	42	BTA	0	0	-5.7%±3.6%

NSD no significant difference

Ethylene glycol, up to coating weights of 133 mg/ft^2, was not detected by either black or white light. Panel strength losses were -0.4 percent, -5.3 percent and -7.3 percent.

Conoco grease was easily detected by white and black light. White and black light inspectors found 100 percent of the grease residue at coating weights of 60 mg/ft^2 and greater. Panel strength loss at this level was -6.1 percent for BTA.

Out of all the possible combinations of the seven most deleterious contaminants and the three TPS applications (i.e., 21 combinations), four bond losses were observed at contamination levels that were not detected by black light or white light. These are shown in table 4.

Table 4 Undetected Contamination Causing Strength Loss

Contaminant/TPS	Control Strength (psi)	Contamination Strength (psi)	Requirement	Percent Adhesive Failure	Comment
Ethylene Glycol/ MSA-2	155	147	75	Fuzz at Surface	Typical cohesive failure
Ethylene Glycol/ Cork	191	177	50	0	Failure in cork not related to contamination
Skin So Soft/BTA	1,470	1,386	100	0	Failure in BTA not related to contamination
Masking Tape Residue/BTA	1,494	1,434	100	50	

CONCLUSIONS

Based on the results of this study, undetected surface contamination from credible sources is not a significant concern with existing SRB TPS processing operations. The epoxy resin system used is sufficiently resistant to a wide range of potential contaminants. Failures were predominantly cohesive and not at the TPS-contaminated substrate interface. In this study, MSA-2, BTA, and cork performed over and above FWT requirements at reject contamination levels. MIL-STD-1246 NVR levels (less than 25 mg/ft^2) are not significant to the lap shear and TPS bonds evaluated in this study. The residue levels found on the two different sets of NVR plates, which were removed from USBI FL Ops, were well below shuttle processing facilities requirements (1.0 mg/ft^2/month). Contamination levels used in this study were much higher than that anticipated on cleaned hardware, a conservative approach.

Contamination effects were insignificant on the MSA-2 panels. The contaminated MSA-2 panels still pulled well above the design minimum. Contamination effects were not effectively realized due to the relatively low cohesive strength of MSA-2.

Some contamination effects were observed on BTA applications, with very small losses in strength. Contamination effects were realized probably due to the higher inherent cohesive strength. Such contaminated BTA strengths were still way above design minimums.

Surprisingly, cork bonding apparently resisted all contamination effects. Like MSA-2, cork is relatively weak cohesively, which explains the lack of sensitivity to contamination affects. All failures were consistently cohesive.

The inherent weakness of SRB TPS materials makes this class of materials less sensitive to surface contamination effects when compared to lap shear testing. For a purely adhesive TPS failure, a contaminant would have to effectively repel the TPS material or bonding adhesive so that it could release at a level below the cohesive strength of the TPS system, which is *much* lower than the design of the adhesive bond system. As a result, the lap shear test revealed more information concerning contamination effects.

New detection methods are not warranted for these three materials based on the magnitudes of bond loss, (i.e., -4 to -6 percent), the high levels of contamination (greater than 42 mg/ft^2), and the low FWT strength requirements.

Spectroscopic Ellipsometry as a Sensitive Monitor of Materials Contamination

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Abstract:

Spectroscopic ellipsometry is demonstrated to be extremely sensitive to contamination layers in the thickness range from 0.1 nm to 10 microns. In the present experiments we deposit either a thin lubricating oil (WD-40) or mineral oil continuously onto Ir, Cu, Al, Au, and V substrates from a bubbler, and monitor its thickness growth from sub-nanometer to tens of nanometers as a function of time. Re-evaporation of contaminant oils is also monitored in real-time by ellipsometry.

Introduction:

Ellipsometry at one wavelength has been used for many years to determine thickness of SiO_2 on Si for example. Recently spectroscopic ellipsometry has been developed in which a wide spectral range enhances the analytical power of the instrument enormously. Secondly, spectroscopic ellipsometers can now be built which acquire data extremely rapidly. For example, the JA Woollam Co. "M-44" ellipsometer acquires data at 44 simultaneous wavelengths in approximately 40 msec. Thus one can monitor processes in real-time.

NASA plans to launch an X-ray telescope using Iridium metal surfaces for mirrors. Extremely thin layers of contaminants will have an enormous effect on the performance of the telescope. This paper demonstrates the sensitivity of spectroscopic ellipsometry to contaminant layers as thin as 0.1 nm (and as thick as 10 microns).

Ellipsometry uses polarized light incident at an oblique angle (typically 70° to the normal) to the material under study. The reflected light polarization state is analyzed to determine the thickness, composition and properties of the film under study. Spectroscopic ellipsometry has been used on multilayer materials to determine thicknesses and compositions of ten and more layers. Thus it is an extremely powerful thin film diagnostics tool.

Experiment:

Substrates used in these experiments were prepared by magnetron sputter deposition from high purity targets of the elements Ir, Cu, Al, Au, and V. These films were approximately 100 nm thick, great enough that the films were considered to be "optically thick"; that is, light could not penetrate through to the silicon substrate.

The oils used in this experiment were WD-40 (a general purpose light lubricating oil) and mineral oil. These oils were deposited onto freshly prepared thin-film samples by bubbling air through a beaker containing the oil as shown in Figure 1. The bubbler worked by flowing clean air into a beaker of oil through a piece styrofoam with several pinholes in it to produce small bubbles. The air suspended oil

was then transported to a sample while an ellipsometer continuously acquired data. This provided real time data from which the optical properties and thickness of the deposited oil were determined. A variable angle spectroscopic ellipsometer (VASE) was used to monitor the growth of mineral oil on Ir, Cu, Au, and Al; and a 44 wavelength fixed angle ellipsometer was used to monitor deposition of WD-40 on V. A WYKO Rough Surface Tester was also used to try to see evidence of contamination of the samples before and after the WD-40 oil depositions.

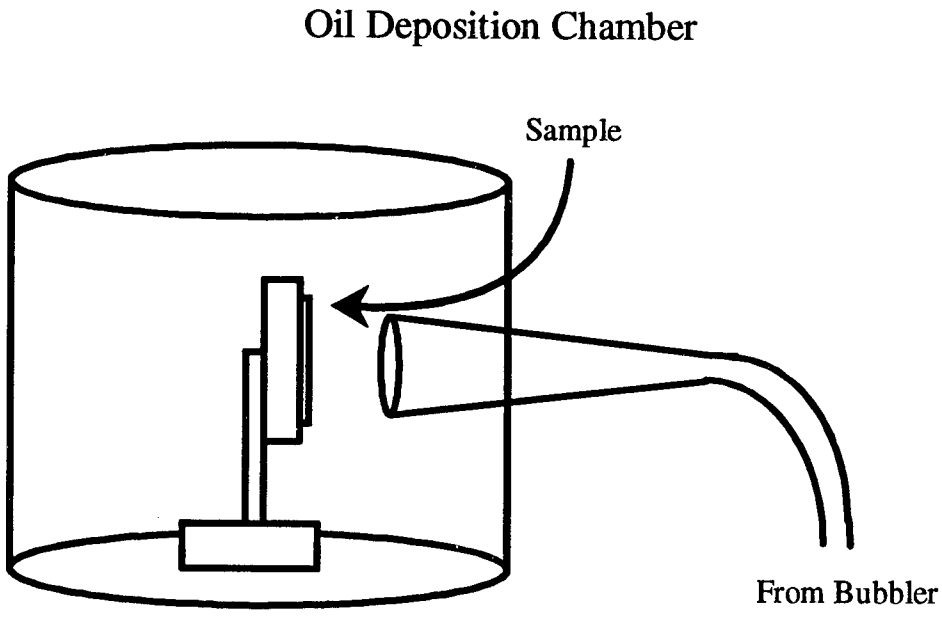

Figure 1. Oil deposition chamber that mounts on the ellipsometer.

Results and Discussion:

The optical constants for the mineral oil were found by depositing 50 nm of oil on Al and then taking VASE data at three angles of incidence. The data fits and optical constants are shown in Figures 2, 3, and 4. A Cauchy dispersion model was used to model the optical constants. These optical constants were then used while monitoring the growth of thin films of mineral oil on Ir, Au, and Cu. The film growth in some cases was not strictly linear in time due to insufficient control of the air flow rate. Spectroscopic ellipsometry data measured during growth showed the film thickness increasing slowly on a sub- monolayer scale. The depositions on Ir and Au were observed as the films grew from 0 nm to around 3 nm (Figure 5 and Figure 6), and the film on Cu was observed as it grew from 0 nm to 8.5 nm (Figure 7).

The bulk optical constants for WD-40 oil (Figure 8) were found by taking ellipsometry data on the oil in a beaker. When using these constants for the oil films, 13% void had to be added in an effective medium mixture model to get good fits to the data. This is likely due to some air being trapped in the film as a result of the bubbler acting as an aerosol. When the bubbler was turned on, a thin layer of oil was rapidly deposited on the Vanadium sample. After the initial layer was deposited the growth rate slowed to around 0.007 nm/sec. When the bubbler was turned off, most of what was deposited evaporated within about one minute leaving only a small additional layer of oil on the surface. Longer depositions resulted in a thicker film being left on the sample after the flow was stopped and re-evaporation took place. Several depositions were done on the same sample so this evaporation could be observed.

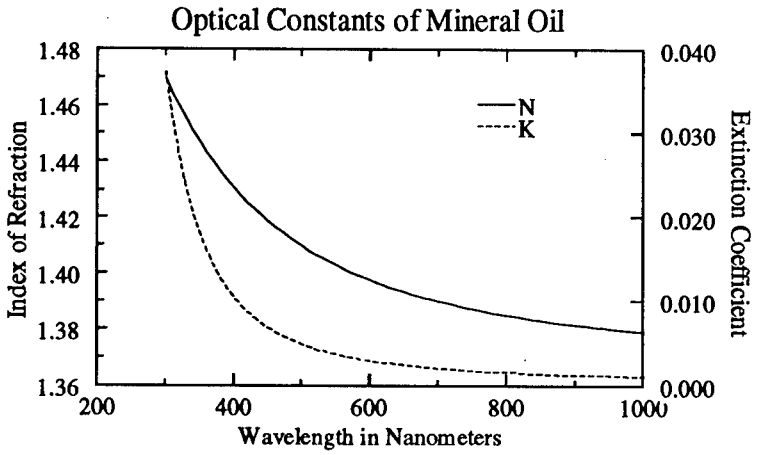

Figure 2. Optical constants of mineral oil modeled with Cauchy dispersion model.

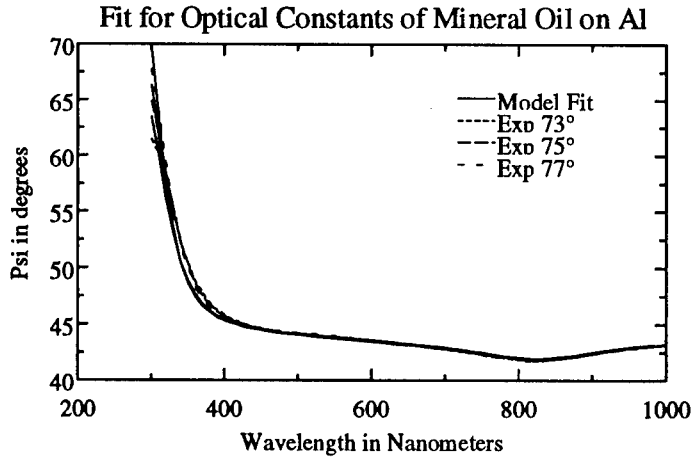

Figure 3. Ellipsometric psi data from fit for optical constants of mineral oil on Al.

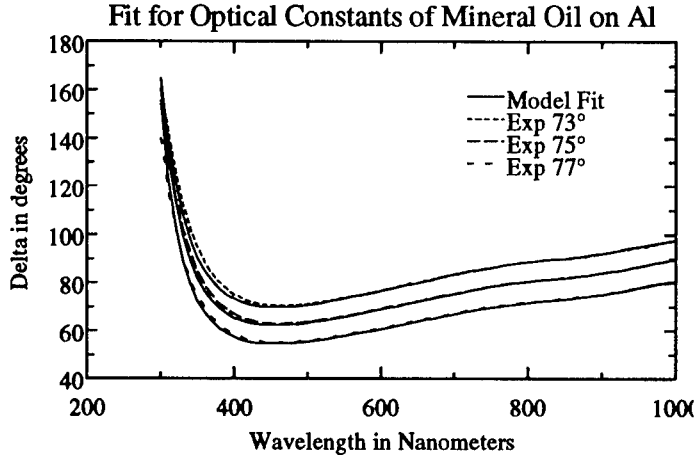

Figure 4. Ellipsometric delta data from fit for optical constants of mineral oil on Al.

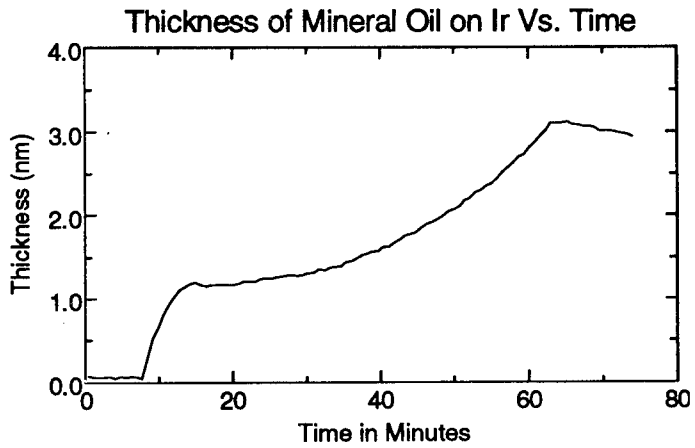

Figure 5. Thickness of mineral oil deposited on Ir thin film versus time.

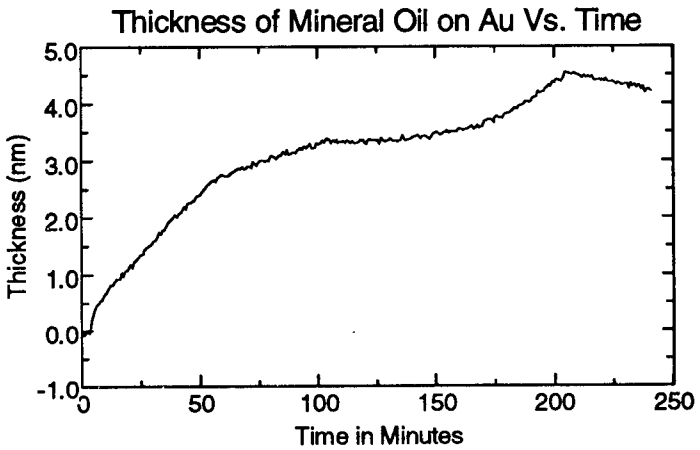

Figure 6. Thickness of mineral oil deposited on a Au thin film versus time.

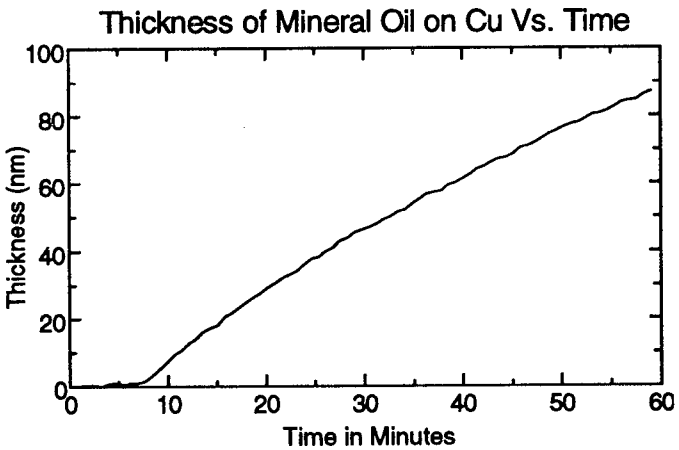

Figure 7. Thickness of mineral oil deposited on a Cu thin film versus time.

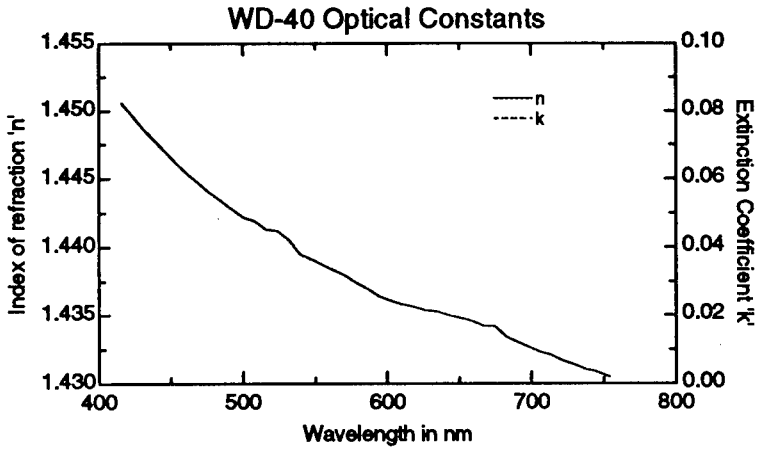

Figure 8. Bulk optical constants of WD-40 found by taking ellipsometry data on oil in a beaker.

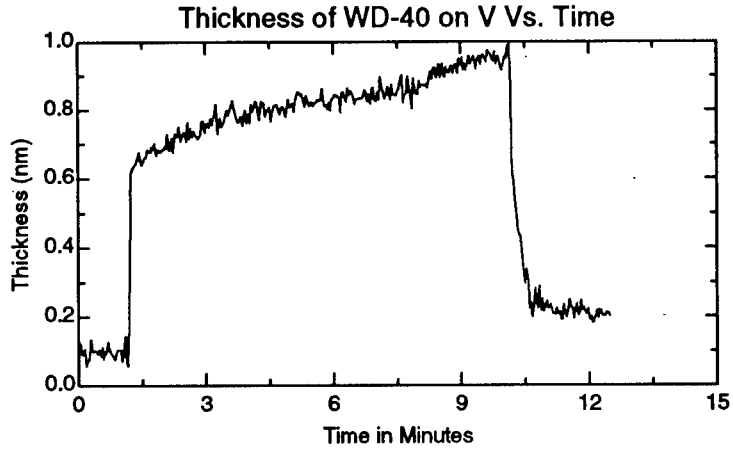

Figure 9. Thickness of WD-40 on V during second oil deposition

WYKO data were also taken before and after the depositions to observe the contamination, but no changes in surface morphology were observed. The first deposition was for 1 minute and the resulting film was only 0.1 nm thick. The second deposition was for 10 minutes, and the ellipsometric data for this deposition are shown in Figure 9. During the 10 minutes an initial film thickness of 0.45 nm was deposited before the growth rate slowed. Just before the bubbler was turned off the film thickness had reached 0.75 nm. After the bubbler was turned off, the film left on the surface was 0.2 nm thick. A third deposition was done for 20 minutes. The film thickness just before the bubbler was turned off was 1.8nm and after it was turned off the thickness was 0.6 nm. By the final deposition the thickness before the bubbler was turned off (after 4.5 hours) reached 11.5 nm and the thickness after the bubbler was turned off was 4.5 nm. Thus the oil film steady-state layer thickness grew as a function of deposition time. Likewise the post-bubbler (long-term) thickness was greater the longer the steady-state deposition was carried out.

Conclusions:

Several general conclusions can be made: these experiments demonstrate the enormous sensitivity of spectroscopic ellipsometry to levels of contamination representing less than 0.1 nm thick layers. Based on our measurements, these levels are apparently below the level detectable by the WYKO microscope. Our experiments were not carried out for long enough to determine when there was sufficient film thickness for the WYKO instrument to be useful, but based on our measurements this will be at least greater than 9 nm thickness. The ellipsometric measurement of sub-nanometer contamination involves only a beam of visible light so the surface is undisturbed. The only other technique with possibly sub-nanometer sensitivity is Auger spectroscopy, which involves use of ultra-high vacuum and small area surfaces. Auger determines the constituent contaminants but not their layer thicknesses. Ellipsometry can be set up to inspect large surface areas in any ambient environment and with sub-nanometer thickness sensitivity to contamination.

The present experiments were done using visible light. We have recently constructed a mid-infrared (2-14 micron) infrared ellipsometer which can be used to help identify contaminant species by identifying the frequency and strength of resonant-like vibrational spectra.

References:

1. J.A. Woollam and P.G. Snyder, "Variable Angle Spectroscopic Ellipsometry", book chapter in Encyclopedia of Materials Characterization, Butterworth-Heinmann Publishers, Boston, page 401 (1992).

2. J.A. Woollam, P.G. Snyder, H. Yao, and B. Johs, "In-situ and Ex-situ Ellipsometric Characterization for Semiconductor Technology", SPIE 1678, 246 (1992).

THE ROLE OF SURFACE CHEMICAL ANALYSIS IN A STUDY TO SELECT REPLACEMENT PROCESSES FOR TCA VAPOR DEGREASING

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ABSTRACT

The role of surface-sensitive chemical analysis (ESCA, AES, and SIMS) in a study to select a process to replace 1,1,1 - trichloroethane (TCA) vapor degreasing as a steel and aluminum bonding surface preparation method is described. The effort was primarily concerned with spray-in-air cleaning processes involving aqueous alkaline and semi-aqueous cleaners and a contamination sensitive epoxy-to-metal bondline. While all five cleaners tested produced bonding strength results equal to or better than those produced by vapor degreasing, the aqueous alkaline cleaners yielded results which were superior to those produced by the semi-aqueous cleaners. The main reason for the enhanced performance appears to be a silicate layer left behind by the aqueous alkaline cleaners. The silicate layer increases the polarity of the surface and enhances epoxy-to-metal bonding. On the other hand, one of the semi-aqueous cleaners left a nonpolar carbonaceous residue which appeared to have a negative effect on epoxy-to-metal bonding. Differences in cleaning efficiency between cleaners/processes were also identified. These differences in surface chemistry, which were sufficient to affect bonding, were not detected by conventional chemical analysis techniques.

1.0 INTRODUCTION

Currently, Thiokol Corporation Space Operations relies on vapor degreasing processes using 1,1,1 - trichloroethane (TCA) for precision cleaning of steel and aluminum parts of NASA's Space Shuttle Redesigned Solid Rocket Motor (RSRM). The purpose of these cleaning operations is to prepare the surfaces of the parts for adhesive bonding and external painting. Because TCA is an ozone depleting chemical (ODC) which will not be available after 1995, it has become necessary to identify alternative cleaning processes which produce adhesive-to-metal bond strengths which are at least as good as those produced by the baseline TCA process.

An effort has been made to understand the effects of the new cleaning processes on the metal surface chemistry (e.g. residues left by cleaners, effect on oxide composition and thickness, cleaning efficiency for process soils, etc.). If bonding data follow the same trends as surface chemistry, the amount of confidence one can have in such data is increased. This increases one's assurance that bond strength differences between cleaners are real and are not the result of anomalies in the bonding tests.

In this paper the use of surface chemical analysis techniques in the initial stages of a program to develop alternatives to TCA vapor degreasing is described. The analytical techniques used were electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and static secondary ion mass spectrometry (static SIMS). These methods are sensitive to changes in the top atomic layers in a surface and, as shown herein, provide unique insights into the effects of the various cleaners on adhesive bonding.

2.0 EXPERIMENTAL

ESCA, static SIMS, and AES measurements were performed at Physical Electronics Laboratories in Eden Prairie, Minnesota. The ESCA and SIMS measurements were made on a Physical Electronics Model 5600 XPS Spectrometer with a model 3700 static SIMS attachment. AES depth profiles were performed on a Physical Electronics Model 650 Scanning Auger Microprobe.

In the ESCA experiments, the sample was irradiated with monochromatic Al Kα X-radiation ($h\nu$ = 1486.6 eV) while the kinetic energies of emitted photoelectrons, from which core-level binding energies are calculated, were measured. Analyses were performed on a 4 x 10 mm rectangular area on each sample. The average analysis depth in ESCA experiments is about 30 Å, or roughly ten atomic layers. Information about surface elemental composition and chemical state (i.e. types of compounds present) can be obtained from the binding energies associated with the peaks in the spectrum.

In static SIMS measurements, an approximately 5 mm square area was bombarded with 4 keV Xe^+ ions, with masses of the resulting positive and negative secondary ion fragments measured by a quadrupole mass spectrometer. The primary ion dose used in the experiments (5×10^{12} ions/cm^2) is low enough to ensure that nearly every Xe^+ ion strikes an undamaged area of the surface and produces fragments which accurately reflect the molecular structure of the surface species. Static SIMS complements ESCA measurements and often provides more precise identification of organic compounds than is possible by ESCA alone. Static SIMS is somewhat more surface-sensitive than ESCA, with a typical analysis depth of 3 - 10 Å.

AES was performed by bombarding the surface with a finely focused 8 keV electron beam and measuring the kinetic energies of emitted Auger electrons. AES provides surface elemental compositions with a sampling depth similar to that in ESCA, but with much better lateral resolution. The electron beam can be rastered over a surface, just as in a scanning electron microscope, providing elemental dot maps and SEM micrographs. AES was used for depth profile measurements to determine oxide thicknesses. These were made by first taking a 1000 X secondary electron micrograph, an average AES scan to determine elements present, and dot maps to determine element lateral distributions. Three small (10 μm square) areas, selected to avoid areas with high levels of grit blast sand, were depth profiled by sputter etching with an Ar^+ ion beam at a rate of 30 Å/minute (calibrated against a SiO_2 film of known thickness) while AES analysis was performed on the three areas.

Metal coupons (D6AC steel and 7075 aluminum) were prepared for subsequent contamination and cleaning treatments by a standard procedure involving TCA vapor degreasing, followed by a heavy zirconium silicate gritblasting, a second TCA vapor degreasing treatment, and finally a light, "cosmetic" zirconium silicate gritblast just before processing. This procedure has been found to yield consistent, repeatable bonding characteristics. The metal coupons were processed under the same conditions as a set of bonding specimens so that surface chemistry and bond strength could be directly correlated.

The overall ODC elimination program is a cooperative venture between two Thiokol laboratories. Three-fifths of the bonding and surface analysis specimens described in this paper were processed at the Thiokol Science and Engineering (S & E) Research and Development Laboratory in

Utah, while the rest were processed at the Thiokol Huntsville Space Operations (HSO) laboratory in Huntsville, Alabama. Differences in operating parameters and how the work was divided between laboratories will be discussed later.

3.0 RESULTS AND DISCUSSION

3.1 Overview of Testing Logic

Down-select 150 → 15 cleaners. At the beginning of the program, samples of about 150 cleaners (organic solvents, aqueous alkaline cleaners, and semi-aqueous cleaners) were obtained and evaluated. Organic solvents were to be used in spray-under-immersion (SUI) cleaning processes followed by a clean solvent rinse. Aqueous alkaline cleaners or semi-aqueous cleaners can be used in a SUI process or spray-in-air (SIA) process followed by a water rinse. The initial list of 150 cleaners was reduced to 15 by such criteria as solubility of process soils (e.g. grease, oil) in the cleaners, contact material compatibility, and bonding tests. Surface analysis was not involved in this phase.

Down-select 15 cleaners/2 processes → 5 cleaners/1 process. Next, a series of bonding tests accompanied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDX), and diffuse reflectance infrared spectroscopy (DRIR) surface cleanliness measurements, was performed to evaluate the 15 cleaners (equally divided between organic, aqueous alkaline, and semi-aqueous categories) applied under both SIA and SUI conditions. The role of ESCA, AES, and SIMS surface analysis in this phase was limited to characterization of cleaner residues. This consisted of evaporating a few drops of each cleaner on aluminum foil and analyzing the residues with ESCA and static SIMS. This simple, inexpensive technique can yield a great deal of information on a cleaner. One semi-aqueous cleaner left a fluorocarbon residue (possible bonding release agent !) · Another organic cleaner left an excessively thick nonvolatile residue which was thick enough (tens of Å or more) to cause concerns about interference with adhesive bonding.

The organic solvents were eliminated from consideration because of poor cleaning efficiency for process soils (as determined by DRIR) and poor epoxy-to-metal bond strengths. SIA cleaning was demonstrated to be superior to SUI cleaning for semi-aqueous and aqueous cleaning. Five cleaners (three aqueous and two semi-aqueous) were selected for further study in SIA cleaning processes. SEM/EDX, FTIR, and DRIR did not detect differences in surface chemistry between samples which had been contaminated with process soils and cleaned with the aqueous and semi-aqueous cleaners. These tests were repeated in the next phase with the same result, i.e. all semi-aqueous and alkaline aqueous candidates cleaned process soils to levels below detection limits, and no cleaner-induced changes in surface chemistry were noted.

Down-select 5 → 2 cleaners. Here the main task was to down-select from the 5 SIA cleaners selected above to two cleaners which would be then subjected to extensive optimization studies. The semi-aqueous cleaners were Du Pont Axarel 52 Cleaning Agent and Dow Prima Clean Semi-Aqueous Cleaner. The aqueous alkaline cleaners were Brulin 815 GD, Metalube 4U Multi-Purpose Cleaner-Degreaser, and Jettacin (Diversey). Surface analysis began to find extensive application in the study at this point.

One objective of the surface analysis studies was to determine what the cleaners themselves do to the surfaces -- what residues they leave behind before and after rinsing, and their effect on oxide thickness and composition. A second objective was to make a preliminary determination of how well the cleaning processes remove soils which come into contact with the steel and aluminum bonding surfaces during RSRM manufacturing. These were Conoco HD-2 grease, which is applied to both steel and aluminum surfaces as a preservative, Magnaflux Magnaglo 20B magnetic particle premix and

Magnaglo WA-4 water conditioner, which are used in magnetic particle inspection of steel hardware, and Shell Diala oil, which is used as a pressure test fluid on steel parts.

Processing on semi-aqueous cleaners (Axarel 52 and Prima Clean) was handled by the S & E laboratory along with one aqueous cleaner (Jettacin, initially considered to be a semi-aqueous cleaner). The HSO laboratory processed the aqueous cleaners Brulin 815 GD and Metalube 4U. Processing conditions used at the S & E laboratory were a 30 % cleaner concentration in water (thought to be appropriate for semi-aqueous cleaners), 135 °F cleaner temperature, and a 70 psi cleaning/water rinsing pressure. At HSO, the parameters used were a 10 % cleaner concentration in water (thought to be appropriate for aqueous cleaners), a 135 °F cleaner temperature, a 1000 psi cleaning pressure, and a 70 psi rinse pressure. The reader should keep in mind that in the study to be described Axarel 52, Jettacin, and Prima Clean coupons were processed differently from the Brulin 815 GD and Metalube 4U coupons.

3.2 Typical ESCA, AES, SIMS Data

Figure 1 shows typical ESCA spectra for freshly grit blasted D6AC steel. The low-resolution "survey" scan, taken to determine what elements were present, shows components of the grit blast sand (Zr, Si, Ti, Ca, and Al). A high-resolution scan of the carbon (1s) region is also shown. The high resolution scans allow one to ascertain what sorts of compounds are present. High-resolution scans were taken on at least one characteristic peak of each element detected.

Figure 2 shows a typical AES depth profile (etch rate 30 Å/min) of freshly grit blasted D6AC steel with minor elements deleted for clarity. Also shown is the method of determining oxide thickness, i.e. by measuring the position of the "knee" of the iron level vs. sputter time curve. (The oxygen level never goes to zero because of the presence of embedded particles of zirconium silicate.) The oxide thickness in this case is about 50 Å.

Figure 3 shows typical static SIMS data (positive ions) for freshly gritblasted D6AC steel. These surfaces are quite clean as they exhibit mainly peaks of the metal and gritblast media.

3.3 Effect of Cleaners on D6AC Steel/7075 Aluminum (No Soils Applied)

Effect of Rinsing Failure. Experiments were performed in which the cleaners were applied to uncontaminated D6AC steel coupons using the SIA cleaning process and dried with no rinsing step. The purpose of such experiments was to determine what would happen in the event of a total rinsing failure. ESCA and static SIMS measurements were performed and ESCA results are given in Table I.

All cleaners leave significant residues (primarily carbonaceous) relative to freshly grit blasted steel. In the case of Jettacin, Brulin 815 GD, and Metalube 4U the layer is thick enough to almost totally suppress the Fe signal from the substrate. This indicates that the layer is on the order of at least tens of Angstroms thick and is likely to interfere with most adhesive bonds. In addition to the carbonaceous residues, the Axarel 52 surface contained significant levels of phosphates which probably are corrosion inhibitors. The Prima Clean coupon was visibly rusted, which may be due to the lack of a corrosion inhibitor as suggested by the ESCA data. Jettacin leaves sulfates, silicates, sodium, and an organic nitrogen species. Brulin 815 GD leaves organic nitrogen, phosphates, potassium, and silicate. Metalube 4U leaves sodium and silicates. The apparent alkaline nature of the deposits from Brulin, Jettacin, and Metalube in particular may have an adverse effect on metal-to-epoxy adhesion, not to mention corrosion problems, if the residues are not adequately removed by rinsing.

Residues Left After Rinsing. To determine what kinds of residues are left after rinsing, freshly grit blasted steel and aluminum coupons were cleaned by the SIA process, rinsed, dried, and subjected to ESCA and static SIMS analysis. (As with the unrinsed panels, the Prima Clean washed D6AC steel panel was visibly rusted.) Figure 4 shows ESCA carbon levels after rinsing as a function of cleaner for steel and aluminum, with the freshly grit blasted and TCA vapor degreased steel data shown for purposes of comparison. All of the cleaners except Axarel 52 on steel and aluminum and Prima Clean on steel leave a clean surface from a carbon contamination standpoint, with carbon levels similar to freshly grit blasted and TCA vapor degreased samples. Axarel 52, on the other hand, leaves a substantial carbonaceous deposit on both steel and aluminum which is not removed by a water rinse.

There is another significant difference between the alkaline cleaners and semi-aqueous cleaners which is displayed in Figure 5, a plot of Si/Zr ratio vs. cleaner for freshly grit blasted coupons which were SIA cleaned with the various cleaners and rinsed. The chart shows significantly higher amounts of surface silicon on coupons cleaned with the aqueous alkaline cleaners Jettacin, Metalube 4U, and Brulin 815 GD. (The Si/Zr atom ratio was plotted to eliminate the effect of variability in the amount of embedded $ZrSiO_4$ grit blasting sand on the apparent surface Si content.) High resolution ESCA scans and static SIMS analysis indicated that the excess silicon is present in the form of a silicate. The silicate levels seem to be highest for Metalube, with Brulin 815 GD the lowest and Jettacin in between, and the effect is stronger for aluminum than it is for steel.

Oxide Thickness Measurements. AES depth profiles were performed on steel and aluminum coupons which were cleaned, rinsed and dried with no precontamination, and also on freshly grit blasted controls and freshly grit blasted controls which had been TCA vapor degreased. With Axarel 52 cleaned samples, the AES dot maps revealed that the carbon coverage detected in the ESCA/SIMS results was non-uniform and "patchy" ; depth profiles were performed on "clean" areas in between the patches of carbonaceous material. The results for oxide/silicate overlayer thickness are displayed in Figure 6. The Prima Clean steel sample was visibly corroded as with the identically processed ESCA/SIMS sample above and, accordingly, the measured oxide thickness on the sample was greater than 300 Å. Apart from that, the cleaning treatments do not significantly increase the steel oxide thickness relative to the baseline TCA vapor degreasing process. With aluminum, all of the cleaners oxidize the surface somewhat, with Prima Clean having the greatest effect.

3.4 Cleaning Efficiency Studies

Cleaning efficiency studies were also performed to make a preliminary assessment of the ability of the cleaners to remove HD-2 grease from steel and aluminum, magnetic particle materials from steel, and Diala oil from steel. The contaminants were applied to the surfaces and placed into the various cleaning processes, and then subjected to a final rinse. In the case of Magnaflux materials, the steel coupons were treated with a solution of Magnaglo 20B magnetic particle premix solution and then rinsed with a solution of Magnaglo WA-4 water conditioner prior to cleaning. It must be remembered that these studies are not conclusive as to which cleaners are most efficient as each cleaner was tested under only one set of processing parameters, and the processing conditions were not the same for all cleaners.

In all data presentations on cleaning efficiency below, the results of the same cleaning/rinsing experiment on a sample with no precontamination (see section 3.3 above) are included so that the reader can judge how much of a particular contaminant can be attributed to the cleaner itself and how much is a result of unremoved soils. Comparative data on the TCA vapor degreasing process are also presented.

HD-2 Grease on Steel and Aluminum. ESCA cleaning efficiency results for HD-2 grease on steel and aluminum are shown in Figures 7 and 8. The ESCA carbon level is a measure of how much

grease is left on the surface after cleaning. None of the cleaning treatments, except possibly Axarel 52 on steel and aluminum, and Prima Clean on aluminum, completely remove HD-2 grease. With Axarel 52 on both steel and aluminum, the static SIMS spectra of the cleaned surface indicate that the carbon residues left after cleaning originate with the cleaner. The carbon levels are actually lower when a surface is precontaminated with HD-2 grease and then cleaned with Axarel 52 than when initially noncontaminated samples are cleaned with Axarel 52. The HD-2 grease overlayer may partially prevent the components of Axarel 52 from adhering to the surface. In the case of Prima Clean on steel, the sample did not rust as was observed in the case of samples with no precontamination, suggesting that the small amount of grease left behind protects the steel from corrosion.

Static SIMS spectra of HD-2 grease precontaminated/cleaned surfaces for all cleaners except Axarel 52 contained high molecular weight (60 - 100 amu) fragments which were not present in spectra of initially uncontaminated samples which had been cleaned with the cleaners and rinsed. These fragments are indicative of HD-2 grease. An extreme example of this is given in Figure 9, which shows a static SIMS spectrum for D6AC steel which has contaminated with HD-2 grease, cleaned with Metalube 4U, and rinsed, and a spectrum of pure HD-2 grease. The cracking pattern of the carbonaceous contaminant on the HD-2 contaminated, cleaned surface matches that of HD-2 grease. It does not match the static SIMS spectra of Metalube residues.

Magnetic Particle Inspection Materials on Steel. In Figures 10 and 11, static SIMS and ESCA cleaning efficiency data for magnetic particle inspected surfaces are shown. Studies of control dried samples of Magnaglo 20B and WA-4 water conditioner indicated that the residues are primarily carbonaceous, so the ESCA carbon percentage is used as a measure of surface cleanliness. The other elements found to be present in 20B particle premix and WA-4 rinse residues (B, N, Na) were effectively removed by the rinsing techniques. All cleaning treatments effectively remove the organic component (Figure 11) except Brulin 815 GD. Static SIMS spectra (Figure 10) show that the cracking pattern of the residue left after Brulin cleaning has characteristics similar to that of a pure WA-4 rinse conditioner control.

Diala Oil on Steel. ESCA showed that all cleaners effectively removed Diala oil (data not shown). In the case of Prima Clean, the cleaning was thorough enough so that the steel sample rusted. With Axarel 52, as before, the cleaner left a heavy carbonaceous deposit of its own.

3.5 Comparison with Surface Free Energy and Bonding Data

Surface Free Energy. Contact angle measurements (using a variety of liquids of various polarities) were made on initially uncontaminated metal specimens which had been cleaned with the various cleaners, rinsed, and dried. The work of adhesion W_{ad} of a liquid can be expressed in terms of contact angle θ by the Young-Dupré equation:

$$W_{ad} = \gamma_l (1 + \cos \theta) \qquad (1)$$

where γ_l is the interfacial free energy of the liquid-vapor interface. For polar systems it is also customary to express the surface free energy γ_s as the sum of a contribution from London dispersion forces (γ^d) and polar forces (γ^p). The work of adhesion is customarily expressed in terms of dispersion and polar forces in the following manner:

$$W_{ad} = 2 (\gamma_l^d \gamma_s^d)^{0.5} + 2 (\gamma_l^p \gamma_s^p)^{0.5} \qquad (2)$$

So, by combining equations (1) and (2), and using contact angle data from a wide variety of liquids of known γ_l^d and γ_l^p, the contributions to surface free energy from dispersion and polar forces can be calculated.

Figure 12 shows the polar contribution to the surface free energy γ_s^p for initially uncontaminated steel and aluminum surfaces which have been cleaned with the cleaners and rinsed. Data from freshly grit blasted surfaces, and surfaces which have been TCA vapor degreased, are included for comparison. It is seen that the semi-aqueous cleaner Axarel 52 produces a highly nonpolar surface for both steel and aluminum, probably as a result of the carbonaceous residue the cleaner leaves behind. TCA vapor degreasing also lowers the surface polarity relative to freshly grit blasted material. The aqueous cleaners Jettacin, Brulin, and Metalube increase the surface polarity, most likely due to the increased silicate content. For a polar adhesive such as an epoxy, we might expect the adhesive to wet the Jettacin, Brulin, and Metalube surfaces better, resulting in better bond integrity, while with the Axarel 52 cleaner we might expect less efficient wetting and poorer epoxy-to-metal adhesion performance.

Adhesion performance tests. Most bonding tests were concerned with bond strength of Hysol EA-913NA epoxy adhesive to gritblasted D6AC steel or 7075 aluminum bondlines. These bondlines are much more sensitive to contamination than others on the RSRM. Bonding tests on more robust bondlines (e.g. NBR rubber-to-metal) cleaned with the five cleaners tended to fail cohesively in the rubber. The EA-913NA to metal bondlines, as expected, proved to be much more sensitive to changes in surface chemistry as shown below. Tests conducted on these were fracture toughness (tapered double cantilever beam or TDCB) and tensile adhesion. Only fracture toughness results on samples which had been contaminated with HD-2 grease, cleaned, and then rinsed will be presented. Tensile adhesion tests generally showed the same trends, but the differences were less pronounced. Fracture toughness is a more discriminating test for this type of system.

Figures 13 and 14 show the EA-913NA bond strength results for steel and aluminum along with results from HD-2 contaminated/TCA vapor degreased surfaces and data from freshly gritblasted surfaces with no grease contamination. All five cleaners perform as well as or better than the baseline TCA process for these bondlines, with the aqueous cleaners (Jettacin, Brulin 815 GD, and Metalube 4U) outperforming the semi-aqueous cleaners Axarel 52 and Prima Clean. (Note: in current practice the EA-913NA to metal bondlines receive a post-clean grit blast prior to application of the adhesive, so the relatively poor bond strength of the TCA vapor degreased specimens is not characteristic of flight hardware. Also, the relative performance of the TCA vapor degreased specimens in tensile adhesion tests is better than in the fracture toughness tests.)

The enhanced performance of the aqueous cleaners correlates with the high surface polarity, which in turn is probably caused by the silicate layer left by the cleaners. This enhancement yields higher bond strengths than a freshly grit blasted surface, and occurs despite the presence of residual HD-2 grease as detected by ESCA and static SIMS. Axarel 52, which creates a nonpolar surface as a result of the carbonaceous residues it leaves behind, does not perform as well as the aqueous cleaners. It was found that a post-clean grit blast to remove the residues was necessary to achieve high bond strengths with Axarel 52. With the aqueous cleaners, on the other hand, a post-clean grit blast actually reduced bond strength. This reduction probably occurs because of the removal of the cleaner-induced silicate layer, which apparently has beneficial effects on epoxy-to-metal adhesion.

Down-select decision and work in progress. At the end of the five cleaner evaluation, it was decided to proceed with further studies on Brulin 815 GD and Jettacin and to eliminate the other cleaners from consideration. Prima Clean was eliminated on the basis of the observed corrosion problems, while Axarel 52 was rejected on issues such as the necessity of a post-clean grit blast to achieve high bond strengths and seriously reduced performance of the cleaner when soil-loaded.

Jettacin, on the other hand, produced the highest bond strengths in the screening program, while Brulin was judged to be the least corrosive of the cleaners in electrochemical tests on steel. Both cleaners showed adequate soil-loaded cleaning ability in preliminary tests.

An additional testing effort to directly compare Brulin 815 GD and Jettacin is now in progress. It includes a two-level fractional factorial study which will determine the effect of such variables as wash and rinse pressures, cleaner concentration/temperature, and lab location on bond strength and surface chemistry.

4.0 SUMMARY AND CONCLUSIONS

The results here show the value of ESCA, AES, and static SIMS for explaining differences in adhesion performance for a contamination-sensitive epoxy-to-metal bondline. Conventional chemical analysis techniques failed to detect differences in surface chemistry among aqueous and semi-aqueous cleaners which in turn had measurable effects on bond strengths. These differences in surface chemistry were readily detected by ESCA, AES, and SIMS. For less contamination sensitive bondlines on the RSRM, such as the vulcanized steel-to-NBR interfaces, the differences in surface chemistry had no effect on bonding results. For such systems conventional techniques are more useful. For example, FTIR and DRIR are capable of easily discerning grease levels which will cause the robust NBR-to-steel bondline to fail.

While all five cleaners provided bond strengths equal to or better than those obtained by vapor degreasing, the aqueous cleaners (Jettacin, Metalube 4U, and Brulin 815 GD) yielded better bond strengths for an epoxy-to-metal bonding system than did the semi-aqueous cleaners (Prima Clean, Axarel 52). The reason for the difference was found to be a silicate layer left behind by the aqueous cleaners which increases the polarity of the surface, thereby increasing epoxy-to-metal bond strengths. This silicate layer probably also provides a measure of corrosion protection. The semi-aqueous cleaner Axarel 52, on the other hand, leaves behind a nonpolar carbonaceous layer which appears to reduce epoxy-to-metal bond strengths. The semi-aqueous cleaner Prima Clean was found to promote rusting of steel surfaces and was therefore dropped from consideration.

In cleaning efficiency studies, it appeared that Jettacin and Axarel 52 removed process soils somewhat more efficiently than Brulin 815 GD and Metalube 4U. (However, Axarel 52 leaves its own carbonaceous residue which more than compensates for its apparently good cleaning efficiency.) It cannot be said at this point, however, which cleaners clean "best" since only one set of process conditions per cleaner was studied, and the conditions were different for different cleaners. More definitive studies involving a wide range of process conditions are underway on two of the cleaners (Jettacin and Brulin 815 GD). These studies will provide a more sound basis for the final down-selection.

5.0 ACKNOWLEDGMENTS

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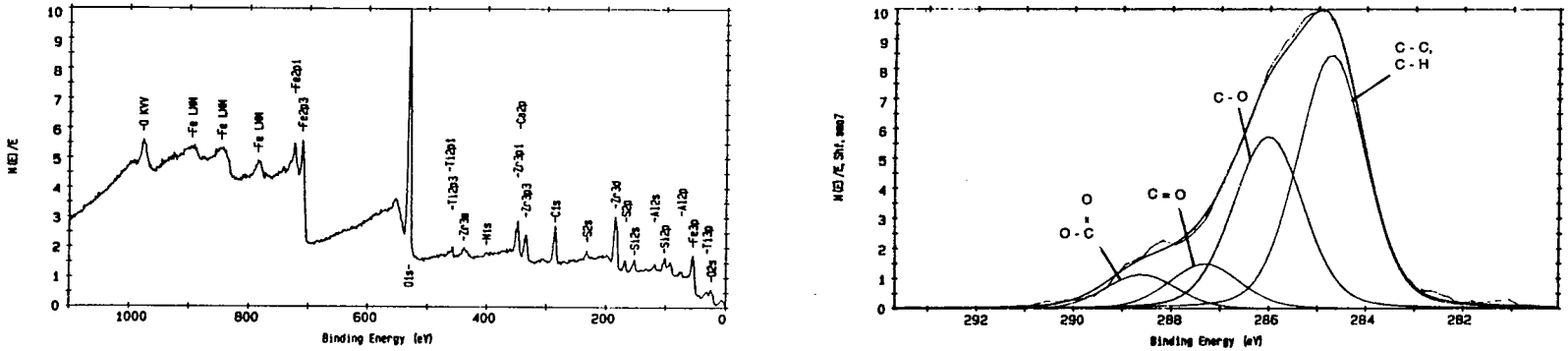

Figure 1. ESCA Spectra of Uncontaminated D6AC Steel. Left: Survey. Right: High Resolution Carbon (1s) Scan.

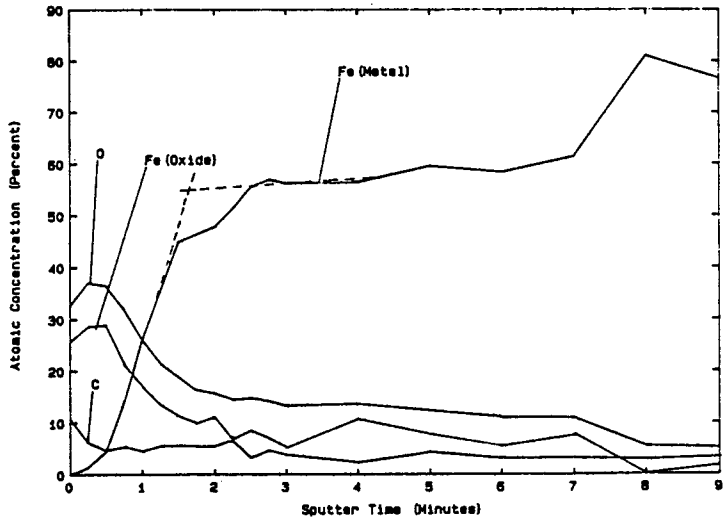

Figure 2. AES Depth Profile of Uncontaminated D6AC Steel

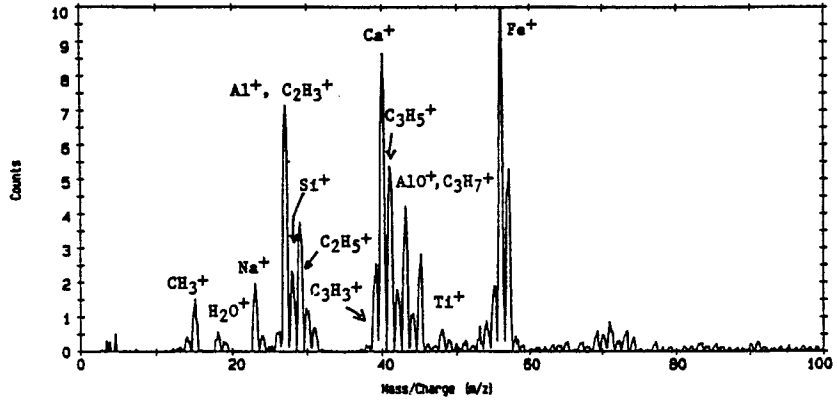

Figure 3. Static SIMS Spectrum (Positive Ions) of Uncontaminated D6AC Steel

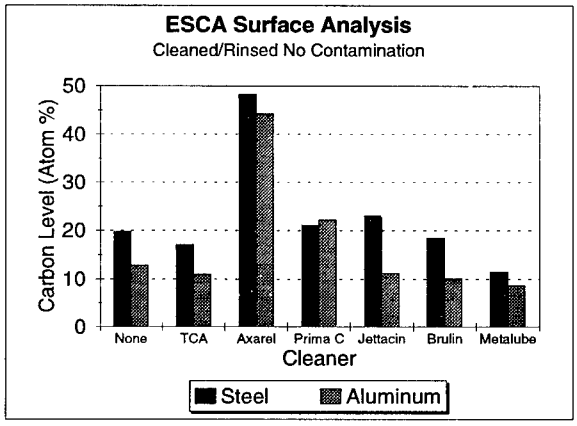

Figure 4. ESCA Carbon Levels on Cleaned/Rinsed Steel and Aluminum

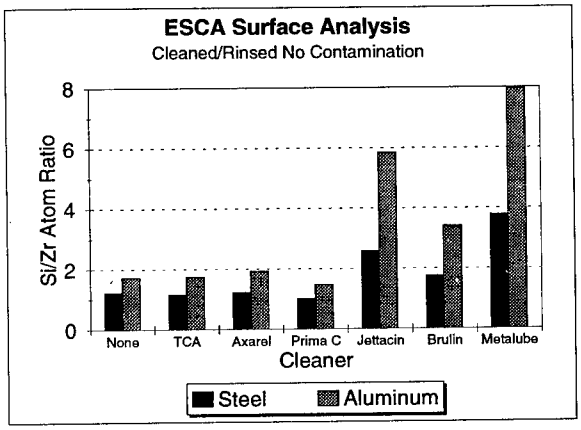

Figure 5. ESCA Silicon Levels on Cleaned/Rinsed Steel and Aluminum

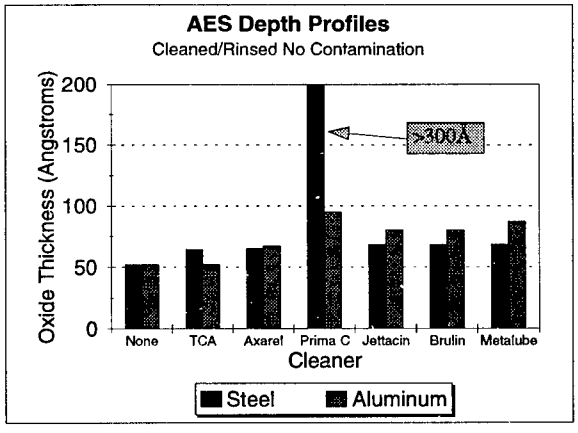

Figure 6. AES Oxide Thickness of Cleaned/Rinsed Steel and Aluminum

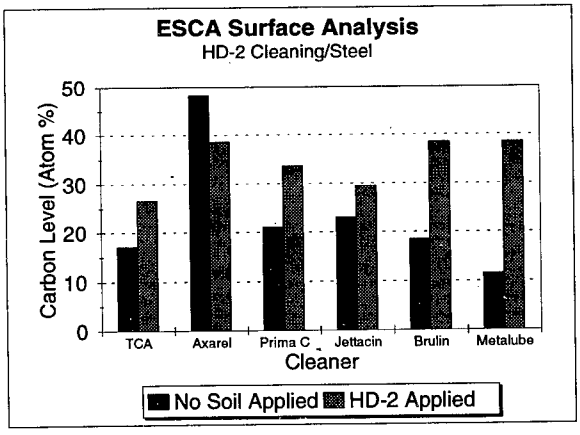

Figure 7. HD-2 Grease Cleaning Efficiency (Steel)

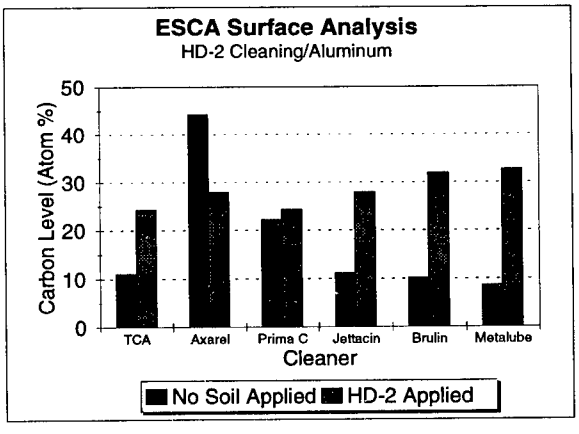

Figure 8. HD-2 Grease Cleaning Efficiency (Aluminum)

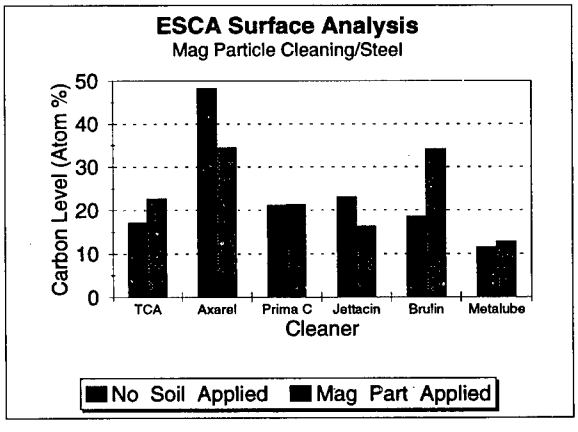

Figure 11. Magnetic Particle Cleaning Efficiency (Steel)

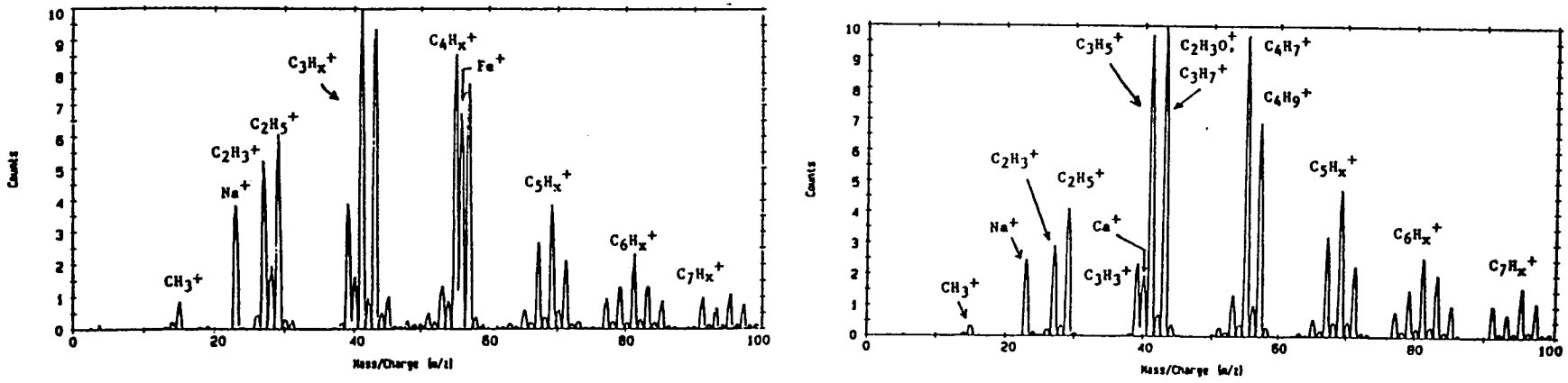

Figure 9. Static SIMS Spectra of (left) HD-2 Contaminated, Metalube 4U Cleaned Steel; (right) Pure HD-2 Grease Reference.

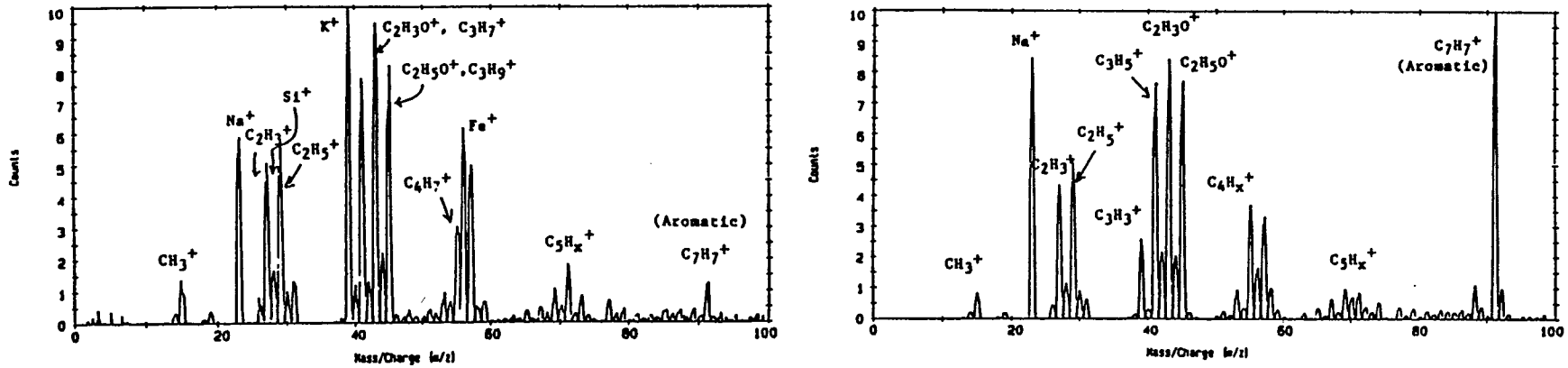

Figure 10. Static SIMS Spectra of (left) Mag Particle Contaminated, Brulin 815GD Cleaned Steel; (right) Pure Magnaglo WA-4 Reference.

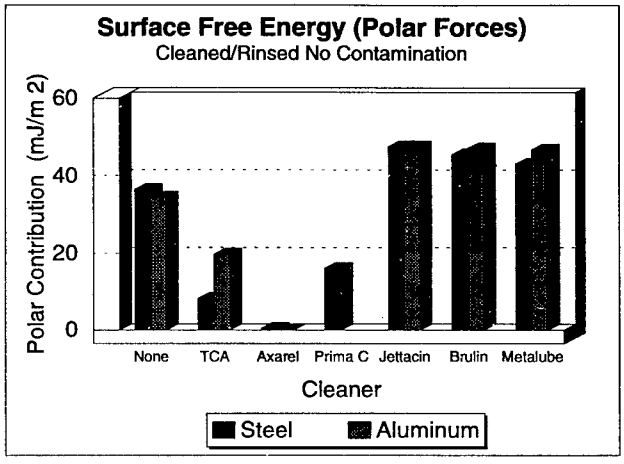

Figure 12. Surface Free Energy (Polar Contribution) of Cleaned/Rinsed Steel and Aluminum

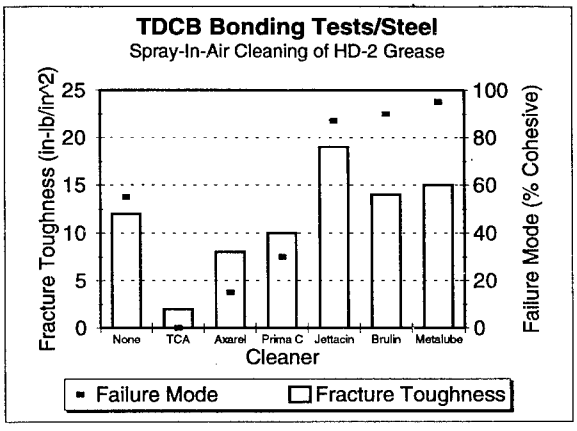

Figure 13. Fracture Toughness Results for HD-2 Contaminated, Cleaned Steel (EA-913NA Epoxy Adhesive)

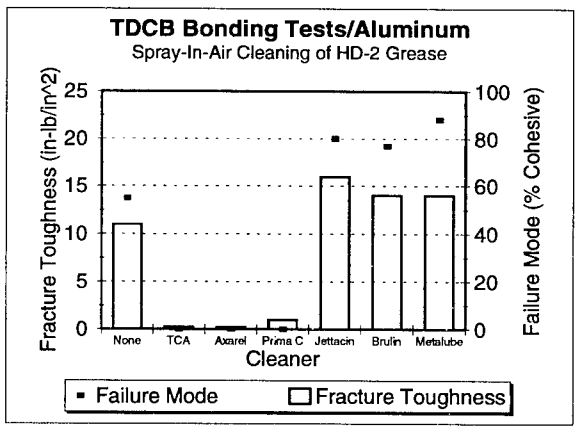

Figure 14. Fracture Toughness Results for HD-2 Contaminated, Cleaned Aluminum (EA-913NA Epoxy Adhesive)

Table I

ESCA Surface Analysis of D6AC Steel Coupons
Cleaned But Not Rinsed

Surface Concentration (Atom %)

Cleaner	Fe	O	Ti	N	Ca	Zr	C	S	Si	Al	Cl	K	P	Na
Steel Control	11.0	50.9	1.0	0.8	2.1	4.4	19.8	2.4	5.4	2.3	--	--	--	--
TCA Vapor	12.6	52.7	0.9	0.4	2.2	3.8	17.1	2.2	4.4	2.0	1.6	--	--	--
Axarel 52	3.8	32.2	0.2	--	0.1	1.9	56.6	0.1	1.8	0.6	0.0	--	2.6	--
Prima Clean	12.9	40.9	--	0.2	--	0.2	45.6	--	0.1	0.1	0.1	--	--	--
Jettacin	0.1	21.3	--	0.8	--	0.1	69.2	1.9	0.8	0.0	0.0	--	--	5.7
Brulin 815GD	0.9	26.7	0.2	2.5	0.1	1.0	60.4	0.2	3.3	0.4	--	1.5	2.6	0.2
Metalube 4U	--	27.5	--	1.9	--	0.1	59.7	3.6	1.2	--	--	0.2	--	5.9

ENVIRONMENTAL TECHNOLOGY INFORMATION SYSTEMS—SPECIFICATIONS, STANDARDS, AND DATA BASES

Environmental Databases and Other Computerized Information Tools

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Abstract

Increasing environmental legislation has brought about the development of many new environmental databases and software application packages to aid in the quest for environmental compliance. These databases and software packages are useful tools and applicable to a wide range of environmental areas from atmospheric modeling to materials replacement technology. The great abundance of such products and services can be very overwhelming when trying to identify the tools which best meet specific needs. This paper will discuss the types of environmental databases and software packages available. This discussion will also encompass the affected environmental areas of concern, product capabilities, and hardware requirements for product utilization.

Introduction

The increasing promulgation of international, federal, state, and local environmental legislation is affecting all facets of business and industry. Such legislation has become the driving force in the development of many new environmental databases, software programs, and other computerized information products. These databases and related products are useful tools when striving for environmental compliance, and are applicable to a broad range of environmental technology areas. The purpose of this paper is to educate the engineer on the increasing environmental legislation and to provide information on the available electronic computerized information compliance tools.

A greater understanding of environmental legislation is a necessity when trying to appreciate the emerging environmental information tools. The Clean Air Act Amendments of 1990 (CAAA), Montreal Protocol, revised Montreal Protocol (also known as the Copenhagen Protocol) and a presidential executive order are the primary legislative environmental drivers which are greatly challenging the traditional aerospace, production and manufacturing practices. This cadre of legislation encompasses but is not limited to enforcement, regulations, and production bans on various chemicals. The needs for engineers to quickly access large amounts of environmental information has greatly increased.

Title VI of the CAAA mandates a U.S. production ban on Ozone Depleting Substances (ODSs). Chlorofluorocarbons (CFCs), methyl chloroform, and carbon tetrachloride production will cease by January 1, 1996. Hydrochlorofluorocarbons (HCFCs) have varying production phase-out dates from 2003 to 2030 (S. Newman, 3). An article entitled Environmental Initiatives at NASA states that ODSs are utilized in many applications such as surface cleaning, cleanliness verification, laboratory analyses, thermal protection systems and many others (141).

The aerospace engineer must also comply with Title III of the CAAA. This legislation classifies 189 chemical and compounds as Hazardous Air Pollutants (HAPs) (Murphree, 4). HAPs are those chemicals which are carcinogenic, mutagenic, or cause reproductive damage. Examples of HAPs include heavy metals such as chromium, lead and nickel. CAAA, Title III requires the Environmental Protection Agency (EPA) to promulgate 156 National Emission Standards for Hazardous Air Pollutants (NESHAPS) (Murphree, 4). This promulgation began in 1993 and must conclude by 2003. NESHAPs establish federal emission limits for HAPS. NESHAPs also require the usage of Maximum Available Control Technology

(MACT) to curb emission rates.

Volatile Organic Compounds (VOCs), as defined by the EPA, are carbon containing compounds which are not ODSs. VOCs are targeted by the EPA because they are precursors to ambient ozone and other forms of air pollution (SPI, 3). Title I of the CAAA, requires the EPA to promulgate Control Techniques Guidelines (CTGs) for the Aerospace Industry and Shipbuilding Industry. These two industries were singled out in part due to the large acreage of hardware encompassed by these industries. The CTGs will set emission limits on VOCs and require states to utilize Reasonably Achievable Control Technology (RACT).

The aforementioned discussion on environmental legislation illustrates the reasons why the aerospace engineer must now consider environmental compliance when designing a new process or maintaining an established process. A thorough understanding of the process from "the beginning -of-the pipe" to "the end-of-the pipe" is a must. The engineer must assume some of the responsibility for identifying the related environmental impacts of the entire process and review these impacts with the facility's resident Environmental Management Office. Materials replacement technology is a relatively new area and many traditional environmental management offices have greater experience with remediation and permitting issues. Many engineers are discovering that the management of everchanging environmental legislation and related impacts upon traditional manufacturing processes is difficult at best. Furthermore, the typical replacement sequence for materials is five years. This five year time span encompasses identification, evaluation, and requalification of materials.

Accessing and Utilizing Computerized Environmental Information as Compliance Tools

The vast majority of engineering work of today is performed on Personal Computers (PCs) (Zanetti, 5). Many engineers have PCs on their desks and utilize these PCs to write reports, design flowcharts, calculate material balances, and handle accounting. Furthermore, many companies are phasing out mainframes and replacing them with Local Area Networks (LANs) and Wide-Area Networks (WANs). WANs link LANS via leased phonelines thereby allowing an engineer in the U.S. to access a database in another country (Zanetti, 5). These databases allow the engineer to retrieve subsets of information from the abstracts, full text articles, periodicals, wire service stories, newspaper editorials, and professional group newsletters that are collected and periodically updated (McCann , 394-395). Attributes of on-line databases include accessing readily available information without extensive training or specialized equipment, and greater flexibility when conducting a search.

Computerized environmental information is available on several formats including on-line databases, stand-alone databases, CD ROM and other software products and cover a wide range of topic areas. Software products include database programs, EPA/OSHA reporting forms, chemical inventory tracking systems, environmental/chemistry calculation programs, emission monitoring, and EPA test methods. The specialized topic areas encompass pollution prevention/control, waste remediation, environmental legislation , and environmental/chemistry research.

The great abundance of such products and services can be very overwhelming when trying to identify the tools which best meet specific needs. The identification of requirements is the initial step in selecting the most accurate tool. One has to determine the type of environmental information that is to be managed or acquired. It is common to utilize several computerized environmental information products to access or determine different types of information. Furthermore, several databases and related products may be used during the life cycle of a project (design, development, operation, and termination). After identifying the type of environmental information to be acquired/managed, the aerospace engineer can select from the several existing databases and other related software products that are on the market today.

Computerized Environmental Information as an Emerging Technology Area

Several companies and federal agencies have identified the need for computerized environmental information and are responding by developing products and services. Microsoft has the WindowChem Software product line. This product line was founded to provide a distribution network for those programmers working in the Microsoft Windows environment, developing software to solve chemistry related problems (WindowChem , 2). Further information about the WindowChem software product line can be obtained by calling **1-800-536-0404.** Also, the EPA developed the Technology Transfer Network (TNN) which houses sixteen environmental databases and related services. The topic areas range from air monitoring to ecosystem protection. The modem access number is **(919) 541-5472,** and the internet address is **TELNET ttnbbs.rtpnc.epa.gov.** Brief descriptions of the available products are provided.

Accessing Legislation/Regulations

The myriad of everchanging federal, state, and local legislation is difficult to track. However, this type of information is essential due to the regulatory impacts upon current and future projects. Several computerized products and services are available to ease this never-ending task.

- **Clean Air Act Amendments BB (CAAA)**
  - on-line database devoted to Clean Air Acts Amendments
  - bulletin board service
  - full text of proposed Hazardous Organic NESHAP
  - EPA sponsored
  - downloadable
  - Technology Transfer Network (TNN)
  - free cost
  - modem # / (919) 541-5742
  - Internet address / TELNET ttnbbs.rtpnc.epa.gov

- **Regscan for Windows and MACs**
  - stand-alone
  - contains final/proposed rules for Code of Federal Regulations (CFR) 40, CFR 49 (and other CFRs), also the complete Federal Register
  - includes state safety and environmental regulations
  - manufactured by Regulation Scanning Company
  - $500 (starting price)
  - company phone # / 1-800-326-9303

Researching Environmental and Chemistry Journals

Oftentimes the aerospace engineer encounters specialized technical challenges. The environmental and chemical journals enable the engineer to stay abreast of the "state-of -the-art" developments in specific technology areas. This on-line capability also allows engineers to search on the needed subject matter, and does not require a lot of space as does hard copies.

- **Chemistry Journals of the American Chemical Society (CJACS)**
  - 127,000 records contained in on-line database
  - approximately 22 journals (e.g. "Environmental Science & Technology,

Chemistry of Materials)
- searchable information (except for some mathematical and chemistry equations)
- Scientific and Technical Information Network (STN)
- $29/hr connect fee (display and search fees applicable)

♦ **Environment Reporter**

- contains complete test of current developments section
- information on federal/state legislation, pollution control
- Westlaw network (offers several environmental databases)
- subscription cost is $125/year
- user cost is $4.05/minute
- CD ROM is $6, 748
- additional networks: Dialog, Lexis
- prices vary per network

Identifying Physical and Chemical Properties of Materials

The engineer will also discover that many environmental databases contain chemistry information and that many chemistry databases contain environmental information. The physical and chemical properties of materials is important information to have when replacing an environmentally non-compliant material with a compliant material. The reactivity and stability data in useful in determining the shelf-lives of materials. Much of this type of information is contained within Chemistry databases.

♦ **Environmental Chemicals Data and Information Network (ECDIN)**

- on-line databases
- chemical identification of 122,400 chemical compounds
- contains 19 files : physical/chemical properties, chemical processes, toxicity information (20,000 compounds)
- internationally produced (Commission on the European Communities & others)
- DIMDI network
- phone #/ 0332 789720

♦ **EM Science Chemicals Information System (EMCIS)**

- WindowChem software
- stand-alone database
- physical/chemical properties
- stability/reactivity data
- toxicity data
- requires Windows 3.x, Excel 4.0
- $395
- phone #/ 1-800-536-0404

Implementing Materials Replacement Technology

Materials Replacement Technology is an emerging technology area. As previously stated throughout the text, the project engineer will have to assume increasing responsibility for ensuring that environmental compliance is achieved and maintained during the life cycle of a project. The NASA Operational Environment Team (NOET) has developed two unique databases to assist with materials replacement tasks.

- NASA Environmental Information System (NEIS)

  - on-line database within the Materials & Processes Environmental Engineering Network (MPEEN) database
  - contains information on legislation/regulations
  - physical/chemical properties of solvents and other cleaning materials
  - cleaning evaluation results
  - free access
  - Internet # /128.158.1.200
  - modem #/1-800-320-6272
  - point of contact /Ms. Beth Cook, (205) 544-2545

- Aero-Mat

  - contains usage and volatile organic content (vc) of materials
  - identifies specification drivers
  - contains specification drivers
  - stand-alone database (will eventually merge into NEIS)
  - currently limited access

Accessing Analytical Test Methods (EPA and Others)

The electronic test methods enable the chemists or engineer to search and identify all the test methods that use utilize a certain chemical as the anlalyte. One can also retrieve several test methods to determine the suitability of needs. These test methods aid in the customization of standard operating procedures because the chemist can "cut & paste" , and combine the appropriate sections of the various methods.

- Electronic Methods for EPA/ National Institute of Occupational Safety and Health NOSH) / Occupational Safety and Health Administration (OSHA)

  - WindowChem product
  - stand-alone database
  - EPA waste & water methods, air toxic methods (and many others)
  - information is searchable by method#, analyte, CAS #, instrumentation
  - prices vary ($300 - $1100)
  - various subscription plans available
  - phone # / 1 - 800 - 536 -0404

- Environmental Monitoring Methods Index (EMMI)

  - EPA sponsored
  - stand -alone database
  - contains information on 2600 of EPA's regulated chemical substances
  - summaries of 926 analytical methods
  - manufacturers of analytical standards
  - regulatory limits
  - $385 - $1995
  - phone # / (703) 487-4650

Complying With Air Emissions Standards

The increasing promulgation of National Emission Standards for Hazardous Air Pollutants (NESHAP) will require closer monitoring of the emissions released from 174 targeted source categories. Several products are available to guide the engineer through the air emissions permitting process. Also, many products have been developed to provide air -dispersion modeling capabilities.

- Breeze Dispersion Models

  - product line contains 35 air dispersion modeling programs
  - several modeling programs approved by the EPA
  - menu -driven programs (help screens, tutorials)
  - guides user through data entry, model execution / plot generation for continuous emissions from stacks, mobile sources & accidental releases
  - access to technical support
  - $450 (starting cost)
  - phone # /(214) 661-8100

- Controlling Air Tonics (CAT) Version 1.0

  - EPA - sponsored
  - stand - alone database
  - assists in review of air emissions permit applications
  - provides guidance on control devices
  - calculates design parameters
  - estimates costs for control devices
  - $55
  - phone # / (703) 407-4650

Chemical Inventory Management

Two common tasks associated with the chemical management process are chemical inventory and the management of Material Safety Data Sheets (MSDSs). Each tasks is extremely important in achieving environmental compliance. However, these tasks are typically time consuming, cumbersome and entails numerous amounts of paper. Several computer programs are available to automate these tasks, and provide paperless chemical management.

- Chemical Inventory Software (CIS)

  - WindowChem software
  - tracks chemicals and other materials
  - provides descriptions of general hazards
  - provides specification of vendor and catalog numbers
  - identifies storage locations
  - $199
  - phone # / 1 - 800 - 536-0404

- Material Safety and Data Sheet (MSDS) Manager Perform Pro Template

  - WindowChem Product
  - designed for the specialty chemical manufacturer
  - allows engineers and chemists to write, publish , store, and distribute their own MSDSs
  - stores all MSDSs in one electronic location
  - merges vendors MSDSs/ extracts vendors MSDSs
  - $199
  - phone # / 1 - 800- 536 - 0404

Performing Mathematical Calculations and chemical conversions

Several computerized products are available to assists the chemist or engineer with chemical conversions, mathematical calculations, and environmental calculations. These products save time and reduce errors caused by calculations. The following programs are WindowChem products and the phone number is 1-800-536-0404.

- Chemical Conversions

  - drop down menus to convert 2000 different unit conversions
  - unit conversion include mass, pressure , volume , flow rates, energy, concentration
  - $89

- Environmental Molecular Weight Calculator 2.0

  - formula database of over 1000 environmentally regulated compounds
  - chemical formulae of compounds from EPA methods (Water & Waste)
  - calculates amount to add to given volume of liquid to make desired solution concentration
  - $119

- Special Environmental Calculations Macros

  - reporting for waste, water, chloride content
  - utilizes Excel to automate reporting of environmental samples
  - macros are same mathematics as used in EPA methods
  - $39 - $1495

Conclusion

Computerized environmental information offers several benefits . The databases provide greater flexibility when searching for specific information resulting in a time savings. This information can be captured and brought in-house. Also, the paperless engineering minimizes the physical space required to store information.

The environmental information products provide services that replace the manual tasks performed by engineers and chemists at one time or another. These services include automation of the chemical

inventory process; customization of MSDSs; ease in creating customized Standard Operating Procedures; and aiding in the air permitting process. Additional benefits from these products are reduction in redundancy of material replacement efforts; current status of environmental regulations and legislation; easy access to EPA analytical test methods; and less manual number crunching when performing chemical /environmental unit conversions.

In summary, engineers will face increasing challenges when striving for environmental compliance. These global challenges will drive the development of emerging technologies for environmental compliance. Computerized environmental information of varying formats and topic areas will be utilized.

A Selected Bibliography

1. McCann, Joseph E., Gomez -Meija, Luis. "Coming On-line in the Environmental Screening Process". IEEE Transactions on Environmental Management, 39, No. 4 (November 1992), 394-99.

2. Murphree Gail., "TitleI/Title III Regulatory Update". Huntsville, AL., September 1993 (Report to the NASA Operational Environment Team

3. Newman Steve., "The Environmental FAX / NASA Office of Space Flight". , June 1993, 3.

4. Schwinghamer, Robert J., Goldberg, Benjamin E., Congo , Richard T. "Environmental Initiatives at NASA : Taking the Lead in Alternative and Replacement Technologies". Federal Facilities Environmental Journal (Winter 1993 -1994), 437-455.

5. Society of Plastics industry. "Clean Air Act of 1990: Impact of implementation on the Polyurethane Industry". SPI Issue Backgrounder (September 1992).

6. Zanetti, R., "The Power of PCs". Chemical Engineering (January 1994), 5.

NEIS
(NASA Environmental Information System)

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Abstract

The NASA Environmental Information System (NEIS) is a tool to support the functions of the NASA Operational Environment Team (NOET). The NEIS is designed to provide a central environmental technology resource drawing on all NASA centers' capabilities, and to support program managers who must ultimately deliver hardware compliant with performance specifications and environmental requirements. The NEIS also tracks environmental regulations, usages of materials and processes, and new technology developments. It has proven to be a useful instrument for channeling information throughout the aerospace community, NASA, other federal agencies, educational institutions, and contractors. The associated paper will discuss the dynamic databases within the NEIS, and the usefulness it provides for environmental compliance efforts.

Evolution of NEIS

In April of 1992, Mr. Goldin, the NASA Administrator, instructed MSFC to proceed with an Agency-wide environment effort. The NASA Operational Environment Team (NOET) was created and given the responsibility to maintain environmental compliance in all operational areas including the design, development, test, production, and use of space flight hardware. The NOET's approach to handle this responsibility is to provide a central environmental technology resource among the many NASA projects to pursue cleaner propulsion systems and to pursue replacement technology for environmentally affected materials and processes.

To disperse the rapidly developing technology among all projects with similar needs, NOET periodically holds Technology Interchange Meetings (TIMs) at which individuals working similar problems can discuss their technology activities. However, another mechanism for providing information on technological advancements was necessary. In addition to technical interchanges for dissemination of replacement technology activities, a NASA-wide environmental database has been established, is updated periodically, and is available to NASA and aerospace contractors. Information from NASA, contractors, and vendor research and development efforts is provided to NOET for addition into the database, titled the NASA Environmental Information System (NEIS).

Structure of NEIS

NEIS is one of three components in a larger information system called the Materials, Processes, and Environmental Engineering Network, or MPEEN. MPEEN is maintained at NASA's Marshall Space Flight Center (MSFC) in Huntsville, Alabama by the Materials and Processes Laboratory. Within this

vast information storage, display and retrieval system are volumes of data on environmental replacement materials information, metallic and non-metallic materials properties, failure analysis research, foreign alloy cross-referencing, specifications and standards, long-duration exposure facility, and more. Once the MPEEN system has been accessed, this information can be reached through three distinct nodes: the Materials & Processes Technical Information System (MAPTIS), Failure Analysis Information System (FAIS), and NEIS. A graphical depiction of the information system's interactive relationship can be seen in Figure 2.

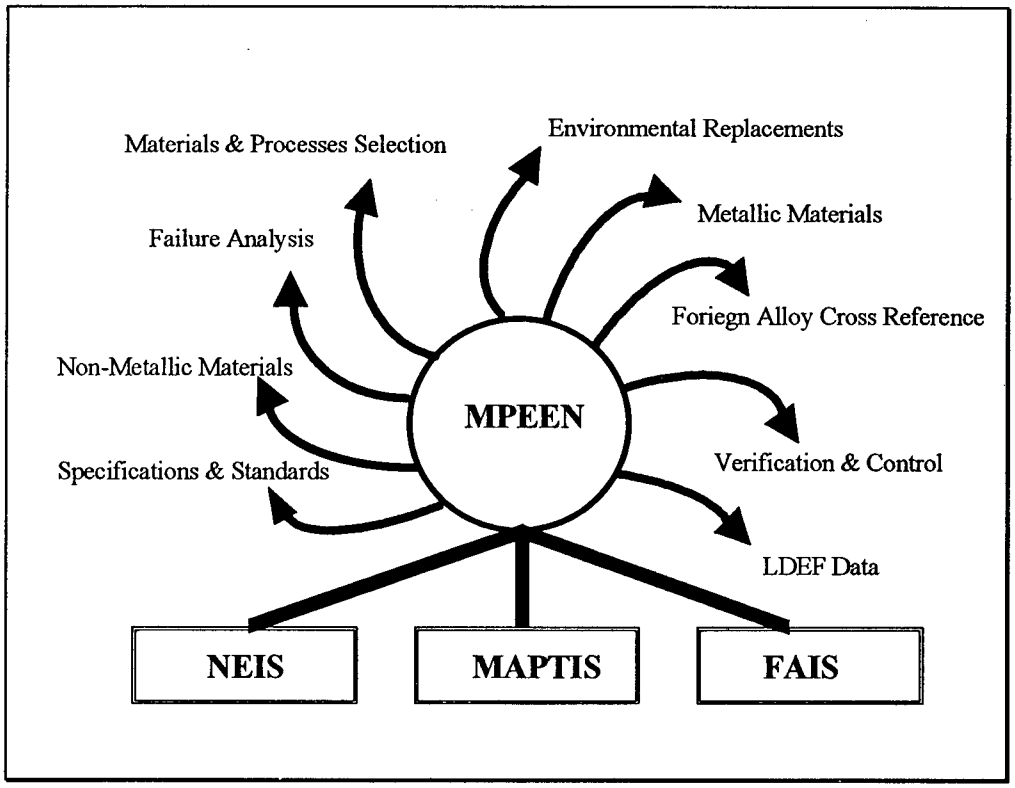

Figure 1

Contents of NEIS

NEIS is designed to provide a central environmental technology resource for all centers and their contractors; to track and access environmental regulations, chemical usages, and environmental technology development; to support program managers who must deliver environmentally compliant hardware; and to provide communication within NASA and among NASA, other agencies, contractors, and educational institutions. To do this, the NEIS keeps tabs on environmentally compliant research and technology designed to replace current aerospace materials and processes. Figure 1 shows the complete set of options available through NEIS as they appear in the NEIS Main Menu.

NEIS Main Menu Options:

1. Regulatory Updates
2. ODS Specifications & Standards
3. NASA-wide ODS Usage
4. Replacement Solvent Summaries
5. Material/Processes Replacement Prioritization Matrix
6. Chemical & Physical Properties
7. Points of Contact
8. Program Tasks
9. In-house Activities
10. Workshop/Conference Minutes
11. Calendar of Events

Figure 2

The **Program Tasks** option of NEIS provides a comprehensive look at each replacement activity NOET monitors within the Shuttle projects. External Tank is developing a new formulation for their foam blowing agent to eliminate CFC-11. Environmentally-friendly solvents are being evaluated to replace CFC-113 and TCA which are currently used in handwipe cleaning operations. High pressure water blast and other methods are being studied to replace current vapor degreasing operations. These activities and more are documented in the Program Tasks option of NEIS. Information can be queried by the task title, the contractor involved, the targeted chemical being eliminated or reduced, or the area of environmental impact. A synopsis of efforts to date and current funding status can also be found here.

The **ODS Specifications and Standards** option contains the results of NOET's 1993 survey in this area. Over 400 documents were identified in this survey, and of those, only 71 identified NASA as the custodian. However, more comprehensive research has since revealed that NASA may need to revise 107 documents total. Many of these changes have already been made and have thus reduced the number of required revisions. Impacted documents can be retrieved from the NEIS by their title, number, or custodian. Other information provided includes and abstract, identified NASA users of the document (by centers), targeted ODS chemical referenced, and forbidden chemicals and suggested alternatives as identified in the document. This data option contains all documents referenced by the survey. They include NASA-owned standards, military specifications, contractor documents, and more.

The **Regulatory Update** option provides informal summaries of interactions with EPA and federal and state and regulations. For example, status's of the Thiokol Essential Use Exemption Request and of NOET's discussions with EPA on the NESHAP for Aerospace Manufacture and Rework are available. Forthcoming NESHAPs and CTGs will also be referenced here. These summaries can be queried by keywords, title, or source of information. Each record contains a summary or status of events to date. Older selections may contradict newer inputs if regulations have been updated or changed.

The NOET-sponsored workshops are cataloged in the **Workshop/Conference Topics** option. For each event, be it a Technical Interchange Meeting, a Video Teleconference, or an All-Centers' Meeting, and agenda of the activities as well as an abstract of each topic is available. This information can be queried by the event title, the presentation title, date of that event, or speaker name/organization.

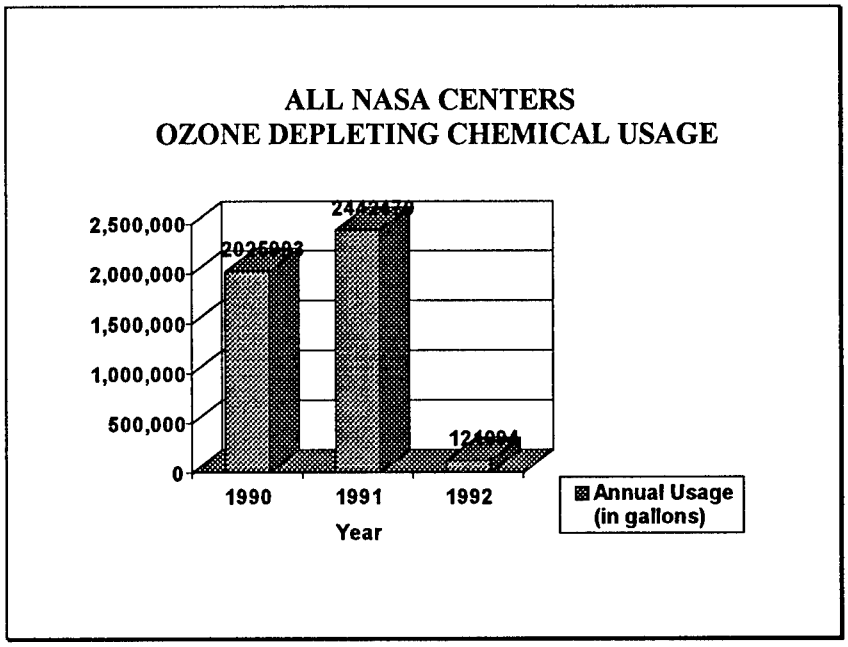

Figure 3

Another useful option is the **NASA-wide ODS Usage**. A user can look at the annual usage trends for each center or for all NASA through this selection. The information is represented by bar graph for the years 1990, 1991, and 1992. Unfortunately, NASA did not

conduct a usage survey for 1993 so data from that year is unavailable. An example of output from this menu option is provided in Figure 3.

Another option within the NEIS is the **Material/Processes Replacement Prioritization Matrix**. This option opens to the user an automated tool for evaluation and prioritization of alternative materials and processes. The analysis is performed based on a Quality Function Deployment (QFD) method of optimization. The series of forms will direct the user to identify a material or process to be replaced. The next step is to identify all areas of concern with the material or process and to assign weighting factors to each concern. These concerns fall into several categories: Regulatory, Process, Chemical, Safety, Environmental, Cost, and Scheduling. This allows the user to list all criteria the replacement must meet and to identify how important each area of concern is to the acceptance of the replacement. For example, if CFC-113 is being replaced as a handwipe, toxicity might rate higher than evaporation rate (as a chemical concern) because of the close proximity in which the operator will be using the handwipe cleaner. Of course safety concerns should also be considered in this situation. This example demonstrates how some concerns are greater issues than others and should be weighted accordingly, and it demonstrates how looking at some concerns can lead to looking at others.

Once all the concerns have been identified and weighted, the user can list each potential replacement and for each concern, can assign a number to rate its ability that previously selected criteria. After all the potential replacements have been added to the system, the user can run a report to determine the optimal solution. To do this, the program multiplies the weighting factor by the rating a potential replacement scored. These products are then tallied per potential replacement and the results are provided in a well organized report. The scoring of each potential replacement on each concern can also be studied by running a long report.

Only six of the NEIS options have been discussed at this point, but the other five options are also available. Two of the remaining five provide lists on points of contacts and upcoming events related to NASA's environmental activities. The **Replacement Solvent Summaries** option lists a variety of materials which have been tested to replace some cleaning solvent or process to be eliminated. Along with the list of materials is a denotation of whether the material passed or failed the particular criteria for that situation, and the name of the person who conducted that test. This is a quick way for one to get a feel for what type of replacements with which to begin a private evaluation as well as a point of contact to gather details about testing already performed. One option, the **Chemical & Physical Properties**, provides a look at some basic properties of various replacement solvents and the materials to be phased-out. Finally, the **In-house Activities** provides a quick summary of replacement activities underway "in-house" throughout the NASA centers.

Future of NEIS

Two major activities will be on-going through the remainder of 1994 to enhance the capabilities of the NEIS. First is the upgrading of the existing MPEEN system. Second is the inclusion of the Aero-Mat database into the existing NEIS.

The MPEEN system currently has a storage capacity of five Gigabytes, a memory capacity of 64Km and an operating speed of 28 MIPS. The system accommodates many users and during prime operating hours, commands are processed rather slowly. An upgrade has been purchased from Digital Corporation from the Alpha 7000 series which is currently on the market. The new system has a storage capacity of six to over 100 Gigabytes, a memory capacity of 128M to two Gigabytes, and an operating speed of 150 to 200 MIPS. This Alpha 7000 upgrade will replace the existing VAX computer cluster system as the active system to be accessed by users. The existing VAX cluster will be used off-line for development of new programs and tasks.

The Areo-Mat Database is a tool that was developed off-line, in a PC environment, for quick accessibility and manipulation of data. This database houses material names, manufacturers, VOC content, annual usage, as well as other data pertinent to aerospace material usage on production lines. Materials included in the data include cleaners, paint thinners, various specialty coatings, foams, adhesives, and sealants. This data has been used to aid the NOET as it evaluates proposed regulations and discusses NASA's unique needs with EPA. This data has proven helpful in justification of the aerospace community's special technical requirements. The data has been compiled from many Centers and contractor facilities. Now that it is in a manageable format, it will be stored within the MPEEN system. With this additional information, the NEIS can address environmental compliance issues other than ODC replacement.

These two expansions of the NEIS will add to its capabilities and to its usefulness. The merging of the Aero-Mat Database with the existing NEIS should take place during the Fall of 1994, and the VAX system improvements are expected to be in place during the 1995 fiscal year. The NEIS is an ever-growing, ever-improving, data storage system which strives to accommodate the varied needs of process engineers, program managers, and materials specialists as they address the increasing requirements for environmental compliance. The demands placed on manufacturers of all types, both federally and locally, are growing increasingly stringent with each issuance of regulation from the EPA. Small businesses do not have the manpower or other resources to independently address all replacement issues, and large companies do not have the budgetary freedom to explore all alternative options. This NEIS provides individuals from various situations with the opportunity to learn from other's activities without unnecessarily duplicating effort. With today's tight budgetary constraints, this opportunity is critical to the survival of many processes and procedures.

THE EFFECT OF ENVIRONMENTAL INITIATIVES ON NASA SPECIFICATIONS AND STANDARDS ACTIVITIES

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ABSTRACT

The NASA Operational Environment Team (NOET) has conducted a survey of NASA centers specifications and standards that require the use of Ozone Depleting Substances (ODSs) (Chlorofluorocarbons (CFCs), Halons, and chlorinated solvents). The results of this survey are presented here, along with a pathfinder approach utilized at Marshall Space Flight Center (MSFC) to eliminate the use of ODSs in targeted specifications and standards. Presented here are the lessons learned from a pathfinder effort to replace CFC-113 in a significant MSFC specification for cleaning and cleanliness verification methods for oxygen, fuel and pneumatic service, including Shuttle propulsion elements.

INTRODUCTION

With the Copenhagen Amendment to the Montreal Protocol, all United States Government agencies and United States industries have had to greatly accelerate their phase-out of ozone-depleting chemicals (e.g. chlorofluorocarbons, chlorinated solvents). NASA organized a team in April of 1992, the NASA Operational Environment Team (NOET), to coordinate environmental compliance activities across the agency's programs. This NOET was chartered to disseminate information across all programs in an effort to eliminate any redundant replacement activities. Since the NOET needed to know just how extensive was NASA's usage of environmentally targeted materials, usage surveys were executed across the agency. It was discovered that many specifications, standards and procedures used at the various NASA centers call specifically for the use of targeted chemicals, such as CFC-113 (1,1,2-trichloro-1,2-trifluoroethane) and TCA (1,1,1-trichloroethane). Each of these specifications will need to be revised or replaced to allow NASA operations to continue in an environmentally compliant fashion. However, these specifications and standards generally have wide applicability, and the implications of revising these requirements are significant with potential cost impacts for the users. This paper will address the approach, methods, magnitude and scope of implementing environmental replacement technology in NASA specifications and standards. In addition, the discussion will show how the activities to replace CFC-113 and TCA in a widely utilized NASA Marshall Space Flight Center (MSFC) fluid system cleaning specification could be used as a pathfinder or model approach for the replacement of targeted materials in specifications and standards throughout the agency.

DISCUSSION

The NOET approach to replacement of non-compliant specifications and standards is implemented through the Replacement Technology Team (RT^2) as a four phase program to: (1) identify current applications that use ODSs; (2) identify the performance requirements of those applications; (3) identify potential replacement compounds with equivalent characteristics; and (4) assure that specifications, standards and procedures are revised, where practicable, to permit the use of alternate compounds (reference 1).

The RT^2, which is a component of the NOET, is responsible for identifying potential alternative and replacement technologies and materials for non-compliant compounds. In addition, an objective of the RT^2 is to identify and revise specifications, standards and procedures that utilize individual or specific groups of non-compliant materials. RT^2 addressed the specifications and standards revision issue by requesting information from all NASA centers on any documents requiring the use of Class 1 or Class 2 ODSs. Responses to this information call were received in 1993 and were compiled to define the size and scope of the revision effort required by NASA. Over 300 specification/standard documents were identified in this survey from all the NASA centers. However, NASA was custodian for only about one-half or 144 of the documents identified, i.e. these specifications or standards were under the direct responsibility and control of NASA. . Therefore, other standards that were not under direct control of NASA were not part of this survey, e.g. Federal, Military, Industry or company standards. Table 1 identifies the number of NASA specifications that reference the use of ODSs and which ODSs these documents specify.

NASA Custodian	# of Documents	CFC 11	CFC 113	CFC 114	CFC 12	HCFC 21	HCFC 22	Halon 1301	CCL 4	TCA
ARC	0									
GSFC	0									
JPL	35		X							X
JSC	26	X	X	X	X	X	X	X	X	X
KSC	55		X	X	X	X	X	X		X
LaRC	1		X							
LeRC	1		X							X
MSFC	16	X	X	X						X
SSC	1		X							
HQ	9		X							X
Total	144	Note: CFC13, 111, 112, 115, 211-217, Halon 1211 and 2402 , and other Class 1 and 2 ODSs not shown were not reported in any NASA documents								

Table 1: ODSs Used In NASA Specifications and Standards

The most widely specified or utilized ODSs identified by this survey, in descending order of their frequency of the appearance in these specifications or standards were CFC-113, TCA, HCFC-21 (dichlorofluoromethane) and CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane). The primary use for these targeted chemicals in the specifications identified were cleaning, cleanliness verification, heat transfer/refrigeration, analytical methods, and reference standards.

NASA's Jet Propulsion Laboratory (JPL), Johnson Space Center (JSC), Kennedy Space Center (KSC), Langley Research Center (LaRC), Stennis Space Center (SSC), and MSFC identified fluid/propellant system precision cleaning specifications that require revision. These and similar specification revision activities to implement replacement technologies could benefit from cooperative efforts among NASA centers for consolidation into common NASA-wide specifications and standards. In fact, a plan for the development of a NASA-wide fluid and propellant system precision cleaning specification was adopted by NASA M&P Working Group at the second annual NASA Materials and Processes (M&P) Standards Committee meeting at JSC in April 1994. The draft of this specification is anticipated by April of 1995. This NASA-wide precision cleaning specification for fluid systems will build on the ODS replacement activities underway at each center by utilizing their environmentally compliant specification revisions as the basis for development of a NASA-wide standard. Examples of NASA specifications that have been or are being updated with alternate cleaning materials and processes are: KSC-C-123, "Specification for Cleanliness of Fluid Systems"; MSFC-SPEC-164, "Specification for Cleanliness of Components for Use in Oxygen, Fuel and Pneumatic Systems"; JSCM 5322, "Contamination Control Program Requirements Manual"; and SSC Standard 79-001, "SSC Facility Cleanliness Requirements for Propellant, Gas and Hydraulic Systems".

The results of this survey were not necessarily intended to encompass all the specifications and standards used by NASA prime contractors and subcontractors. This relationship is very complicated, making it difficult to identify whether certain requirements are actually tied to a NASA specification , standard or derived requirement. In addition, some subcontractors consider their internal standards to be proprietary. Typically, these contractor specifications are internal company or industry standards, and specify the design, development, manufacturing and testing requirements for hardware systems. As a result, these specifications could easily specify a significant number of materials, substances and chemicals, of which the numbers of specifications and standards utilizing targeted ODSs should far exceed those reported here by the NASA centers.

NASA Custodian	Handbook	Plan	Procedure	Requirement	Specification	Standard	Total
ARC	54	4	1	5	43	18	125
GSFC	57		2	12	7	21	99
JPL	448	181	17	104	289	78	1117
JSC	398	10	2	40	118	136	704
KSC	170	5	8	3	153	62	402
LaRC	135	2	4	3	99	122	365
LeRC	85	7	26	12	307	260	697
MSFC	437	3	26	10	645	200	1321
HQ	48				2		50
Totals	1832	212	86	189	1663	897	4880

Table 2: ESDB Contents

It has been noted that this survey was intended to take into account primarily those specifications and standards which are baselined, controlled, maintained, and approved for use by each NASA center. These specifications and standards are generally contained in a NASA Engineering Standards Data Base (ESDB), which is a part of the Materials, Processes and Environmental Engineering Network (MPEEN) residing on a VAX cluster at NASA's MSFC. The ESDB is a reference index of NASA baseline specifications and standards which provides the following information:

document number and release date; document title; Federal stock classification number; custodian (who maintains document); discipline (area of use); user (NASA center); metric compatibility; and abstract. The total number of specifications and standards contained in the ESDB is 4880, with Table 2 showing the breakdown by NASA center and type of document. Therefore, approximately 6% of the standards contained in the NASA ESDB utilize ODSs. When considering only those specifications and standards for which NASA is custodian and maintains control, fewer than 3% of the standards in the ESDB contain ODSs that NASA can directly replace by revising the standard to implement alternative technologies.

As a example, at NASA's Marshall Space Flight Center (MSFC), only 16 of the 1321 total approved and baselined MSFC standards contained Ozone-Depleting Substances (ODSs). Table 3 identifies these NASA MSFC standards, the corresponding ODSs, and gives indication of how the chemicals are used. However, several of these documents have broad use or are imposed on major programs and contracts, such as the MSFC Shuttle propulsion elements. As a result, any modifications to the requirements in these standards could have significant impacts to the users. JSC, JPL, and KSC, combined, maintain at least 106 specifications which must be addressed. Some of these may be Standard Operating Procedures (SOPs) and easily changeable. Moreover, most specifications and standards must be revised and go through many levels of approval before they can be implemented. Even prior to revision, new materials must be tested and selected as suitable replacements if a "how-to" type of specification is used as the alternate. If a performance driven or "performance-based" specification is used as the replacement document, the expected results must be clearly defined. Each of these approaches requires a significant amount of work, yet the "performance-based" specification becomes virtually timeless.

Any approach to implementing replacement technology in NASA specifications must also consider NASA Standards Policy (NMI 8070.6) requirements that encourage participation in development and use of "voluntary" or consensus standards when practical, and common, non-project unique NASA standards when this is not practical. Specifically, this policy requires: the adoption of, and gives preference to, non-government or "voluntary" standards where they meet NASA needs; support of NASA's participation in the development of standards by other government and non-government organizations; and developing and maintaining NASA Standards where need cannot be met by other sources. The NASA Standardization Procedures Manual (NHB 8070.3) describes the control procedures for engineering specifications and standards implemented at each center, as illustrated by the following approach utilized by MSFC. The MSFC Engineering Documentation Standard (MSFC-STD-555) describes reasonably straightforward requirements for the expeditious release of MSFC engineering specifications, standards and drawings. General specification, standards, and drawings require the approval signature of the designer or the preparer (designated as the Office of Primary Responsibility (OPR), a designated Materials and Processes (M&P) and Stress engineer, with Safety, Producibility and Inspectability as required depending on the type of document. Project specific specification, standards, and drawings require the same approval signatures as before, but additionally must be approved for release by Engineering Change Request (ECR) through the Project Configuration Control Board (CCB) with resulting Directive (CCBD). NASA-wide or NASA Handbook (NHB) type standards have a much more broad and complex review, release and concurrence process. All MSFC baseline specifications and standards are identified by OPR in the Approved Baseline List (MSFC-MNL-2348) of over 1000 documents of various types, of which approximately 40% are materials and processes type standards that would most likely specify the use of targeted materials. NASA specifications and standards, including those maintained as Goddard Space Flight Center (GSFC), KSC, MSFC, NHB standards are found on commercially available Military & Federal specification/standards services, such as searchable microfilm or CD-ROM systems.

Specification	Title	ODS	Usage
MSFC-SPEC-164	Cleanliness of Components For Use in Oxygen, Fuel & Pneumatic Systems	CFC-113 TCA	Cleaning/Verification (MSFC, ET, SSME, SRB)
MSFC-SPEC-250	Protective Finishes For Space Vehicle Structures & Associated Flight Equipment, General	CFC-113	Cleaning/Surface Prep. (MSFC, ET, SSME, ATP/ATD, SRB)
MSFC-PROC-166	Hydraulic System Detailed Parts, Components, Assemblies, and Hydraulic Fluids for Space Vehicle Cleaning, Testing, and Handling	TCA CFC-113	Cleaning
MSFC-SPEC-233	Nitrogen, Instrument Grade	CFC-113	Cleanliness Verification
MSFC-STD-366	Penetrant Inspection Method, Standard	TCA	Cleaning (Shuttle)
MSFC-SPEC-1870	Guidelines For Evaluation of Corrosion Inhibiting Preservatives	CFC-113	Cleaning
MSFC-SPEC-1919	Thermal Ablative Compound, Application and Cure of	TCA	Cleaning (MSFC, SRB, RSRM)
MSFC-PROC-1831	Analysis of Nonvolatile Residue Content Based on ASTM F331-72	CFC-113	Cleanliness Verification
MSFC-PROC-1832	Sampling and Analysis of Nonvolatile Residue Content on Critical Surfaces	CFC-113	Test Media/Cleaning Test Equipment
MSFC-PROC-404	Gases, Drying and Preservation, Cleanliness Level and Inspection Methods	CFC-113	Cleanliness Verification
MSFC-PROC-639	Procedure For Potting Connection Using Heat Shrinkable Boots/Tubing and RTV Silicone Compounds	TCA	Cleaning
MSFC-SPEC-592	Specification For The Selection and Use of Organic Adhesives in Hybrid Microcircuits	CFC-113	Cleaning
MSFC-10A00527	Sealing of Fasteners subject to Sea Water Exposure on the Solid Rocket Booster (SRB)	TCA	Cleaning SRB
MSFC-10A00528	Protective Finishes for Aluminum and Steel Alloys Subject to Sea Water Exposure on the SRB	TCA	Cleaning SRB
MSFC-SPEC-2083	Polyurethane Foam Insulation	CFC-11	Blowing Agent (ET/Orbiter)
MSFC-SPEC-2084	Mix, Application and Cure of Polyurethane Foam	CFC-11	Blowing Agent (ET/Orbiter)

Table 3: MSFC Specifications to be Revised for Environmental Compliance

From the beginning, the implementation of replacement technology in NASA specifications and standards adopted a Continuous Improvement (CI) teaming approach coordinated by NOET RT^2. NASA specifications and standards were tailored using CI through Product Development Teams (PDTs) involving both NASA and the specification customers/users, i.e. contractors, other NASA centers and other engineering disciplines. This approach had been utilized with much success by MSFC's Materials and Processes (M&P) Laboratory to effectively tailor project/program materials and processes requirements, deliverable Data Requirements (DRs), and consolidate multiple company specifications into common NASA specifications. The M&P laboratory experience with using this cooperative CI/PDT approach resulted in cost savings and launch flow/processing enhancements. Base on this positive experience, PDTs were also used to implement environmental compliance by replacing and updating NASA specifications that utilized ODSs with alternate materials, processes and technologies. These PDTs adopted the following groundrules to facilitate the effectiveness of their activities:

- Solicit direct input from the users of the specification.
- Empower team members with the responsibility for product specification.
- Empower team members to speak and make decisions for the organizations they represent.
- Operate the team and make team decisions based on a consensus.
- Encourage sharing of data.
- Eliminate "how to's" and lessons learned as specification requirements.
- If "how to" and lessons learned are considered essential, provide this information in the specification as guidance and not as added requirements.
- Base specification requirements on essential performance criteria.
- Start specification with zero-base requirements, where each new requirement must "buy their way in" based on value added.
- Challenge all requirements.
- Eliminate unnecessary requirements that do not "add value".

This CI/PDT approach proved to be an advantage to implementation of environmental initiatives in the NASA specification revision process. It provided an efficient and cost effective mechanism for: expediting evaluation of supporting data; streamlining and consolidating data reporting requirements to only essential and required information that would be evaluated by the approving authority; allowing for real-time assessment of potential impacts and costs associated with specification changes prior to their inclusion in program requirements; creating a cooperative teaming arrangement conducive to sharing data, common problems and experiences; and eliminating redundant and duplicative replacement technology development activities. However, the task of implementing replacement NASA specifications for ODS still requires a significant effort. "How-to" specifications require new replacement materials to be tested and selected, while "performance-based" specifications must be clearly defined the expected results. Ultimately, if suitable to the intended application of the resulting specification, "performance-based" specifications can becomes virtually timeless, eliminating the need for subsequent revision.

The most widely used ODS at MSFC, where this usage was specified in standards was CFC-113. As was the case generally for NASA in general, CFC-113 usage applications at MSFC were primarily for cleaning solvents and cleanliness verification media, with some usage for coolants, analytical methods and reference standards. The specification that required the most significant use of CFC-113 by MSFC, as well as by the MSFC Shuttle propulsion elements contractors was MSFC-SPEC-164A, "Specification For Cleanliness Of Components For Use in Oxygen, Fuel and Pneumatic Systems." MSFC-SPEC-164A applied to MSFC fabrication and testing activities and required the use of CFC-113 (and/or TCA) as a precision cleaning solvent for immersion and vapor degreasing, as well as a cleanliness verification test media for Nonvolatile Residue (NVR) and particulate analysis. Recent

historical usage amounts of CFC-113 by MSFC are shown in Table 4. The figures for MSFC alone are the usage amounts for the fabrication, precision cleaning and analysis facilities in MSFC's M&P Laboratory where, due to facility constraints, very little if any of annual usage rate of about 65,000 pounds is recycled and recovered. As was stated earlier, MSFC-SPEC-164A is also applicable as contract requirement to MSFC Shuttle propulsion elements, including the External Tank (ET), Space Shuttle Main Engine (SSME), Alternate Turbopump Development (ATD) and Production (ATP), and Solid Rocket Booster (SRB). The total amounts used by MSFC and their Shuttle propulsion element prime contractors combined has been on the order of 200,000 pounds annually, with the recycle and recovery rates indicated in Table 4 being primarily due to Shuttle contractor efforts. Therefore, replacement of CFC-113 by substances without an ozone depleting potential would have a significant benefit to the environment. The steps necessary for replacement of CFC-113 in MSFC's precision cleaning and field cleaning operations requires identification of acceptable replacement materials for cleaning operations, NVR and particulate analysis, followed by revision of MSFC-SPEC-164.

Calendar Year	MSFC	Total (MSFC & Shuttle Contractors)
1991	65,052	221,582
1992	59,556	158,273
1993	64,300	175,000 (est.)

Note: 45% recycled/15% recovered

Table 4: MSFC CFC-113 Usage (pounds)

As the MSFC organization with prime responsibility for the materials selection and cleaning processes for on-site operations, as well as the Shuttle propulsion elements, the M&P Laboratory initiated a study of the center's Ozone-Depleting Chemical (ODC) replacement activities. Initially, in order to address the in-house activities in the fabrication and precision cleaning areas of the M & P Laboratory, a CI Chemical Replacement Team of Laboratory representatives was chartered to investigated ways to accommodate the elimination of ODCs. Operating as a PDT by consensus under the guidance of a facilitator, the specific recommendations of this team were as follows:

1.) Initial substitution of trichloroethylene (TCE) for CFC-113 in the final cleanliness verification process of MSFC-SPEC-164, with long range goal to eliminate halogenated solvent and pursue aqueous or semiaqueous cleaners. A significant data base existed from Saturn to Shuttle to implement TCE as alternate, with an overlap planned during the implementation approach period that would allow for revalidation of TCE data. TCE has very short atmospheric lifetime, is not a ODS, and costs significantly less than CFC-113 with no foreseeable punitive taxation/restrictions. TCE was removed from the list of suspect carcinogens and is not suspected as a human carcinogen according to ACGIH (reference 2). In addition, TCE is not currently listed as a carcinogen or potential carcinogen by NTP, IARC and OSHA according to the Materials Safety Data Sheet (reference 3). TCE is hazardous air pollutant, water pollutant and has toxicity problems requiring use of available control technology. In addition, the current use of CFC-113 at MSFC was more than was required for cleanliness verification and significant quantities were being used as a final rinse, with only the last 500 ml. being collected for verification, wasting significant quantities (up to 13 liters) per procedure. Therefore, with care and improvement in shop usage practices, the usage of TCE could conceivably be less than was required with CFC-113. The accelerated replacement of CFC-113 with TCE requires:

a.) Discontinued used of solvents as an unnecessary final rinse and redundant cleaning step, with final verification limited to the quantities specified in MSFC-SPEC-164. During an

initial validation period, a duplicate verification will be conducted using both TCE and CFC-113.

b.) Installation of an exhaust system with scrubbers in the precision cleaning facility. The system should minimize personnel exposure to TCE in the laboratory environment to below the 25 ppm Personnel Exposure Limit (PEL) utilized by MSFC.

c.) Installation of a catch basin and pump to minimize exposure of TCE to the laboratory environment, minimize emissions in the laboratory and to aid in the collection of samples for cleanliness verification.

d.) Upgrade of facility pumps to accommodate conversion from CFC-113 to TCE may be required to accommodate materials compatibility issues.

e.) Personnel respirators with remote air service as personnel protective devices for routine operations, and in case of solvent spills. TCE is a potentially hazardous material when exposure exceeds 25 ppm and decomposes to produce toxic fumes if exposed to flames.

f.) Installation of TCE distillation/recovery system for reuse of the solvent.

g.) Installation of an isopropyl alcohol (IPA) cleaning station since materials compatibility issues could necessitate a second cleaning system. IPA precision cleaning systems are commercially available with distillation and fire suppression capabilities, and should be investigated for cleaning small specialty items.

2.) Replacement of solvent cleaning/verification with aqueous or semiaqueous cleaners as a long term goal to eliminate the use of chlorinated hydrocarbon solvents. Considerable effort will be required to select and qualify these replacement materials.

3.) Other recommendations under consideration include: replace existing degreasers with Low Emission Vapor Degreasers (LEVD); eliminate vapor degreasers and convert to aqueous spray precleaning stations; and select and qualify (long term) aqueous or semiaqueous cleaners.

Even though the initial recommendations identified trichloroethylene (TCE) and isopropyl alcohol as potentially acceptable alternatives to CFC-113 for MSFC operations, neither material is universally applicable and must be considered as complementary. Cost estimates for implementation of TCE and IPA slightly favored TCE. This was due in part due to the flammability, higher boiling point and need to assure complete removal in oxygen components of IPA. Other considerations included: the incompatibility of residual IPA in oxygen systems; IPA was not as mature a replacement alternative as TCE; and data indicated IPA had a low recovery efficiency for certain fluid system contaminants. Due to these factors, MSFC selected TCE as the intermediate cleaner/verification solvent, with a longer term goal to qualify aqueous and semiaqueous materials. Yet the prime contractor for the ET is proposing to use IPA (in addition to TCE) for selected precision cleaning/cleanliness verification applications, including cleanliness verification media for hydrogen and oxygen lines, vessels and components. This is being proposed utilizing proper control methods and will be substantiated by qualification/validation data consistent with the requirements of the new replacement specification for MSFC-SPEC-164A.

Additionally, it was recognized that instrumental analytical verification methods, e.g. Optically Stimulated Electron Emission (OSEE), Fourier Transform Infrared (FTIR) analysis , etc.

could ultimately replace the chemicals used for NVR and/or particulate analysis. In order to accommodate these potential changes in the future, MSFC-SPEC-164 would have to become a more adaptable standard, versus it's more traditional role as a "how to" specification. By using the approach of developing a "performance-based" standard, the requirements could be easily tailored to accommodate alternate approaches or changes essential for future programs, without creating significant procedural constraints or producing unnecessary cost impacts for the users. The "performance-based" specification approach was ideally suited to the user needs.. Ultimately, this new specification would be a verification standard, defining the general data requirements and design considerations that would be required for approval of the cleaning and cleanliness verification process by the procuring activity. As such, the cleanliness verification performance requirements could be derived from the significant and successful data base developed over the last 25 years, from Saturn and Shuttle through the current advance propulsion technology test bed experience at MSFC .

In order to initiate this "performance-based" specification approach and replace the ODSs in this fluid system cleanliness specification, all principal users or customers of MSFC-SPEC-164, including the Shuttle prime contractors for whom MSFC-SPEC-164 was a Contract End Item (CEI) specification requirement, were invited contribute to the revision effort as members of a CI team during the initial Technical Interchange Meetings (TIMs). Participants that formed the PDT included representatives from all Shuttle propulsion element prime contractors organizations, and MSFC organization representatives from M&P Laboratory, fabrication services, facilities, propulsion test operations, component assembly and refurbishment, analytical chemistry, materials selection and control, contamination control, propellant compatibility testing and quality assurance. This approach allowed the participants to take ownership in the product and follow the CI/PDT groundrules discussed earlier. Ultimately, this enthusiastic team participated in numerous reviews, as the MSFC-SPEC-164 rewrite progressed. Copious input and comments were assessed through many iterations of the specification, with the team's consensus recommendations being incorporated into the final team product.

The resulting product, an environmentally compliant NASA cleanliness specification for components used in fluid systems, does not discard the established materials utilized successfully for so long to perform these processes, but rather uses these materials and processes, as well as their associated data bases to establish a baseline that all subsequent replacements must meet or exceed. In this replacement specification, the "performance-based" approach defines general data requirements and design considerations for producing data necessary to support approval of alternate cleaning and cleanliness verification processes by procuring activity. The performance criteria are particulate and NVR cleanliness verification levels based on successful performance experience in the field, during testing and in flight. The new specification strengthens particulate criteria by deemphasizes particle counting and bases requirements on maximum absolute particle sizes with a prohibition against silting. This aspect has an added benefit of simplifying analytical procedures. In addition, this revision establishes tape lift testing as an alternative for cleanliness verification when component flushing is impractical. New packaging material requirements take advantage of the substantial data generated by another center (KSC) to define appropriate material selection requirements. This replacement MSFC-SPEC-164 establishes new in-service and field cleaning criteria for ground test systems are based on accumulated history of successful propulsion test bed operations at these levels of cleanliness. New considerations allow for utilizing cryogenic cold shock to aid the cleaning process for the fluid system components prior to conducting cleanliness verification. Verification and inspection frequency and sample size are clearly defined for all testing required by the specification. Drying effluent gas verification analysis assures no residual accumulation of organic solvents or moisture that would be detrimental to system performance, e.g. IPA in oxygen system components. Less stringent purge gas requirements for tanks and vessels eliminate the need for "missile grade" air or gaseous nitrogen, based

on the successful and cost effective performance history of ET. Requirements for approval of alternate verification procedures define specific criteria for sample selection, verification test quantities and minimally acceptable statistical significance for data. The CI/PDT approach to teaming of specification customers and users has produced a viable specification that will benefit NASA-wide standardization activities for cleaning processes. This example will serve as a pathfinder and a model for the significant efforts that are required to bring the remaining NASA specifications and standards that reference targeted materials into compliance with environmental initiatives.

Already other MSFC specifications identified in Table 3 are being revised for replacement of ODSs using this same approach. For example, in MSFC-SPEC-1919, " Application and Cure of Thermal Ablative Compound," TCA is used as a solvent to clean and prepare various surfaces on the SRB and RSRM for application and bonding of the ablative compound. The revision will implement the downselected aqueous or organic hand wipe cleaners, e.g. Jettacin, Prime, Reveille, and/or PF Degreaser, and provide for consistent processing across Shuttle interfaces, launch flow enhancement at KSC and data sharing among the Shuttle element prime contractors. MSFC-SPEC-2083, "Polyurethane Foam Insulation (PDL-4034-2.5)," consolidates ET, Shuttle Orbiter and KSC requirements for into a common material procurement specification that provides common acceptance criteria and consistent material procurement requirements. The revision will implement HCFC-141B as the alternate blowing agent to replace CFC-11 without degrading the properties of this critical Thermal Protection System (TPS) material. MSFC-SPEC-2084, "Mix, Application and Cure of Polyurethane Foam (PDL-4034)," is the process specification that corresponds to the pervious TPS material specification, and consolidates ET, Oribter and KSC processing requirements for enhanced launch processing and commonalty. The revised specification implements the HCFC-141B alternate blowing agent as a replacement for CFC-113 to assure process consistency.

Finally, in all these activities, the teams utilized the NASA Environmental Information Network System (NEIS) as a tool and data source for ODS replacement in MSFC specifications. NEIS is a system of environmental data bases which are a part of the MPEEN system residing on a VAX cluster maintained by MSFC, which is available through the Materials and Processes Technical Information System (MAPTIS). NEIS is a tool currently being developed to support the NOET functions and is designed to: provide a central environmental technology resource drawing on all NASA centers' capabilities; support NASA programs to deliver hardware compliant with performance specifications and environmental regulations; track and access environmental regulations, usage, and new technology developments; and provide a channel of communication throughout the aerospace community. All data is dynamic, continuously updated and is intended to be flexible in order to meet the environmental community needs as they become know. NEIS is designed to aid in environmental compliance efforts, such an the implementation of replacement technology in NASA specifications and standards. The point of contact for more information is Marcia Clark-Ingram, NASA/MSFC/EH44, at 205-544-6229.

CONCLUSIONS

The discussion presented herein indicates that NOET and RT^2 are implementing a planned approach for accommodating environmental compliance through alternate replacement technology in NASA specifications and standards. Numerous NASA specifications and standards call specifically for the use of targeted materials. Because these specifications and standards generally have wide applicability, the impact of changing them to implement replacement technology has potentially serious and broad implications for the users. However, Continuous Improvement (CI) and teaming of

customers, users and the procuring activity is a productive approach to gaining consensus, when common/consolidated specifications that minimize impacts to projects and programs are required. Tailoring specifications and standards to meet environmental initiatives while precluding unnecessary project costs and data requirements is essential for success in the current environment. NASA is encouraging and pursuing implementation of common NASA-wide solutions to environmental issues. Through the NOET, NASA is actively sharing data and coordinating data and results to producing specifications and standards that are compliant with current environmental needs and requirements. NASA policy is to use of "voluntary standards" or existing consensus industry standards and actively participate in their development. When voluntary standards are unavailable or do not meet agency needs, replacement specifications and standards for environmentally hazardous materials and processes must rapidly establish and implement solutions, maintain currency and support program requirements as well a future needs without compromising or degrading performance. "Performance-based" specifications that clearly defined the expected results and are adaptable to new developments become virtually timeless, providing a distinct advantage in the task of implementing alternate technology to replace ODSs in NASA specifications and standards.

REFERENCES

1.) Schwinghamer, R. J., Congo, R. T., and Goldberg, B. E., "Environmental Initiatives at NASA: Taking the Lead in Alternative and Replacement Technologies," Federal Facilities Environmental Journal, Winter 1993-94, pages 437 through 455.

2.) American Conference of Governmental Industrial Hygienists (ACGIH), "1992-1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices," pages 40 through 45.

3.) PPG Industries, Inc., "Trichloroethylene," Materials Safety Data Sheet (MSDS), Form 6372 Rev 3-88, 07/12/93, pages 1 through 3.

An Overview of NASA Testing Requirements for Alternate Cleaning Solvents Used in Liquid and Gaseous Oxygen Environments

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Abstract

The elimination of CFC-containing cleaning solvents for oxygen systems has prompted the development of a number of alternative cleaning solvents that must now be evaluated not only for clean-ability, but compatibility as well. NASA Handbook 8060.1 (NHB 8060.1) establishes the requirements for evaluation, testing, and selection of materials for use in oxygen rich environments. Materials intended for use in space vehicles, specified test facilities, and ground support equipment must meet the requirements of this document. In addition to the requirements of NHB 8060.1 for oxygen service, alternative cleaning solvents must also be evaluated in other areas (such as corrosivity, non-metals compatibility, non-volatile residue contamination, etc...). This paper will discuss the testing requirements of NHB 8060.1 and present preliminary results from early screening tests performed at Marshall Space Flight Center's Materials Combustion Research Facility.

The NASA Handbook 8060.1C (NHB 8060.1C) establishes the requirements for evaluation, testing, and selection of materials that are intended for use in space vehicles, associated ground support equipment and facilities used during assembly, test, and flight operations. A portion of this specification deals specifically with all materials that are exposed to liquid oxygen (LOX), gaseous oxygen (GOX), and other reactive fluids. Materials for use in LOX/GOX must be evaluated for compatibility with the fluid in their use application (pressure and/or impact energy potential). In the case of alternative cleaning solvents the evaluation is made in LOX and/or GOX. Test 13A and Test 13B of NHB 8060.1C outlines the test procedures and criteria for evaluation of materials compatibility in these environments.

Test 13A of NHB 8060.1C defines the test procedure for the evaluation of the mechanical impact sensitivity of materials in ambient pressure LOX environments. Test 13B of NHB 8060.1C is the test procedure for the evaluation of mechanical impact sensitivity of materials in variable elevated pressure LOX or GOX environments. Both of these procedures have ASTM equivalents -- ASTM D2512-82 for Test 13A, ASTM G86-84 for Test 13B. The basic criteria of these tests are to impact samples with 72 ft-lb. (98 J) of impact energy to determine if a material reacts in various oxygen environments when mechanically impacted. The data presented in this paper, along with the initial screening test matrix, concentrates on the results produced from NHB 8060.1C, Test 13A, for initial evaluation.

The test unit utilized for these initial evaluations is the ambient pressure LOX impact test unit. This unit uses a 20 lb. plummet on nylon roller bushings, guided by 6 legs, to deliver impact energy to the sample being tested. This plummet can be dropped from various heights in order to obtain varying amounts of impact energy to the sample being tested. All testing performed for this evaluation utilizes a drop height of 43.3 inches to obtain the required 72 ft-lb. (98J) of impact energy. An electromagnet holds the plummet at the desired drop height until the test technician is ready to impact the sample. When the technician is ready, all lights in the testcell are turned off, and the technician releases the plummet and observes the impact for a flash or audible report (both are indications of a reaction taking place during testing).

The NHB 8060.1C, Test 13A, was chosen as the initial screening method for alternative cleaning solvents' compatibility with oxygen environments. This testing method is an aerospace industry standard and was chosen to establish a baseline of data comparable to historical data available from other sources. It should be emphasized that the results presented from this study are *only preliminary* and the overall goal of this program is to provide *a relative rating of each material as they compare to other candidate materials* that have been tested. **The data presented is not intended in any way as a recommendation or endorsement for the use of one product over any other**.

After the establishment of a standard testing method, sample preparation for testing and evaluation were then examined. Two different methods of sample preparation were chosen to reflect the wide range of possible use conditions that might be encountered by the various cleaning solvents. Sample preparation techniques follow those outlined in ASTM D2512-82, in paragraph 10.1 and paragraph 10.3. Paragraph 10.1 details the preparation of liquid samples in cups that are approximately 0.625 inch inside diameter and 0.050 inch deep. Sample material is placed in each cup in sufficient volume to fill each cup; then the cups are chilled in a container of liquid nitrogen to freeze the sample prior to impact testing in LOX. Paragraph 10.3 details the preparation of liquid samples on sulfuric acid anodized 6061-T6 Aluminum disks. Test disks are allowed to soak in the sample solution for approximately 15 minutes, then removed and allowed to drain at a 90 degree angle for approximately 15 minutes. The purpose of each of the above described preparation methods is to test a material for compatibility in bulk form and in residue form.

The test plan matrix (shown in Figure 1) was then developed. This matrix is designed so that all candidate materials are prepared and tested in a similar manner. Included in this test matrix is an option that allows for materials to be tested in the manufacturer's suggested solution strength, if it is different from the non-diluted full strength concentration. This allowance is made to cover the broadest possible range of end-use concentrations for each material. The matrix has been devised so that each material is tested at least twice, once as a full strength bulk solution and once as a residue. For each concentration of solution tested that is not "full strength", both test methods (0.050 inch bulk solution and residue) are utilized to test the various manufacturers suggested solution concentrations. The rationale for this test matrix is to test a material in the two most likely end-use conditions. Testing the sample in a bulk form (0.050 inch deep sample cups) examines the possible reactivity of a material in situations where a pocket of the fluid in question has been trapped somewhere in an oxygen system. Residue testing of a material examines the possible reactivity of the remnants of the fluid in question in an oxygen system.

Table 1 describes some of the historical data available for the various tested materials. A complete listing of all data presented in this report is available for review and analysis on the Materials And Processes Technical Information System (MAPTIS) resident at Marshall Space Flight Center (MSFC). The format of the data presented in Table 1 is altered from the standard MAPTIS output format for ease in comparison and presentation in this paper. The data in Table 1 shows historical data by product trade name, a unique NASA Material Code (a five digit number assigned to a specific material for tracking and identification purposes on MAPTIS), the test conditions (test fluid, test temperature, and sample form), and the number of reactions per tests. The standard acceptance criteria utilizing the

methods described for a given energy level in NHB 8060.1C is less than 2 reactions per 20 samples tested. If only 1 reaction is noted during the initial 20 sample drops, then an additional 40 samples must be tested with no further reactions noted in order for the material to be considered passing this test (i.e. 0/20 or 1/60 is passing, 2 or more reactions failing, 1/20 is considered inconclusive).

Table 2 describes a partial list of the alternative solvent results produced to date in this testing program. The results are reported in the same format as Table 1, described earlier. It should be emphasized again that these preliminary results are meant only as a relative rating of the liquid and gaseous oxygen compatibility of the tested materials and are not meant to imply any endorsement of any material. The preliminary results indicate that, under certain conditions, some replacement materials should be considered for further oxygen compatibility study. Again, this paper only deals with the area of oxygen compatibility. There are a number of other areas (such as corrosion, metals and non-metals compatibility, etc...) for which each of these materials must be evaluated prior to implementation as a cleaning solvent.

Table 1. Historical Data

Product Name	MAPTIS Material Code	Test Pressure (psia)	Test Fluid	Test Temp. (°F) 68XC5dem	Sample	Reactions/ Tests	Concentration
Blue Gold	87992	14.7	LOX	-297	Bulk	0/20	Full Strength
Amway SA8	88157	14.7	LOX	-297	Residue	1/20	Full Strength
CCS-4000	00961	14.7	LOX	-297	Bulk	0/20	Full Strength
					Residue	0/20	Full Strength
Neugenic 4175	89936	1050	LOX	-297	Residue	0/20	Full Strength
		1050	GOX	75	Residue	0/20	Full Strength
Turco Spray-eze LT	01352	10,000	LOX	-297	Bulk	0/20	Full Strength
		10,000	LOX	-297	Bulk	0/20	5 oz./gallon deionized water

Table 2. Program Data

Product Name	MAPTIS Material Code	Test Pressure (psia)	Test Fluid	Test Temp. (°F)	Sample Form	Reactions/ Tests	Concentration
Isopropyl Alcohol	01524	14.7	LOX	-297	Bulk	9/20	Full Strength
					Residue	0/20	Full Strength
Amberclean L12	01241	14.7	LOX	-297	Bulk	0/20	Full Strength
					Bulk	0/20	75% deionized water/ 25% sample fluid
					Residue	7/20	Full Strength
Amberclean L21	01249	14.7	LOX	-297	Bulk	0/20	Full Strength
					Bulk	0/20	90% deionized water/ 10% sample fluid
					Residue	19/20	Full Strength
TCE (Hi-Purity Grade)	01257	14.7	LOX	-297	Residue	0/20	Full Strength
DOT 111/113	01252	14.7	LOX	-297	Bulk	0/20	Full Strength
					Bulk	0/20	90% deionized water/ 10% sample fluid
					Residue	6/20	Full Strength
					Residue	0/20	90% deionized water/ 10% sample fluid

Figure 1. Test Plan Matrix

PHASE 1 - Prepare and test in accordance with NHB 8060.1C, Test 13A per instructions for liquid samples as described in ASTM D2512, Para. 10.1 (0.050 inch deep Aluminum grease cups, samples to be tested full strength). Start testing at 72 ft-lb. impact energy, theshhold for energy as required.

PHASE 2 - Prepare and test in accordace with NHB 8060.1C, Test 13A per instructions for emulsifiers as described in ASTM D-2512, Para. 10.3 (unsealed sulfuric acid anodized Aluminum disks, soaked in full strength solution 15 minutes then drain at 90 degrees for 15 minutes). Start testing at 72 ft-lb. impact energy, thershhold for energy as required.

PHASE 3 - Prepare and test in accordance with NHB 8060.1C, Test 13A per instructions for liquid samples as described in ASTM D2512, Para. 10.1 (0.050 inch deep Aluminum grease cups, samples to be tested in solution prepared according to manufacturer's recommendations). Start testing at 72 ft-lb., threshhold for energy as required.

PHASE 4 - Prepare and test in accordace with NHB 8060.1C, Test 13A per instructions for emulsifiers as described in ASTM D-2512, Para. 10.3 (unsealed sulfuric acid anodized Aluminum disks, soaked in solution prepared per manufacturer's recommendations for 15 minutes then drain at 90 degrees for 15 minutes). Start testing at 72 ft-lb. impact energy, thershhold for energy as required.

PHASE 5 - Prepare a container of full strength solution and evaporate to dryness for analytical testing. Perpare a second container of solution prepared according to manufacturer's recommendations and evaporate to dryness for analytical testing.

DEVELOPMENT OF A CFC CRITICAL AREA RESPONSE (CAR) PACKAGE

Dr. J. Wayne McCain

ABSTRACT

During the past two years, the NASA Marshall Space Flight Center (MSFC) has studied means to improve the transfer of technology from a major federal lab to a significant portion of an industrial segment. In the past, technology transfers had taken place with individual firms, or small groups of firms. This method of "customized" transfer is often time consuming and can reduce the effectiveness of a response. Thus, a method was achieved to develop a standardized package on replacement of Chlorofluorocarbons (CFCs) that could be sent out to a large number of firms with minimum follow-up.

INTRODUCTION

The usual role of a technology transfer agent is to convey an existing technology from the originator to prospective users. This is typically accomplished by locating reports or other descriptions of the technology and then transferring them to the requesting entities. Often this process is aided by use of special seminars or workshops surrounding a particular technology. Also, brochures explaining the technology sources may be circulated for an increased effect. This paper describes a more proactive approach to technology transfer. In this approach, a technology transfer product was developed as a stand-alone method of transferring a very specific type of technology. At the NASA Marshall Space Flight Center (MSFC), this product is known as a Critical Area Response (CAR) package. This concept was developed to serve the technology transfer process in specific industry-critical areas where information is needed urgently.

Dr. **J. Wayne McCain**, Associate Professor, Management of Technology, Athens State College (Athens, Alabama) and Owner of HyTek Associates, has a PhD in Engineering from the University of Alabama in Huntsville (UAH). He was responsible for the CFC CAR development while consulting at the Marshall Center for UAH and most recently as a consultant for ERC, Inc.

This may be considered a handbook or workbook approach to technology transfer. That is, a stand-alone, user-friendly data package is produced that should, in one operation, solve a majority of the user's needs for knowledge of a specific technology. In the case of mature technology, such a data package product would remain current for a considerable period. However, there are also urgent industrial needs for data packages in areas of major ongoing development such as CFC replacement.

BACKGROUND

The Criticality of CFC Replacement

The natural ozone umbrella that helps protect life on our earth from the harmful effects of ultraviolet (UV) radiation from the sun is being damaged by extensive use of chlorofluorocarbons (CFCs). The ozone layer of our atmosphere circles the earth performing two important functions. This pale blue gas, a variation in the oxygen molecule, is toxic if breathed but, in the stratosphere 10 to 30 miles above the surface of the earth, the layer acts as a filter to protect us from UV and as a "blanket" to stabilize earth's temperatures. Every 1-percent drop in ozone levels can lead to a 3-percent increase in non-melanoma skin cancers in light-skinned people, dramatic increases in blinding eye cataracts, lethal melanoma cancers, and damage to the human immune system. In addition, timber production sags and crop losses increase.

Stability of the ozone layer itself is fragile and is being adversely affected by man's use of CFCs in various industrial processes and in mechanical systems. CFC molecules that are vented or allowed to evaporate in these processes, make their way to the stratosphere where, when coming into contact with ozone, they act to deplete it from the air. **One** CFC-generated chlorine atom alone can catalyze the destruction of as many as **100,000** ozone molecules.

The effects of a CFC molecule on ozone has been demonstrated in the laboratory as well as by computer modeling.

The depletion process, shown in Figure 1, is as follows:

1-2. A CFC molecule uses its chlorine atom to break down an ozone atom into an oxygen atom. An ozone molecule is lost in the process;

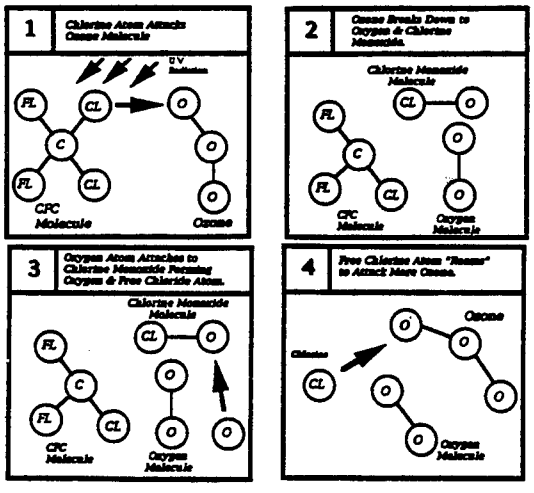

Figure 1 - Ozone Depletion By CFCs

3. Another chlorine atom is freed;

4. The new chlorine eventually comes into contact with another ozone molecule, starting the process over.

Substantial Ozone depletion is the result of these interactions between CFCs and the atmosphere. Ozone levels have dropped an estimated 40 percent in certain spots over the last decade. At the South Pole (and the North Pole to a lesser extent) the depletion is severe enough that a measurable hole has appeared. It is estimated that over the next decade, stratospheric chlorine levels will continue to rise at a rate of about 5 percent per year. Today's level is 3.5 parts per billion, almost six times the normal "background" level .

In 1991, NASA launched the Space Shuttle Discovery carrying a 7 and one-half-ton satellite whose primary purpose is to learn more about the ozone depletion problem. This $700 million dollar investment shows the magnitude of importance placed upon Ozone depletion by NASA and the United States Government.

A world-wide effort is underway to control and limit the amount of CFC gases released into the atmosphere. The drive began in 1978 when the use of CFCs in aerosol cans were banned in the United States. In 1987 the first meeting of 23 major industrialized nations met in Montreal, Canada to address future plans for controlling CFCs. It was agreed that CFC production would be phased down to fifty percent of that year's level by 1998. According to Dow Chemical, the U. S. produced 1.7 billion pounds of chlorinated solvents in 1989.

In 1990, nations again met and agreed to accelerate the phase out schedule. The result of this London meeting was an agreement to totally ban CFC production by the year 2000. Then in February 1992, President George Bush announced that production of CFCs in the U. S. would be banned altogether after January 1, 1996. This accelerated schedule is shown in Figure 2.

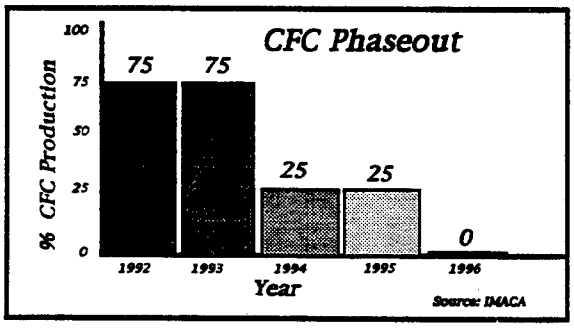

Figure 2 - U.S. CFC Phase out Schedule

Additional legislation has been passed in the U. S. to further control the release of CFCs. For instance, in 1990, the Federal Clean Air Act was amended to require the recapture and recycling of any refrigerant removed from automotive air conditioning (A/C) systems. The Act requires that all technicians handling CFC compounds must be properly trained and certified and imposed an excise tax on the

purchase of new R-12 refrigerant (freon). As shown in Figure 3, the tax on a pound of CFC-12 for automotive use was $1.67 in 1992. By 1999, if CFCs were available, the tax would add $4.90 per pound to cost. Other aspects of industry are also affected. Cleaning operations that have previously used solvents such as 1, 1, 1 Trichloroethane, Freon, MEK, Acetone, and other potentially harmful solvents must be modified. Generation of foams requiring CFC blowing agents must be revisited and the CFC hazards curtailed. Table 1 shows a listing of common CFC compounds affected.

Table 1 - CFCs Ins and Outs [Source IMACA]

Compound	Lifetime (years)	Ozone Depletion Potential (avg.)	Global Warming	Primary Uses
What's Out				
CFC-11	60	1	1	Refrig., A/C, foams
CFC-12	120	1	3	Refrig., A/C, foams
CFC-113	90	0.8	1.4	Solvents
CFC-114	200	0.7	3.9	Foam packaging, aerosols
CFC-115	400	0.4	7.5	Refrigeration
What's In				
HCFC-22	15	0.05	0.34	Refrig., A/C, foams
HCFC-123	2	0.02	0.02	Refrig., foams, solvents
HCFC-124	7	0.02	0.1	A/C, insulating foams
HCFC-141b	8	0.1	0.09	Insulating foams, solvents
HCFC-142b	19	0.06	0.36	Insulating foams, solvents
HFC-125	28	0	0.58	Refrigeration
HFC-134a	16	0	0.26	Refrigeration, A/C
HFC-152a	2	0	0.03	Insulating foams, aerosols

The Basic MSFC Tech Transfer Approach

Generally, the technology transfer field does not think of its stock-in-trade (technical information) as a product or service in the way that is used in a manufacturing or technical services company. Marketing of a package of data like the CFC Critical Area Response is approached typically in a non-commercial manner. This situation is best seen in the "shotgun" approach to achieving technology transfer as is used at many federal laboratories. A typical "shopping list" of general technical areas of capability used by the NASA Marshall Space Flight Center (MSFC) describing each laboratory's primary capabilities is distributed. Other federal labs use similar lists. This information is widely circulated and results in a certain number of requests for technical assistance. However, the matching of technical capability to requestor needs is often difficult. Thus the capabilities of the "shopping list" are not targeted to a specific market.

At MSFC, technology assistance has been promoted for many years. The general approach has been to depend on the shopping list of technical expertise and hope that one or more technologies would appeal to significant numbers of a general audience.

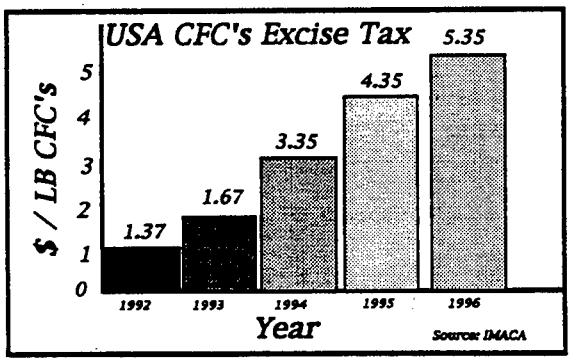

Figure 3 - Excise Taxes On CFC's

In addition, numerous technology transfer workshops or seminars have been held in Alabama and the Southeast to attract clientele. In recent years, these "road shows" have been improved by highlighting specific technology transfer projects or "success stories" to demonstrate the existence of successful transfers.

The ORNL Approach

Further justification of the CAR approach is noted at Oak Ridge National Laboratory (ORNL), where technology transfer has been handled by the operating contractor, Martin Marietta Energy Systems, for more than a dozen years. As an industrial firm, Martin Marietta took a more commercial approach to marketing ORNL technology than did typical federal labs such as MSFC. The ORNL approach was to hire seven full-time technology transfer personnel, most of whom had business degrees. This group then began to search the totality of the diverse ORNL technology base to locate a few new technologies deemed ready to begin the process of commercialization. Then the ORNL technology transfer (T^2) team began a market

survey of possible firms that might be interested in commercializing each of the subject new ORNL technologies. Because these new technologies tended to be specific and esoteric, the market survey was very focused. This focused marketing approach has been rather successful at ORNL. A significant number of companies have signed agreements (CRADAs) for joint product or process development and a number of laboratory patents have been licensed.

Developing the CAR Package

Partly as a result of the success of **focused** technology transfer marketing at ORNL, the MSFC Technology Utilization Office (TUO) with the assistance of the University of Alabama in Huntsville (UAH) developed the concept of a basic technology transfer product (stand-alone data package). The product, a Critical Area Response (CAR) package, is developed to respond to a known critical area of technology transfer need. Critical technology transfer areas have certain criteria as follows:

* **Must be important to industry,**

* **Must be important to a broad sector of a single industry or to several industries,**

* **Must be resolvable with MSFC resources.**

With this CAR approach, MSFC felt that it could focus on a few broad, receptive targets for the transfer of some of its capabilities, notably CFC replacement technologies and information.

UAH working with NASA MSFC developed the first CAR package on another subject: the modular manufacturing process simulation for the apparel industry. Over 300 copies of that CAR package were distributed during 1992 and 1993. Only about 10% of the requestors had difficulty using the supplied software and contacted UAH for help. Most were helped by telephone and/or mail. In addition, semi-annual $1^1/_2$ day seminars were provided at modest cost for those persons who needed hands-on help. Based on its wide acceptance in industry, the modular manufacturing CAR was judged 90% successful as a stand-alone item.

The CFC package reflects the need to quickly replace CFC compounds as well as other ozone-depleting chemicals such as methyl chloroform. In this package, federal regulations on the use of CFCs and other ozone depleters are discussed. Also, details of replacement refrigerants and solvents are provided. This is, however, a difficult package to maintain because of the need to update it frequently as new products and/or processes reach the market.

The purpose of the CFC CAR document is to provide interim information which has been compiled by the Marshall Space Flight Center regarding CFC replacement, alternate processes, and other related information. These data, while incomplete at any given time, will hopefully be of use in identifying potential sources, processes, and chemical replacements. This document will be updated periodically as additional information becomes available.

Contents of the CFC CAR Package

The CFC CAR consists of a brief introduction to the CFC replacement problem with the majority of the data contained in related appendices. Contents of the appendices are as follows:

Appendix A - General references on CFC's and replacement.

Appendix B - Addresses potential replacements and sources for solvent cleaning chemicals. The information provided is not an exhaustive list and other options are available.

Appendix C - Provides information regarding industrial refrigerant replacements and procedures for handling CFC chemicals used for refrigeration purposes. Excerpts from some applicable Federal documents are provided. Again, these data are not exhaustive and much more information exists.

Appendix D - Includes information on alternate cleaning methods and processes which may be applied to replace methods previously using CFC-containing chemicals.

Appendix E - Provides preliminary information extracted from MSFC's .NASA Operational Environment Team (NOET) CFC Replacement workshops.

Appendix F - Provides a listing of government agency and industrial sources for additional information, equipment, and chemical replacements.

Promotion of CAR Packages

It is not sufficient to develop a data package that is needed by a large industrial segment unless that segment can be made aware of the package so that they can request it. Fortunately, there are various means available to contact industrial groups. Many industries or major industrial segments are represented by specific industry associations. For the sewn products (apparel) industry, the principal organization is the American Apparel Manufacturers Association (AAMA). Another method to contact an industrial group is through trade journals. Often there are a number of these publications and it is desirable to select the two or three with the most circulation.

Future CAR Packages

The success of the original CAR Modular Manufacturing Simulation and CFC packages has resulted in the NASA MSFC Technology Utilization Office seeking to develop other Critical Area Response packages. One such package for **corrosion preventive coatings** is currently being compiled.

CONCLUSIONS

The idea of a widely usable, stand-alone technology transfer product is not new. Publishing companies have long tried to accomplish data transfer with technical handbooks and special commercial software packages. An early federal example is the "Fastener Design Manual", NASA Reference Publication 1228, produced by the NASA Lewis Research Center in 1990. The concept of federal "handbooks" to promote technology transfer is considered valid because these documents can be produced as soon as the need arises, which is not always the case with their commercial counterparts. Also, federal lab data is more likely to be current because it is being produced by persons who are leaders in their specific fields, as compared to commercial editors. Consequently, Marshall Space Flight Center (MSFC) will continue to develop and promote CAR packages for unmet industrial needs.

It is felt that the CFC CAR package will become more popular as its existence becomes more widely known. It has general use in industries that form metals, manufacture electronics and make foam insulation. After the initial announcement of the availability of this package, more than 200 requests from firms have been received.

The CFC Critical Area Response (CAR) data package is sponsored by NASA Marshall Space Flight Center (MSFC) and is thus **free of charge**.

Should your company or organization provide or have knowledge of additional pertinent information on CFC replacement that would be appropriate for inclusion into the CFC CAR document or should you desire to obtain a copy of the latest release, please contact the NASA MSFC Technology Utilization Office at the following address:

Marshall Space Flight Center
Technology Utilization Office
CFC Replacement CAR
Attention: Dr. Ken Fernandez, Code LA20
Huntsville, Alabama 35812

Phone: (205) 544-3825
FAX: (205) 544-3131

BIBLIOGRAPHY

McCain, J. Wayne and M. C. Ziemke; (June 1994); *A Product Development Approach To Marketing Technology;* Proceedings, Technology Transfer Society (T^2S) 1994 Annual meeting; Huntsville, Alabama.

McCain, J. Wayne; (May 1994); *CFC Critical Area Response;* Revision C, NASA, Marshall Space Flight Center, Technology Utilization Office, Code LA20; Huntsville, Alabama.

McCain, J. Wayne; (August 1993); *CFC Critical Area Response;* Draft, NASA, Marshall Space Flight Center, Technology Utilization Office, Code LA20; Huntsville, Alabama.

Schroer, Bernard J.; (Aug., Sept., Oct. 1992); *Manufacturing's New Crystal Ball, Parts 1, 2 and 3,* Bobbin Magazine.

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The mandated elimination of CFC's, Halons, TCA, and other ozone depleting chemicals and specific hazardous materials has required changes and new developments in aerospace materials and processes. The aerospace industry has been involved for several years in providing product substitutions, redesigning entire production processes, and developing new materials that minimize or eliminate damage to the environment. These activities emphasize replacement cleaning solvents and their application verifications, compliant coatings including corrosion protection systems, and removal techniques, chemical propulsion effects on the environment, and the initiation of modifications to relevant processing and manufacturing specifications and standards.

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