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*Pollution Prevention Wipe Application Study

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Abstract

As part of a pollution prevention program, a study was conducted at Sandia National Laboratories and at the Amarillo, "Pantex Plant" to identify a suitable replacement solvent(s) for cleaning hardware during routine maintenance operations. Current cleaning is performed using solvents (e.g. acetone, toluene, MEK, alcohols) that are classified as Resource Conservation and Recovery Act (RCRA) materials. The Environmental Protection Agency (EPA) has assigned four characteristics as the criteria for determining whether a material is identified as hazardous under RCRA: Ignitability, Corrosivity, Reactivity and Toxicity. Within the DOE and DoD sector, these solvents are used with hand wipes to clean surfaces prior to O-ring replacement, to remove decals for new labeling, to clean painted surfaces prior to reconditioning, and for other general maintenance purposes. In some cases, low level radioactive contamination during cleaning necessitates that the RCRA solvent-containing wipes be classified as mixed waste. To avoid using RCRA materials, cleaning candidates were sought that had a flashpoint greater than 140 F, a pH between 2.5 and 12.5, and did not fail the reactivity and toxicity criteria. Three brominated cleaners, two hydrofluoroether azeotropes and two aliphatic hydrocarbon cleaner formulations were studied as potential replacements. Cleaning efficacy, materials compatibility, corrosion and accelerated aging studies were conducted and used to screen potential candidates. Hypersolve NPB (an n-propyl bromide based formulation) consistently ranked high in removing typical contaminants for weapons applications. The results of the study are presented.

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DISCLAIMER

I. Introduction

Sandia National Laboratories (SNL) and the Amarillo, "Pantex Plant" have teamed on a pollution prevention project to identify suitable replacement solvent(s) for nuclear weapons maintenance operations. Field weapons maintenance is currently performed using solvents (e.g. acetone, toluene, MEK, alcohols, etc.) that are classified as Resource Conservation and Recovery Act (RCRA) materials. These solvents are used with hand wipes to clean weapon surfaces prior to O-ring replacement, to remove decals for new labeling, to clean painted surfaces prior to reconditioning, and for other general maintenance purposes. The EPA has assigned four characteristics as the criteria for determining whether a material should be identified as hazardous under RCRA: Ignitability, Corrosivity, Reactivity and Toxicity. In some cases, low level radioactive contamination from weapon surfaces necessitates that the RCRA solvent-containing wipes used during the maintenance operations be classified as mixed waste. To avoid using RCRA materials, cleaning candidates were sought with a flashpoint greater than 140 F, a pH between 2.5 and 12.5, and did not fail the reactivity and toxicity criteria.

The primary goal of the project is to reduce and/or eliminate mixed waste streams for the DOE weapons complex and DoD in DOE-directed nuclear maintenance applications. A significant cost savings can be realized if this goal is achieved. Disposal of mixed waste is significantly more expensive than the disposal of radioactive waste alone. The DOE complex-wide potential estimated savings are 1370 cubic meters of mixed waste and 457,000 kg of hazardous waste. This equivocates to estimated cost savings of $16M. Although DoD's waste is smaller, the waste is relatively more expensive per unit volume because it is generated in smaller quantities at many different sites. This waste cannot then be consolidated into a larger mixed waste depository due to state laws governing shipment of RCRA-regulated hazardous waste. The Air Force estimates potential annual savings of over $300K and the Navy's estimates are on the order of $150K. The total expected annual savings to the government are $16M for the DOE and $450K for the DoD, for a total of 6.45M.[1]

The major tasks of this study included: 1) cleaning efficacy tests, so that the candidate cleaner(s) selected "cleaned as well as or better than" the existing baseline cleaners, 2) corrosivity effects of the cleaners on the various metal alloys of interest, 3) compatibility effects of organic materials, 4) accelerated aging studies and 5) ES&H issues associated with the cleaners.

II. Experimental

1. Cleaning Efficacy Study - For the purpose of this study and for ease of analysis, 38.1 mm OD, 16 RMS 6061 aluminum (Al) and 304 stainless steel (SS) discs were utilized. For statistical purposes, five samples per condition were analyzed. In order to obtain an initial uniform surface, the discs were first precleaned using an n-propyl bromide based cleaner, a.k.a. Nu Tri Clean followed by an isopropyl alcohol rinse (IPA). It was determined in an earlier study that precleaning with Nu Tri Clean was comparable to cleaning with trichloroethylene (TCE). This in effect eliminated residual chlorides as a variable in the process. After the discs were precleaned, a contaminant in the amount of 0.2 cc was applied to the disc. The contaminant was allowed to dry for 1/2 hour before it was wiped clean. Each disc was then wiped a total of three times using wipes furnished by the Amarillo, "Pantex Plant". Three methods were used to determine cleanliness levels. Goniometer/Contact angle measurements and MESERAN analyses were performed at SNL. X-ray photoelectron and Auger electron spectroscopy was performed at the Amarillo, "Pantex Plant".

A Rame Hart Model 100 Contact Angle (CA) Goniometer was used to determine surface cleanliness. The test measures the contact (tangent) angle that is formed between a drop of water and its supporting surface. The method is a relative measurement of surface wettability. In general, the cleaner and less oxidized a surface, the lower the CA measurement. The CA measurement is a qualitative test that is used as an initial screening tool.

A MESERAN Surface Analyzer was the second analytical method for determining quantitative measurement of microorganic residues to nanogram/cm^2 levels using a slope technique. The MESERAN is a non-destructive test method available for in process organic contamination detection and measurement.[2] Its measurement is based on Evaporative Rate Analysis technology. The technique measures the rate of evaporation of a carbon-14 tagged radioactive chemical with a Geiger counter. The optimal slope of the log count versus time evaporation curve, expressed as a positive integer, is a valid inverse measure of the amount of residue, i.e., the higher the slope the less the residue.[3] Calibration curves have been established for common organic contaminants and can be used to convert slope values to contamination levels in nanograms/cm^2.

X-ray photoelectron spectroscopy (XPS) is a surface sensitive analytical technique in which only the first few monolayers (0-100 angstroms) of the surface of a material are examined. The technique measures the binding energy of valence and core electrons in atoms and molecules. The binding energy of an element can be related to its oxidation state. This gives molecular bonding information about the surface constituents of a material. XPS is based upon the photoelectric effect.[4,5] Irradiation of a surface with monochromatic x-rays results in the ejection of photoelectrons from valence and core levels. The energy of a monochromatic incident x-ray is transformed into the kinetic energy of an ejected electron. By experimentally measuring the kinetic energy (E_k) of the expelled photoelectron and knowing the x-ray photon energy (hu, the binding energy (E_b) of electrons can be found using the following relationship: $E_b = hu - E_k - \omega$ where ω is the work function unique to the spectrometer.

XPS uses two modes of analysis to produce its information. Low-resolution or survey XPS spectra can give qualitative information and atomic composition of the sample surface. High-resolution XPS spectra can resolve elemental peaks further and give more detailed chemical bonding information on each element of interest. The binding energy of an element is unique to the element as well as unique to its chemical environment. E_b can change by several eV due to changes in oxidation state. Upon examination of inner shell electrons, the binding energies of these electrons in any element, X, can be directly related to the oxidation state of that element in a molecule in the following sequence: $X^- < X^{\delta-} < X^0 < X^{\delta+} < X^+$. This is to say, as the positive charge on an atom increases, so does the binding energy of the atom. This would seem logical because the remaining electrons would experience a greater nuclear affinity and, thus, would be more tightly bound than in a neutral atom. In the same way, as an atom acquires a negative charge, the electrons would be less tightly bound by the nucleus and the binding energy of the ejected photoelectrons would decrease.

A Kratos Analytical AXIS HSi XPS spectrometer was used in this study. The x-ray source was an aluminum anode. A quartz crystal, with a Johann geometry, focused monochromatic aluminum K_α photons of 1486.6 eV onto the samples. Roughly one hour per sample was required to accumulate the low resolution scans, while high resolution scans required about twice the counting times.

Three sets of the 1.5" metal coupon discs were analyzed by XPS and compared to goniometer/contact angle and MESERAN data. The discs were 38.1 mm in diameter and 6.35 mm thick. The first set of discs consisted of 6061 Al that were polished with 1200 grit SiC. These samples were studied to determine if a relationship existed among the three analytical techniques. The second set of discs consisted of both 6061 Al and 304 SS that were solvent cleaned only. This second set of discs consisted of two types: the first type was cleaned by ultrasonicating in TCE for two minutes, which was then followed by another ultrasonication for two minutes in IPA and in the second type the TCE was replaced by an n-propyl bromide based cleaner. The surface of these samples was examined with XPS to test for incompatibility of these metals with the solvents. The third set of discs was the wipe study samples that was discussed in the first paragraph of this section.

XPS spectra were recorded in at least four different areas on each disc surface. The analysis area was ~ 0.004 in^2 (2.5 mm^2). The four areas were located equidistant in a 0.5 in (13 mm) diameter circle which was centered on the disc. The XPS spectra were recorded with a minimum of 5×10^3 counts (above background) in each peak, and were deconvoluted to a best fit using peak shapes of 70% Gaussian and 30% Lorentzian character. It should be noted that hydrogen is omitted in the atomic percent determinations. It is very difficult for the XPS technique to quantify hydrogen due to the fact that its electron is in the valence level. These valence electrons are often associated with, or shared between, two or more elements and thus cannot be easily used for elemental quantification of the surface.

2. Compatibility Tests on Materials - Materials compatibility tests on organic materials and other materials, such as paints and ceramics were performed in the event of an inadvertent spill. The compatibility test defined for this study consisted of a 2-minute immersion of representative weapons materials in the candidate and baseline solvents. Weight change and visual analyses (discoloration, swelling, dissolution, texture change, etc.) of the materials were recorded before and after immersion.

3. Corrosion Tests - Two corrosion tests including a "Sandwich Corrosion Test" per ASTM Standard F 1110-90 and an "Immersion Corrosion Test" per ASTM Standard F 483-91 were performed.

The Sandwich Corrosion Test is a comparative accelerated aging test used to determine the corrosivity of cleaners, generally on aluminum alloys. In this case, the study was expanded to include 304 SS and titanium 6A14 vanadium. Briefly, metal alloy samples (51 mm" X 102 mm X 1 mm) having clad (bare), anodized or alodined surfaces, were sandwiched together (with a filter paper saturated with the candidate solution between the two metals). The sandwiches (replicates of three per condition) were cycled between warm (100 F) dry air and warm humid air (100 F, 95-100% RH) for five days and then put into the warm humid air environment over the weekend for a total of 168 hours exposure. After the exposure cycle was complete, the samples were inspected with the naked eye and 10X magnification to determine whether corrosion had occurred. A relative corrosion severity rating system (Table 10) was used to numerically rank order the results. Only the surfaces that were in contact with the saturated filter paper were compared. Any corrosion at the edge of the sandwich was disregarded. Any corrosion in excess of that shown by the control group was cause for rejection per the ASTM standard definition.

The Immersion Corrosion Test determines the corrosiveness of maintenance chemicals on metals (25.4 mm X 51 mm X 10 mm) under conditions of total immersion by a combination of weight change measurements and a visual qualitative determination of change. The procedure was as follows: 1) three replicate samples of each alloy were precleaned with TCE and IPA, 2) the samples were weighed to the nearest 0.1 mg prior to immersion, 3) the samples were immersed in the cleaner for a 24 hour period, 4) at the end of the 24 hour period, the samples were removed from the solution and reweiged and inspected (for discoloration, dulling etching, presence of growth, pitting, presence of selective or localized attack etc.), and compared to the control sample. The prescribed temperature of the solutions was 100 F.

The metal alloys tested included, bare 6061, 7075, and 2024 Al, anodized 6061, 7075 and 2024 Al, alodined 6061, 7075, and 2024 Al, bare titanium, bare 304 SS, and passivated 304 SS. The anodized, alodined, and passivated surfaces were prepared at the Amarillo, "Pantex Plant".

4. Accelerated Aging Studies - Representative test materials were placed in canisters that contained candidate solvent vapors. Accelerated aging studies were then commenced. A 320-day accelerated aging thermal cycle was used to determine the effect of different materials to weapons environments. The profile consisted of five 64-day cycles, with different ramp and soak times and temperatures (–60 C to 70 C).

5. Candidate Solvent Selection Process - Preliminary tests at the Amarillo, "Pantex Plant" identified a chlorobromomethane-based product, a.k.a. Borothene, as a potential candidate. Borothene was subsequently dropped from consideration after the EPA Stratospheric Ozone Protection Division deemed it unacceptable due to its ozone depletion potential. A linear dibasic ester was also considered but eventually excluded due to personnel safety concerns, (i.e., the low threshold limit value of 1.5 ppm would require the use of a respirator or other protective measure).

Candidate solvents that were tested included n-propyl bromide based cleaners Nu Tri Clean, Abzol VG, and Hypersolve NPB. These brominated formulations contain predominately n-propyl bromide with minor differences in their inhibitor package. Two hydrofluoroether azeotropes including HFE-71DE and HFE-71DA were tested. Two aliphatic hydrocarbons, Exxsol D80 and Exxsol D60, were also tested. Exxsol D80 was eventually dropped from the study because of its low evaporation rate and substituted with Exxsol D60, which has an evaporation rate that is 12 times faster. Traditional baseline cleaners included 1,1,1 trichloroethane, acetone, and IPA. The cleaners that were tested and typical properties are shown in Table 1.

6. Contaminants and Substrates for Cleaning Efficacy Study - Three contaminants were evaluated on two metal alloy (6061 Al and 304 SS) surfaces. The three contaminants included DC4 silicone grease, Hangsterfer's Hard Cut #225 oil and Dust Sebum Emulsion simulated fingerprint oil. The contaminants selected were a representative cross-section of those found on weapons surfaces.

7. Worker Safety Issues - An SNL toxicologist addressed Industrial Hygiene concerns with the proposed cleaners. As with most chemicals, there were personnel protective measures required, but the relative risk (due to the proposed replacement solvents) to personnel exposed in the amounts that are used for weapons maintenance work is comparable to the risks associated with solvents now in use.

Toxicity concerns with the n-propyl bromide based formulations warranted air-monitoring studies. The EPA has proposed a 100 ppm Permissible Exposure Limit (PEL) for the n-propyl bromide based cleaners. Although the n-propyl bromide based cleaners have yet to be SNAP (Significant New Alternatives Program) approved, they are exempt for wiping applications. Nevertheless, worker safety remains a concern and exposure levels or 8-hour time weighted average tests were conducted. Personal breathing zone and area monitoring was conducted for Hypersolve NPB (95% n-propyl bromide) during an experimental process at Amarillo, "Pantex Plant". The process was conducted out in a laboratory tabletop. The substrate was continuously cleaned for forty-five minutes wearing butyl gloves and using presaturated Hypersolve wipes. No task exhaust was used and a respirator was used during the test.

III. Results & Discussion

1. Cleaning Efficacy Tests - Prior to data collection on the wipe study specimens, preliminary measurements of contact angle, MESERAN and XPS were made on 6061 Al discs. To minimize the effect of surface roughness, all discs were polished with 1200 grit SiC. The samples were then inadvertently cleaned in a commercial detergent and rinsed with copious amounts of deionized (DI) H_2O. The contact angle, MESERAN and XPS data are shown in Table 2 for these samples. The data show these surfaces have very large contact angles (77° and 83°), large MESERAN values (785 and 337 ng/cm^2), and from the XPS data, high surface carbon contents (70 atomic %). All of these results support the conclusion that the surface of the polished 6061 Al to be highly contaminated with a carbonaceous material, presumably the detergent.

An attempt was made to remove the detergent by ultrasonication first in TCE and then in npb (Nu Tri Clean). The results showed that there was very little success in removing the contamination from the metal surface, since all three techniques still showed large values (CA = 70 and 74 ; MESERAN = 1368 and 367 ng/cm^2 ; and XPS 69 atomic % carbon). In order to remove the detergent, the metal surface was re-polished and thoroughly rinsed with DI water; the contact angles and XPS data were retaken. The results show that both the contact angles and the carbon signals from XPS decrease by approximately 50%. A lower contact angle indicates the surface of the metal alloy is more easily wettable suggesting the alloy surface contains less contamination, i.e., less non-polar, carbon-containing material, that inhibits wetting. This result is also supported by the XPS surface chemistry data. These studies indicate a good correlation of surface cleanliness as measured by the three analytical techniques discussed in this paper.

Next, discs of 6061 Al or 304 SS were exposed to various solvents, e.g. npb, to determine if there was an alteration in the alloy surface chemistry. In order to determine if the solvent reacted with the base metal, high resolution XPS spectra of the base metals were recorded before and after exposure to the solvent. The metals were ultrasonicated in Nu Tri Clean for two minutes and then in IPA for two minutes. The surface composition of 6061 Al before and after cleaning in npb were measured and found to be, before: C - 62, O - 22, Al - 12, Cl - 0.13 and Br - <0.06 atomic % and after: C - 31, O - 44, Al - 21, Cl - 0.16 and Br - 0.17 atomic %. For 304 SS, the values were, before: C – 68, O – 25, Fe – 3.3, Cr – 0.7, Ni – 0.2 atomic % and after: C – 33, O – 57, Fe – 6.8, Cr – 1.5, and Ni – 0.3 atomic %. The XPS scans for 304 SS and for 6061 Al are shown in Figures 1a and 1b, respectively. Although, the surface composition of residual carbon is cut in half, the aluminum spectra from 6061 Al, and the iron and nickel spectra from 304 SS, do not show significant changes before and after exposure to the npb solvent. Thus, it can be concluded that the npb solvent is cleaning without altering the surface chemistry of the base metals. However, it was found on all studies involving npb-based solvents that a slight increase in bromide surface concentration from < 0.1 to ~ 0.2 atomic % occurred. The high resolution scans on the Br $3d_{5/2}$ and $3p_{3/2}$ levels; the bromine oxidation state was characterized as Br^{-1}. The other solvents were characterized similarly, again, no alteration in the surface chemistry of the base metals was found.

Another example of contact angle, MESERAN and XPS test results is shown in Table 3a and 3b. Preclean values for 6061 Al discs cleaned with Nu Tri Clean and IPA are shown on the left-hand column and post clean values for discs that were contaminated with dust sebum emulsion and subsequently wiped with acetone are shown on the right hand column (Table 3a). The XPS data are shown in Table 3b for 6061 Al discs: (1) in the as-received condition before cleaning, (2) precleaned in Nu Tri Clean followed by IPA, (3) contaminated with a layer of dust sebum emulsion, and (4) after wiping the dust sebum emulsion with acetone. An average contact angle (CA) of 81.4 ±3.1 was obtained for precleaned 6061 aluminum and an average contact angle of 95.4 ±1.8 was obtained for discs contaminated and wiped with acetone. The higher post clean CA value indicates that the original preclean surface was not restored. The same trend is noted with the MESERAN method. An average slope value of 2588 (which translates to a contamination level (CL) of 5 ng/cm^2 ±9) was obtained for precleaned discs and an average slope value of 2383 or CL of 36 ng/cm^2 ±51 was obtained for post-cleaned discs. Although not shown, similar results were obtained for the other contaminants and cleaners on 6061 aluminum and 304 stainless steel. The XPS data show that roughly 82% of the dust sebum emulsion was removed by wiping with acetone, thus 18% still remains on the surface of the base metal.

A relative ranking of how well each cleaner performed for the removal of contaminants from 6061 aluminum and 304 stainless steel is shown in Tables 4 through 9. For both the MESERAN and contact angle methods, the rank order was derived by subtracting the average precleaned value from the average post clean value. In the case of XPS, the amount of contaminant left on the surface of the metal was determined by measuring the carbon levels for the dust sebum emulsion study, the silicon levels for DC4 silicone grease, and the carbon, silicon and chlorine levels for Hard Cut #525 oil. In Table 4, both Exxsol D60 and Hypersolve NPB solvents were very efficient in removing the dust sebum emulsion from 6061 Al. In fact both left the aluminum alloy surface free of any of any detectable emulsion. Therefore, these two cleaners were given an equivalent ranking of 1 and/or rated the best. On the other hand, 1,1,1 TCA and IPA were found to be very ineffective in removing the dust sebum contaminant; leaving 24% of the sebum on the metal surface after wiping, and are subsequently given a rating of 4. The other cleaners are rated between; wiping with Absolv VG, Nu Tri Clean or Exxsol D80 did remove a significant amount of the sebum, but not all. These were given a rating of 2. Similarly, acetone was given a ranked number of 3. Note that the differences between a number 2 and a number 3 ranking are considered minor.

The effectiveness of the cleaners for the removal of DC4 silicone grease from 6061 aluminum can be seen in Table 5. None of the cleaners were very effective in removing the silicone; Hypersolve NPB was ranked number 1 but still left 28% of the grease on the surface. To the other extreme, wiping with acetone was not effective and left a film of grease on the 6061 alloy; therefore, acetone was given a rating of 5. The effectiveness of the cleaners for the removal of Hard Cut #525 oil from 6061 Al can be seen in Table 6. In this case, acetone, Nu Tri Clean and Hypersolve NPB were ranked number 1 and the rest of the cleaners (with the exception of Exxsol D80) were ranked number 2. Exxsol D80 was dropped from the study because of a slow evaporation rate.

The effectiveness of the cleaners for the removal of Dust Sebum Emulsion from 304 stainless steel can be seen in Table 7. All of the cleaners were given a number 1 ranking with exception of 1,1,1 TCA, which was given a number 2 ranking. Note again that there is very little difference between a number 1 and 2 ranking. The relative rank order for the removal of DC4 silicone grease from 304 SS can be seen in Table 8. Again, as before with the aluminum alloy it also very difficult to remove the silicone grease from the 304 SS; however, less silicone is left on the steel surface as compared to the aluminum alloy. Abzol VG and Hypersolve NPB were ranked number 1; again, acetone was found to be the least effective. Finally, the effectiveness of the cleaners for the removal of Hard Cut #525 oil from 304 SS can be seen in Table 9. In this case, all cleaners were given an equivalent rank order of 1 or 2.

Preliminary tests with the HFE solvent azeotropes (including HFE-71DA and HFE-71DE) has commenced but has not been completed.

2. Sandwich Corrosion Tests - The relative corrosion rating system per ASTM F1110-90 is listed in Table 10. Sandwich corrosion test results for 7075 aluminum can be seen in Table 11. With the exception of one panel in the Nu Tri Clean group, a relative corrosion severity rating of 4 was assigned to all panels. A rating of 4 corresponds to extensive corrosion exhibited on 25% or more of the total surface area exposed. Additional Microprobe analysis identified the observed black residue as aluminum hydroxide. This type of residue is typically found in oxidized and hydrated Al samples and is a major material in many kinds of corroded Al. Similar tests were performed for the other metal alloys with no significant corrosion observed.

3. Immersion Corrosion Tests - Immersion corrosion test results for bare 2024 aluminum can be seen in Table 12. No corrosion effects were observed for any of the cleaners after exposure for 24 hours. Similar tests were performed for the other metal alloys with no corrosion effects observed.

4. Materials Compatibility Tests On Other Materials - An example of a yellow paint sample on aluminum is shown in Table 13. The average percent weight change after a 2-minute exposure was insignificant for all cleaners tested; however, the visual analysis of the painted surface after exposure was severe in some cases. Similar tests were run

on many other materials that are found in weapon systems, sometimes with no reaction and other times with moderate to severe reactions observed.

5. Preliminary Results on Accelerated Aging Studies - Preliminary results of the first 64-day cycle indicate no surprises or problems associated with the materials exposed to the various candidate solvents. A detailed analysis on the test materials is progressing.

6. Toxicity Results – The results for the breathing zone test was 4.1 mg/m^3 (0.8 ppm) time-weighted average (TWA) and the area sample indicated an amount of 117 mg/m^3 (23 ppm) of normal propyl bromide. The currently recommended TWA for normal propyl bromide is 503 mg/m^3 (100 ppm). The breathing zone results are well below this level. Direct monitoring was also performed. Direct readings ranged from 0 to 4 ppm in the breathing zone area for a very short period of time.

7. Other Results - A cure inhibition compatibility test with potting compounds and adhesives was performed. Briefly, the test procedure specifies the evaporation to dryness of a candidate cleaner in an aluminum container, followed by the mixing and curing of an adhesive or potting compound into the bottom of the same container where the cleaner was evaporated. After cure, any sign of stickiness, wetness or excessive softness as compared to the control should be interpreted as cure inhibition. In this case, no cure inhibition was noted with any of the materials tested.

Two different tests were performed to determine the stability of high explosive materials in the presence of the candidate cleaners. Differential Scanning Calorimetry (DSC) was performed to determine the temperature at which thermal decomposition (exothermic reaction) of an explosive occurred. A Chemical Reactivity Test (CRT) was performed to determine the amount and type of gases evolved when an explosive was heated for a stated period of time at an elevated temperature in the presence of the material in question. No reactions were noted in either case.

IV. Summary

A cooperative study between the Sandia National Laboratories and the Amarillo, "Pantex Plant" to identify a suitable replacement solvent for hand wipe cleaning applications was conducted. Many non-hazardous solvents, those not defined by RCRA criteria, were identified and a few were evaluated for efficacy in cleaning material surfaces. Three brominated and two aliphatic hydrocarbon cleaner formulations were evaluated as potential replacements. Three surface analytical techniques (contact angle, MESERAN and XPS) were used to study the cleaning efficiency of removing common contaminants by these replacement solvents. In addition to cleaning efficiencies, materials compatibility, corrosion and accelerated aging studies were performed to screen potential candidate solvents. The results showed the brominated solvents and Exxsol D-60 to clean and to remove surface contaminants as least as good as, and in many cases better, than the commonly used solvents of 1,1,1 TCA, acetone and IPA. No materials incompatibility or corrosion was found for passivated and unpassivated 304 SS; for bare, anodized and alodined 6061 and 2024 Al alloys; and for bare titanium.

V. Future Work

Non-volatile residue (NVR) studies will be performed to determine the purity of the candidate cleaners. NVR will be determined by conventional gravimetric methods and through the use of a new analytical instrument, called a "MicroSolventEvaporator". The "MicroSolventEvaporator" utilizes the MESERAN method for quantifying residues to 100 ppb levels. Outgassing of solvents will also be performed using NASA outgassing standards. Finally, bonding of critical interfaces will be addressed.

VI. Acknowledgements

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VII. References

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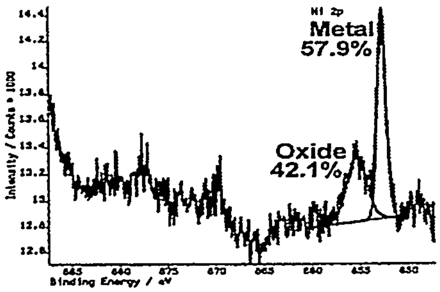
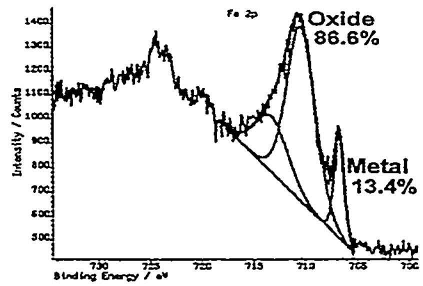
Figure 1a - XPS data showed that cleaning with these solvents did not affect the oxide on the 304 SS discs

Before solvent clean Nickel 2p Spectra



Before solvent clean Iron 2p Spectra



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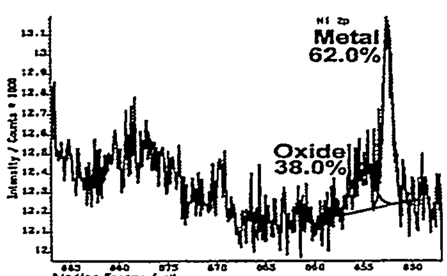

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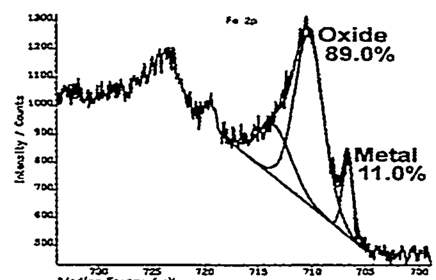
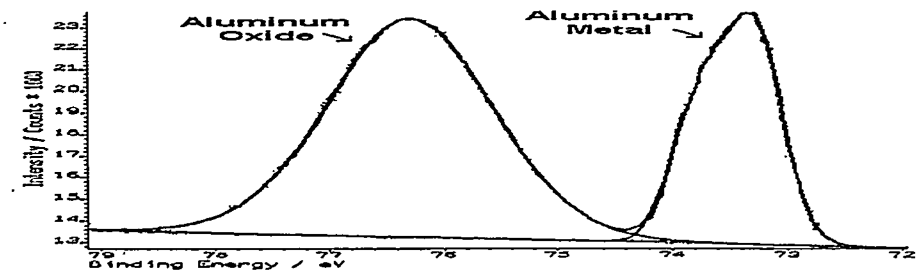


Figure 1b - XPS data showed that cleaning with these solvents did not affect the oxide on the 6061 Al discs

Before solvent cleaning



After solvent cleaning

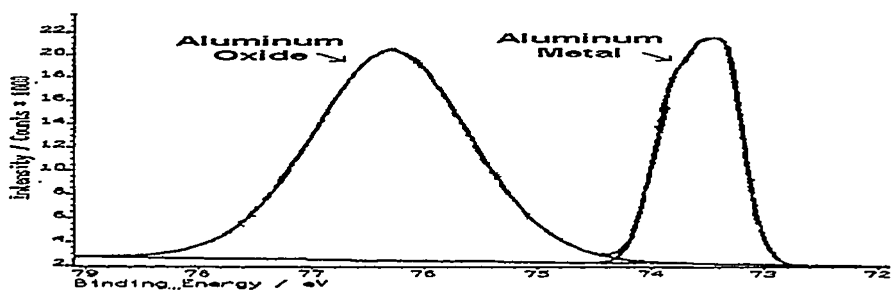


Table 1 - Baseline and Candidate Cleaners Tested				
Cleaner	Ingredients	Toxicity (ppm)	Kauri butanol solvency	Flashpoint
1,1,1 TCA	Methyl chloroform	100	124	None
Acetone	2-propanone	750 TLV	-	4 F
Isopropyl Alcohol	2-propanol	400 TLV	-	53 F
Nu Tri Clean	n-propyl bromide, inhibitors	EPA Proposed 100	125	None
Abzol VG	n-propyl bromide, inhibitors	EPA Proposed 100	125	None
Hypersolve NPB	n-propyl bromide, inhibitors	EPA Proposed 100	125	None
Exxsol D80	Aliphatic hydrocarbon	Exxon OEL 300	29	180 F
Exxsol D60	Aliphatic hydrocarbon	Exxon OEL 300	32	143 F
HFE-71DA	52.7% by wt. HFE-7100, 44.6% trans-1,2-dichloroethylene and 2.7% ethanol	HFE 7100-600 Trans 1,2 - 200 EtOH - 1000	33	None
HFE-71DE	50% by wt. HFE-7100, 50% trans-1,2-dichloroethylene	HFE 7100 - 600 Trans 1,2 - 200	27	None

Table 2 - Summary of Contact Angle, MESERAN and XPS Data on Polished 6061 A1 Discs That Were: Cleaned in Commercial Detergent and Rinsed in DI(a), Then Ultrasonicated in Nu Tri Cleanor in TCE (b), and Re-polished and Cleaned in Solvent (c)

Analysis Technique	No of Analysis	(a) Polished, Washed in Detergent, and Rinsed DI	b) Ultrasonicated in Nu Tri Clean (npb)
Contact Angle, AVE	5	77	70
Contact Angle, STD		5.8	5.9
MESERAN, AVE	5	785 ng/cm^2	1368 ng/cm^2
MESERAN, STD		761 ng/cm^2	807 ng/cm^2
		(a) Polished, Washed in Detergent, and Rinsed DI	(b) Ultrasonicated in TCE
Contact Angle, AVE	5	83	74
Contact Angle, STD		8.2	8.7
MESERAN, AVE	5	337 ng/cm^2	367 ng/cm^2
MESERAN, STD		290 ng/cm^2	591 ng/cm^2
		C Al O	C Al O
XPS, AVE	32	70. 12. 18.	69. 12. 18.
XPS, STD		1.0 1.1 <1	1.0 <1 <1
		(c) Re-Polished and Rinsed DI	
Contact Angle, AVE	5	3.8	
Contact Angle, STD		4.8	
		C Al O	
XPS, AVE	10	28. 24. 46.	
XPS, STD		<1 <1 1.2	

Table 3a – Contact Angle and MESERAN data: 6061 Aluminum Preclean w/NTC/IPA, Then Wipe w/Acetone After Dust Sebum Emulsion Application

Sample	Contact Angle Preclean With NTC/IPA	Contact Angle Wipe w/Acetone	MESERAN Slope: ng/cm^2 Preclean With NTC / IPA	MESERAN Slope: ng/cm^2 Wipe w/Acetone
1	80	96	3084 0	1859 115
2	86	93	2545 1	2909 0
3	79	98	2407 2	2327 5
4	79	95	2763 1	2843 0
5	83	95	2142 21	1975 61
AVE	81.4	95.4	2588 5.0	2383 36
STD	3.1	1.8	357 9.0	483 51

Table 3b – XPS data: 6061 Aluminum Preclean w/NTC/IPA, Then Wipe w/Acetone After Dust Sebum Emulsion Application

XPS data	Carbon	Aluminum	Oxygen	Bromine	Silicon
As –received	62	12	22	<0.06	0.07
Precleaned w/NTC/IPA	31	21	44	0.17	0.07
After Dust Sebum Emulsion	80	-	18	-	-
After wiping with Acetone	45	17	34	<0.05	0.05

Table 4 - Relative Rank Order Effectiveness of Cleaners for Removal of Dust Sebum Emulsion from 6061 Aluminum

Cleaner	Contact Angle Difference	MESERAN ng/cm^2 Difference	XPS Data*				% Sebum left from XPS Results**	Rank Order
			C	Al	O	Br		
Acetone	14	31	45	17	34	<0.05	18	3
1,1,1 TCA	13.2	83	50	16	30	0.14	24	4
Nu Tri Clean	17.6	383	33***	22***	41***	0.15***	2***	2
IPA	19.2	398	50	16	30	<0.05	24	4
Exxsol D80	3 (better)	1	42	18	36	<0.05	14	2
Abzol VG	1.2	3 (better)	34	21	42	0.15	4	2
Hypersolve NPB	1.6	6	31	23	43	0.16	0	1
Exxsol D60	2.4	14 (better)	31	22	43	<0.05	0	1

* Other elements analyzed include Mg, Zn, Cu, Cr, N. F, Ca, Na, C1, and S.
** Assumes a clean surface to be precleaned condition.
***Average of 8 runs; 4 runs each made by two different operators.

Table 5 - Relative Rank Order Effectiveness of Cleaners for Removal of DC4 Silicone Grease from 6061 Aluminum

Cleaner	Contact Angle Difference	MESERAN ng/cm² Difference	XPS Data*					% DC4 left from Silicone XPS Data	Rank Order
			C	Al	O	Si	Br		
Acetone	14.6	5077	46	2.7	29	19	<0.04	100	5
1,1,1 TCA	2	414	40	16	34	7.9	0.14	41	3
Nu Tri Clean	5.2 (better)	396	40	16	36	5.8	0.13	30	3
IPA	3.4	683	38	14	34	12	0.08	63	3
Exxsol D80	25.2	405	10	15	57	16	0.11	84	4
Abzol VG	6.6	2846	32	19	41	5.2	0.08	27	3
Hypersolve NPB	0.2	49	16	24	52	5.5	0.18	28	1
Exxsol D60	3 (better)	100	36	11	40	11.4	<0.05	59	3

*XPS Spectra of DC4 gave atomic % of: carbon - 43, oxygen - 38 and silicon - 19.

Table 6 - Relative Rank Order Effectiveness of Cleaners for Removal of Hard Cut #525 Oil from 6061 Aluminum

Cleaner	Contact Angle Difference	MESERAN ng/cm² Difference	XPS Data						% Hard Cut left from XPS Data	Rank Order
			C	Al	O	Si	Br	Cl		
Acetone	16 (better)	5 (better)	34	23	37	2.7	0.14	0.7	7	1
1,1,1 TCA	8.2 (better)	42	41	18	35	1.8	0.08	1.0	15	2
Nu Tri Clean	7 (better)	63	32	21	43	1.6	0.18	0.60	3	2
IPA	7.8 (better)	16	36	20	39	1.9	0.11	1.0	9	2
Exxsol D80	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Abzol VG	10.4 (better)	33	35	18	42	2.4	0.19	0.42	7	2
Hypersolve NPB	10 (better)	28	32	20	42	2.3	0.12	0.5	4	1
Exxsol D60	11.6 (better)	1 (better)	40	18	40	2.3	0.14	0.67	14	2

Table 7 Relative Rank Order Effectiveness of Cleaners for Removal of Dust Sebum Emulsion from 304 Stainless Steel									
Cleaner	Contact Angle Difference	MESERAN ng/cm^2 Difference	XPS Data					% Sebum left from XPS Data	Rank Order
			C	Total Metal	O	Si	Br		
Acetone	4.4	0	29	8.6	60	<0.1	<0.1	0	1
1,1,1 TCA	9.0	1	39	7.7	51	0.4	<0.1	17	1
Nu Tri Clean	3	83 (better)	33	8.6	57	0.2	<0.1	0	1
IPA	0.8 (better)	2	32	8.5	57	0.2	<0.1	0	1
Exxsol D80	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Abzol VG	0.8 (better)	65	32	8.4	56	0.1	<0.1	0	2
Hypersolve NPB	0	0	35	8.4	55	0.1	<0.1	6	1
Exxsol D60	8.6 (better)	0	34	8.4	55	0.1	<0.1	4	1

Table 8 - Relative Rank Order Effectiveness of Cleaners for Removal of DC4 Silicone Grease from 304 Stainless Steel									
Cleaner	Contact Angle Difference	MESERAN ng/cm^2 Difference	XPS Data					% DC 4 left from XPS Data	Rank Order
			C	Total Metal	O	Si	S		
Acetone	9.2	190	40	4.2	42	12.5	<0.1	65	3
1,1,1 TCA	10.2	196	27	6.0	58	4.4	0.4	23	3
Nu Tri Clean	5.6	438	23	5.6	59	10.2	0.2	54	4
IPA	4.2	518	33	5.0	53	5.0	0.4	26	4
Exxsol D80	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Abzol VG	3 (better)	0	35	7.8	53	1.2	<0.1	6	1
Hypersolve NPB	2.8	73	34	8.0	53	1.0	<0.1	5	2
Exxsol D60	2.2	917	30	6.0	57	3.5	<0.1	18	4

Table 9 - Relative Rank Order Effectiveness of Cleaners for Removal of Hard Cut #525 from 304 Stainless Steel											
Cleaner	Contact Angle Difference	MESERAN ng/cm² Difference	XPS Data						% Hard Cut left from XPS Data	Rank Order
			C	Total Metal	O	Si	Cl	S		
Acetone	4.4 (better)	11	32	7.8	53	2.4	0.2	0.6	4	1
1,1,1 TCA	2.2	16	28	8.4	58	1.8	<0.1	<0.1	2	1
Nu Tri Clean	0.8 (better)	17	35	7.0	52	1.0	<0.1	<0.1	4	1
IPA	0.6	10	36	7.0	51	3.0	1.0	<0.1	9	2
Exxsol D80	N/A	N/A	N/A	N/A	N/A	N/A		N/A	N/A	N/A
Abzol VG	0.6 (better)	7	32	7.4	54	2.0	<0.1	0.2	3	1
Hypersolv NPB	0.2	3	34	7.0	53	1.0	1.0	1.0	4	1
Exxsol D60	1.2	5	40	6.2	46	2.8	1.0	0.2	14	2

Table 10 - Relative Corrosion Severity Rating System	
0	No visible corrosion
1	Very slight corrosion or discoloration
2	Slight corrosion
3	Moderate corrosion
4	Excessive corrosion or pitting
0	0%
1	Up to 5% of the surface area corroded
2	5 to 10% of the surface area corroded
3	10 to 25% of the surface area corroded
4	25% or more of the surface area corroded

Table 11 - Sandwich Corrosion Test Results Bare 7075 Aluminum

Sandwich	Solution	Corrosion Severity	Corrosion Percentage
1	IPA	4	4
2	IPA	4	4
3	IPA	4	4
1	Acetone	4	4
2	Acetone	4	4
3	Acetone	4	4
1	1,1,1 TCA	4	4
2	1,1,1 TCA	4	4
3	1,1,1 TCA	4	4
1	Exxsol D80	4	4
2	Exxsol D80	4	4
3	Exxsol D80	4	4
1	Nu Tri Clean	4	4
2	Nu Tri Clean	4	4
3	Nu Tri Clean	2-3	2-3
1	Abzol VG	4	4
2	Abzol VG	4	4
3	Abzol VG	4	4

Table 12 - Immersion Corrosion Test - Bare 2024 Aluminum Samples			
Cleaner	Weight Change	Visual Before	Visual After
Nu Tri Clean	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect
Isopropyl Alcohol	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect
Exxsol D80	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect
1,1,1 TCA	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect
Abzol VG	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect
Acetone	Negligible	Longitudinal machine marks, shiny polished silver appearance	No Effect

Table 13 - Material Compatibility Test - 2" Long Aluminum Strip with One Side Painted Yellow			
Cleaner	Avg % Wt. Change	Std. Dev.	Visual
Nu Tri Clean	-.113	.079	Severe paint peel
Isopropyl Alcohol	.115	.074	No change
Acetone	-.368	.021	Paint peeling
TCA	.510	.035	Severe pain peel
Exxsol D80	N/A	N/A	N/A
Abzol VG	-.114	.017	Paint curling, discolored solution
Hypersolve NPB	-.143	.081	Paint curling, discolored solution
Exxsol D60	.057	.047	No change