

SURFACE ANALYSIS EVALUATION OF HANDWIPE CLEANING FOR THE SPACE SHUTTLE RSRM

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ABSTRACT

In this paper we discuss the role of surface-sensitive spectroscopy (electron spectroscopy for chemical analysis, or ESCA) in the selection of solvents to replace 1,1,1-trichloroethane in handwipe cleaning of bonding surfaces on NASA's Space Shuttle Reusable Solid Rocket Motor (RSRM). Removal of common process soils from a wide variety of metallic and polymeric substrates was characterized. The cleaning efficiency was usually more dependent on the type of substrate being cleaned and the specific process soil than on the solvent used. A few substrates that are microscopically rough or porous proved to be difficult to clean with any cleaner, and some soils were very tenacious and difficult to remove from any substrate below detection limits. Overall, the work showed that a wide variety of solvents will perform at least as well as 1,1,1-trichloroethane.

INTRODUCTION

About eight years ago Thiokol Propulsion began a comprehensive effort to eliminate the use of 1,1,1-trichloroethane (TCA) for adhesive bonding surface preparation in the manufacture of NASA's Space Shuttle Reusable Solid Rocket Motor (RSRM). TCA is an ozone-depleting compound (ODC) whose production has been banned by international agreements.

TCA had been the solvent of choice for both vapor degreasing of large steel and aluminum rocket motor parts and handwipe cleaning of

metal and polymer bonding surfaces. Vapor degreasing of steel and aluminum parts has been replaced by a spray-in-air aqueous cleaning process, eliminating 90 percent of the TCA usage in RSRM processing. Two papers describing the role of surface analysis in these efforts have been recently published^{1,2}. An effort to eliminate TCA (currently being drawn from a stockpile and used under an essential use waiver) from handwipe cleaning operations is now nearly complete.

In the majority of handwipe cleaning studies on this program, bonding tests have not discriminated between cleaners that have been demonstrated to effectively dissolve the process soils that are being removed. Most RSRM bondlines are robust and can tolerate significant amounts of contamination before they fail. We desired to determine, despite the equivalence often observed in bonding tests, if there were differences in cleaning efficiency between solvents. Obviously, one would want to show that a replacement cleaner removed the process soils at least as well as TCA.

In this paper we discuss the role of surface-sensitive spectroscopy in measuring the cleaning efficiencies of a wide variety of organic solvents on both metallic and polymer substrates.

EXPERIMENTAL

Description of Technique

All surface analysis results were acquired using the electron spectroscopy for chemical analysis (ESCA) technique. In ESCA, a sample is irradiated with X-rays that cause electron emission from core levels of the surface atoms. By measuring the electron kinetic energies, one can determine surface elemental compositions and information about the types of chemical compounds present. Only photoelectrons that originate in the topmost atom layers have a significant chance of escaping without scattering. Most of the analytical signal comes from the top 30 - 50 Angstroms or 10 - 15 atomic layers, although some signal will typically be observed from as deep as 100 Angstroms.

Equipment and Analysis Procedures

All ESCA studies were conducted on a Kratos XSAM 800 ESCA spectrometer. The system

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was equipped with a hemispherical electron energy analyzer and a dual anode (Al and Mg) X-ray excitation source. All studies on metals (steel and aluminum) used Al K α X-radiation to stimulate electron emission. For polymer samples, Mg K α X-radiation was used except for a few instances where Al K α was used due to the wearing out of the Mg side of the anode. A 90 degree take-off angle was employed in all tests.

Analyses consisted of low resolution "survey" scans (0 - 1100 eV binding energy, 160 eV pass energy), followed by high resolution "detail" scans (20 eV pass energy) on characteristic peaks of each element (e.g. Al (2p), Si (2p), Cl (2p), C (1s), N (1s), O (1s), Fe (2p), etc.) detected in the survey scan. The high resolution scans provide accurate peak areas for quantitative analysis, and the peak positions can be used to identify the various chemical compounds present.

In some cases where multiple chemical states of an element were encountered (especially carbon), the curves were fit with multiple peaks to allow them to be distinguished. For purposes of chemical state identification, peaks were referenced to the binding energy of the C-C bond (284.8 eV) to correct for charging effects. The analysis area in these studies was approximately a 3 x 4 mm rectangle.

The surface analysis system is equipped with a multi-sample motorized stage that permits the analysis of up to 24 specimens (1/2-in. x 3/4-in. coupons) without operator intervention. With many of the polymeric materials, however, putting this many specimens in the vacuum system at one time was not feasible due to their vapor pressures.

Samples and Sample Preparation

Samples were mostly in the form of 1/2-in. x 3/4-in. coupons, typically 1/8-in. thick. They were prepared alongside bonding specimens (mostly tensile buttons and peel specimens). Contaminants were applied to the samples in a controlled manner and then cleaned off with solvent-wet cotton (Rymple™) cloth. The operators (only two operators were used to reduce variability) rubbed the coupons until they "felt" clean, and the soil was visually removed, much as would be done on the production line. Typically only one coupon for each soil/substrate/cleaner combination was analyzed.

Admittedly, there are concerns with this approach due to operator subjectivity and the lack of multiple replicates on each sample. It would have been preferable to analyze samples at least in triplicate to get statistical measures of the variability in the handwipe method, but the large scope of the testing effort prohibited this. Approximately 900 specimens were analyzed in the course of this study.

RESULTS AND DISCUSSION

Types of Substrates Evaluated

The general types of substrates evaluated were:

Metallic. D6AC steel and 7075 aluminum, both gritblasted with Biasill XL® aluminosilicate gritblast media. These are used in case and nozzle assemblies and are later bonded to phenolics with epoxy adhesives or to rubber with Chemlok® rubber-to-metal adhesives.

Phenolic Composites. These included carbon cloth phenolic (CCP), glass cloth phenolic (GCP), and silica cloth phenolic (SCP) substrates. These are used in nozzle assemblies and are bonded to phenolic prepreg overwrap or with epoxy adhesives. Both zero-degree (cleaned surface parallel to the plies) and 90 degree (cleaned surface perpendicular to the plies) specimens were evaluated.

Rubber. Evaluated materials here mostly consisted of asbestos-filled NBR case insulation, which is bonded to steel cases and igniters with Chemlok® adhesives, and coated with liner which bonds it to the solid propellant. A small amount of testing was conducted on EPDM rubber formulations.

Painted Substrates. These were painted steel and aluminum surfaces typical of the external surfaces of the motor. Most bonds involving these materials involve epoxy adhesives.

Miscellaneous Substrates. These included: Rencothane® polyurethane, the AP-based composite propellant (TP-H1148), nylon, cork and epoxy/cork composite material (K5NA), two silicone rubber sealants (DC93-104 and DC90-006) used in nozzle assemblies, inhibitor that is applied to certain exposed propellant surfaces, etc.

Solvents

A wide variety of solvents were considered. Not all were used on every substrate/soil combination. The cleaners, followed by their abbreviations used in this paper, included 1,1,1-trichloroethane (TCA), Ionox BC® (Ionox), PF145 HP® (PFH), Ecosolv 5® (EC5), PF Ionsol® (PFI), PF Degreaser® (PFD), PF D'Ink® (PFK), BIOACT PCG® (PCG), BIOACT 145 ®(BA4), BIOACT 113 ®(BA1), Oxsol 100® (OX1), Plus 4 ®(PL4), and Reveille® (REV). These solvents had previously been shown (in preliminary handwipe cleaning tests) to dissolve most common process soils reasonably well.

Example ESCA Spectra

Figure 1 shows sample ESCA survey spectra (0 - 600 eV binding energy only) of carbon cloth phenolic that has been wiped with TCA, and carbon cloth phenolic that has been contaminated with a hydrocarbon-based, corrosion inhibiting calcium grease (Century Lubricants HD-2® grease) and then TCA solvent wiped. (From the elemental analysis obtained by measuring detail scan peak areas, one can also get a table of surface elemental concentrations.)

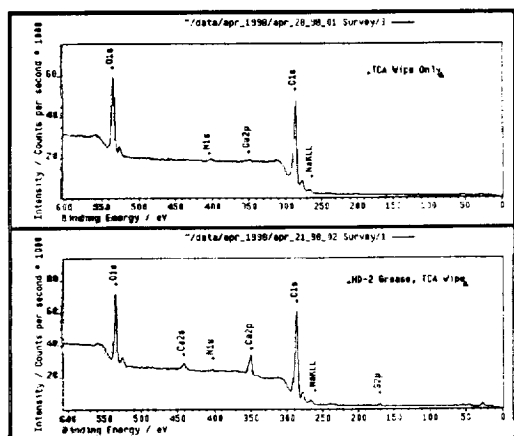


Figure 1. ESCA Survey Scans of Carbon Cloth Phenolic, 90 Degree Ply Orientation, Cleaned with TCA

From the elemental analysis alone one can see that some residual calcium is not removed by the cleaning treatment. However, it is not straightforward to determine the extent to which the hydrocarbon component of the grease was removed from elemental analysis alone.

Fortunately, we can determine this from the carbon (1s) detail scans. By curve fitting the carbon (1s) region, we can measure quantitative ratios that allow the hydrocarbons to be distinguished from the oxygen-containing functional groups in the carbon phenolic. This is shown in Figure 2. There also appears to be some residual carbonate on the surface from the calcium carbonate in the grease. One of the powerful features of ESCA is that one can readily determine the extent to which different components of a contaminant are removed.

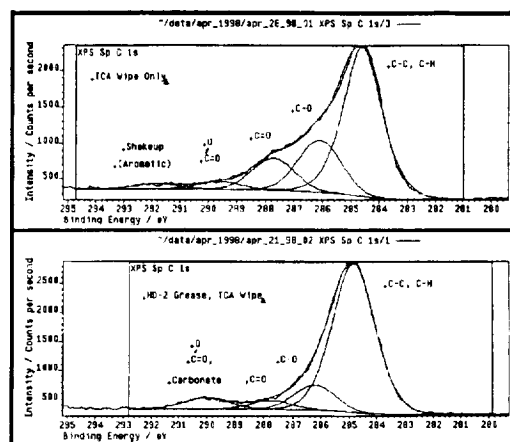


Figure 2. ESCA Detail Scans, Carbon (1s) Region, of Carbon Cloth Phenolic, 90 Degree Ply Orientation, Cleaned with TCA

Data Interpretation Strategy

As mentioned above, because of the large scope of the handwipe cleaning program and the limitations of the ESCA instrument, only one sample of each soil/substrate combination was prepared and tested.

Generally speaking, to determine if a difference in performance between cleaners was real and not the result of variability in the handwipe method, we looked to see if similar differences were observed with the same or a chemically similar soil on other substrates. In addition, one can check to see if the results correlate with other information, such as bond data. If there is a correlation with other data on the same or similar substrate/soil combinations, the difference is probably real.

For most substrates a set of solvent-wiped control samples, i.e., samples that had not been precontaminated with soils before wiping, was prepared and analyzed. This was done so that the effects of the cleaners on the substrates could be evaluated. A control sample that had not been cleaned with any solvent or cleaner or exposed to any soil was also typically included in the sample set.

A series of bar charts were made from the ESCA results to facilitate interpretation of the data. These included the following:

- Plots of substrate tag element levels as a function of the cleaner used. The lower the levels of these constituents, the more contaminated the surface.
- Plots of soil tag elements as a function of cleaner. The higher the levels of these constituents, the higher the level of unremoved soil on the surface.
- Plots of organic (carbon) functional group distributions versus cleaner. As demonstrated by Figure 2, this is another sensitive indicator of differences in surface chemistry and can sometimes differentiate between the soil and the substrate.

For the tag element charts, data from both soiled/cleaned surfaces and cleaned surfaces with no precontamination were plotted on the same axes. This facilitates easy comparison of the effect of a solvent on the soil and its effect on the substrate.

Metallic Substrates

The metallic substrates considered here were grit blasted D6AC steel and 7075 aluminum. Process soils included HD-2 grease, Permacel yellow tape adhesive, and DC90-006 silicone sealant. Cleaners evaluated were: BA1, BA4, EC5, PCG, PFH, PFK, OX1, and TCA.

The first thing that was noticed was that the Rympel cloth wiping leaves a carbonaceous residue on the steel and aluminum coupons. This is illustrated in Figure 3, which is a bar chart comparing overall carbon levels of the wiped coupons (no contaminants applied beforehand, so the contamination comes from the wiping treatment). Figure 4 shows that the

nature of the residue (rich in C-O functionality) is similar for all of the solvents, suggesting that the residues originate with the cloth and not the solvents themselves.

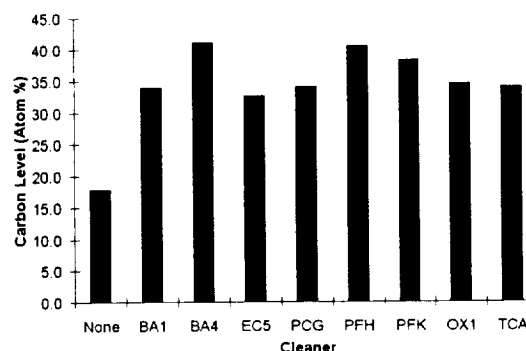


Figure 3. ESCA Carbon Levels of Solvent-Wiped Steel Coupons (No Soils Applied)

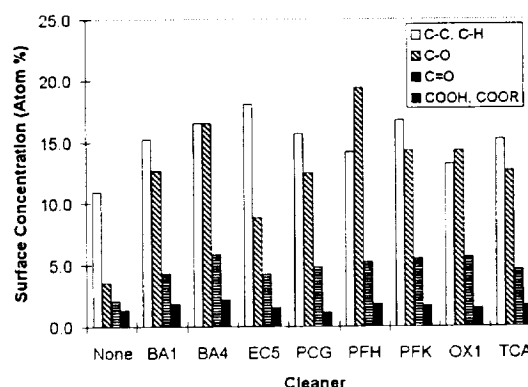


Figure 4. ESCA Organic Functional Group Distributions of Solvent-Wiped Steel Coupons (No Soils Applied)

With the HD-2 grease, yellow tape, and silicone sealant contaminants, it was observed that no cleaner consistently performed better than TCA, i.e. if minor differences were observed on steel they were not observed on aluminum, and vice versa. The cleaners seemed to have reasonable cleaning efficiency for grease and tape residue, but none of them (including TCA) effectively removed the DC90-006 silicone sealant. This is illustrated in Figure 5, which shows silicon levels on noncontaminated/wiped steel substrates (here the Si is from the grit blast sand) and contaminated/wiped steel substrates.

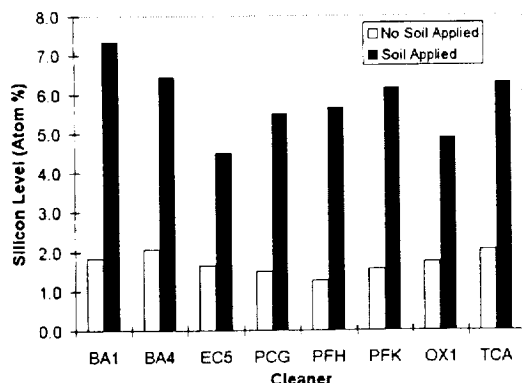


Figure 5. ESCA Silicon Levels of Solvent Wiped Steel Coupons, With and Without DC90-006 RTV Silicone Precontamination

Phenolic Substrates

Here carbon cloth phenolic, glass cloth phenolic, and silica cloth phenolic materials, in zero and 90 degree ply orientations, were contaminated with a variety of soils including HD-2 grease, DC90-006 RTV silicone sealant, silicone adhesive from Teflon tape, Permacel P-32 yellow tape adhesive, two uncured epoxy adhesives, hydraulic oil, and a polysulfide sealant. Solvents evaluated included BA1, BA4, EC5, PCG, PFH, PFK, OX1, and TCA. Not all soils were tested on all substrates.

The solvents by themselves occasionally (not consistently) left oxygen functionalized carbon species on the surfaces. This could originate with residues leached from the cleaning cloths or air oxidation of solvent residues on the surface. Several of the cleaners contain terpenes (e.g. PCG is pure terpene with no anti-oxidant) that are prone to form oxidized residues when spread out in a thin layer and exposed to air. Indentations in the samples can hold solvent and give it time to oxidize before it dries.

Figures 6 and 7 show an example of typical data on phenolics (HD-2 grease on 90 degree silica cloth phenolic). Figure 6 shows plots of a substrate tag element (Si). For samples that have been exposed to grease, the levels are lower, suggesting the presence of contamination. Figure 7 is a chart of the hydrocarbon level (C-C, C-H peak in Figure 2) as a function of cleaner. The charts show that all cleaners leave behind small but similar amounts of grease residue. (All

cleaners left ~ 1 - 2 atom percent of calcium from the grease as well.) The cleaner BA1 seems to leave more hydrocarbon residue than the other cleaners. However, this observation was not true for the same soil on the other phenolic substrates, and hence it is probable that the difference with the other cleaners is due to normal variability in the cleaning method.

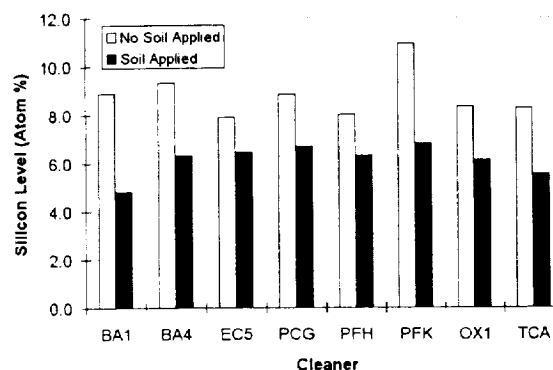


Figure 6. ESCA Silicon Levels of Solvent Wiped 90 Degree Silica Cloth Phenolic Coupons, With and Without HD-2 Grease Precontamination

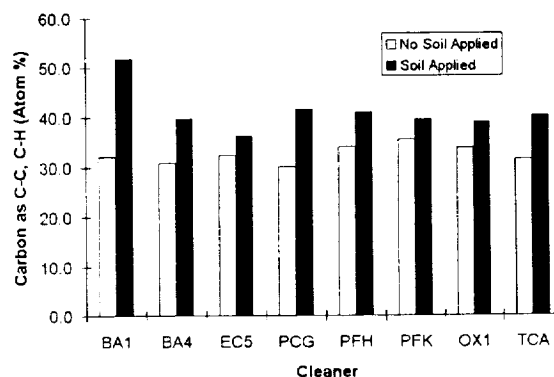


Figure 7. ESCA Hydrocarbon Levels of Solvent Wiped 90 Degree Silica Cloth Phenolic Coupons, With and Without HD-2 Grease Precontamination

With the phenolic substrates, cleaning efficiency seemed to be considerably more dependent on the soil and the substrate being cleaned than on the solvent used. Substrates with a zero degree ply orientation were generally easier to clean than those with a ninety degree orientation, probably because the 90 degree substrates are

rougher on a microscopic scale and thus hold contamination more tenaciously.

There were some soils (polysulfide and silicone sealants, and the silicone adhesive from Teflon tape) that were not consistently effectively removed by any cleaner, including TCA. However, in tests on zero and ninety degree glass cloth phenolic, TCA seemed to remove polysulfide better than all of the cleaners except possibly PFK. Apart from this, no cleaner among those tested consistently performed differently from TCA.

Rubber Substrates

Most of the rubber studies were done on cured, asbestos-filled nitrile-butadiene rubber (ASNBR) case insulation contaminated with uncured liner, HD-2 grease, dried Chemlok rubber-to-metal adhesive, yellow tape adhesive, and uncured polysulfide adhesive. Tests were also done on uncured ASNBR with HD-2 grease and yellow tape adhesive. A few tests were also done with EPDM rubber substrates. Solvents evaluated were PFI, PFK, PFD, PCG, BA4, EC5, REV, and TCA. (No solvent-wiped controls were analyzed for PFI.) The cured NBR insulation had been cured against a patterning cloth, giving it indentations that can hold contamination.

The number of tests that could be done on rubber (especially uncured) was limited, as large numbers of samples could not be put into the vacuum system at one time. Sulfur-containing vapors from the rubber tend to react with copper components of the system to form black copper sulfides and with titanium surfaces in the ion pump, leading to pump failure. These samples can still be safely analyzed one at a time.

For rubber, it seemed that the solvents REV (a straight hydrocarbon) and, to a lesser extent, PFD (a straight hydrocarbon with a few percent of terpene) were somewhat less effective than the other, more aggressive cleaners. These cleaners were more likely than the others in any given soil/substrate dataset to show lower than average cleaning efficiency. An example of this is (for REV) is shown in Figure 8, a cleaning study on uncured liner (mostly a hydrocarbon) from cured asbestos-filled NBR. Clearly, in this test at least, REV is less effective than the other cleaners. This single result could be the result of variability in cleaning technique, however it is

more likely to be a real difference as REV had a tendency to be less effective than TCA for cleaning other types of hydrocarbon-containing contaminants from rubber samples.

Another interesting example is a cleaning study of dried Chemlok adhesive from cured NBR (Figures 9, 10). This Chemlok contains both a

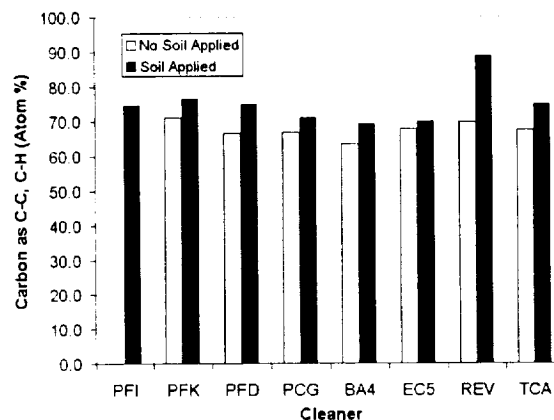


Figure 8. ESCA Hydrocarbon Levels of Solvent-Wiped, Cured ASNBR With and Without Uncured Liner Precontamination

chlorinated polymer and an isocyanate, so Cl is a tag for the contaminant, and N appears in both the substrate and the soil.

As shown in Figures 9 (nitrogen level) and 10 (chlorine level), the surfaces cleaned with PFD and REV are qualitatively different. They are higher in nitrogen than a solvent wiped control (indicating they are enriched in the isocyanate component of the Chemlok) and are lower than any of the others in chlorine (indicating less of the chlorine-containing component of the Chemlok). While no cleaner, including TCA, effectively removes this contaminant, the surface chemistry of the samples cleaned with PFD and REV will be different than the others.

With polysulfide sealant on cured ASNBR, none of the solvents removed the contaminant (as measured by the residual S levels on the rubber) as well as TCA, although PFK seemed to clean nearly as well. This is probably a real difference as a similar effect was noticed for polysulfide on glass cloth phenolic. Sulfur levels of solvent-wiped cured ASNBR are shown in Figure 11.

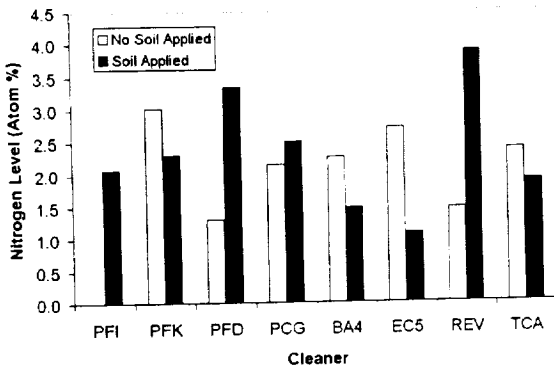


Figure 9. ESCA Nitrogen Levels of Solvent-Wiped, Cured ASNBR With and Without Chemlok Adhesive Precontamination

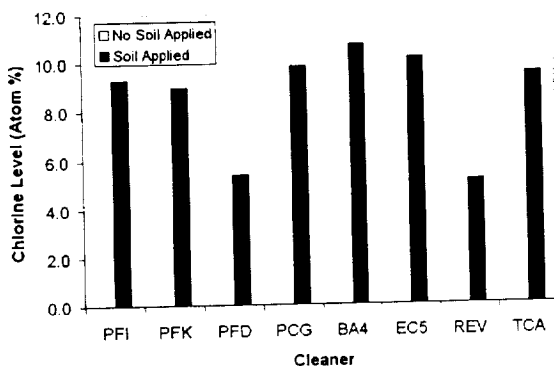


Figure 10. ESCA Chlorine Levels of Solvent-Wiped, Cured ASNBR With and Without Dried Chemlok Adhesive Precontamination

For all soils except polysulfide, ESCA showed that all cleaners, for the most part, removed contaminants from rubber samples as well as TCA. It seemed that, in a number of cases, however, the performances of REV and (to a lesser extent) PFD were not as good as other solvents. Specific additional instances included the following: PFD and REV were less effective in removing yellow tape adhesive residues from cured ASNBR; PFD and REV were less effective in removing calcium grease residue from uncured ASNBR; and REV did a poor job of removing the hydrocarbon component of HD-2 grease from cured silica-filled EPDM.

Any one of these instances, if it occurred in isolation, could probably be dismissed as variability in the cleaning method. However, since the same behavior was observed with these

solvents in multiple contexts, it may reflect a real difference in cleaning efficiency. This is also supported by bonding tests carried out in conjunction with the rubber study, which revealed overall lower adhesion performance for surfaces cleaned with REV and PFD.

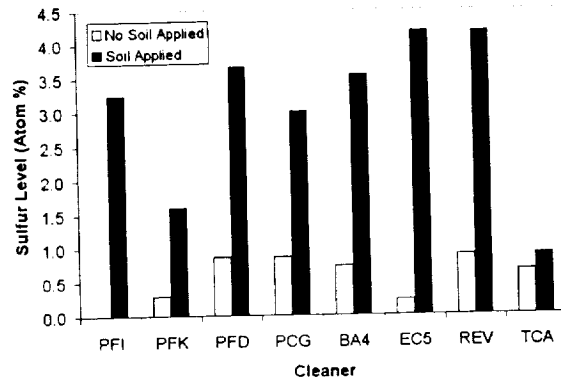


Figure 11. ESCA Sulfur Levels of Solvent-Wiped, Cured ASNBR With and Without Uncured Polysulfide Precontamination

Painted Substrates

This part of the study was concerned with smooth, painted aluminum and steel coupons. Different (white) epoxy paints are used on steel and aluminum. Process soils included: HD-2 grease, yellow tape adhesive, vacuum putty, Diala oil (a hydrocarbon proof test oil), Celvacene grease, Immunol (a fluid used in case inspection), DC90-006 RTV silicone, storage deck black rubber marks, and zinc chromate primer. Solvents evaluated were BA4, EC5, OX1, PCG, PFD, PFH, REV, and TCA. Not all contaminants were applied to both substrates.

In most cases there was no discernible difference in cleaning efficiency between cleaners and the cleaners effectively removed the soils. A typical result (cleaning efficiency for the hydrocarbon component of HD-2 grease from painted aluminum) is shown in Figure 12. While there appear to be traces of hydrocarbon left, the cleaners all perform at least as well as TCA.

With the 90-006 silicone sealant, cleaning efficiency was difficult to gauge because of

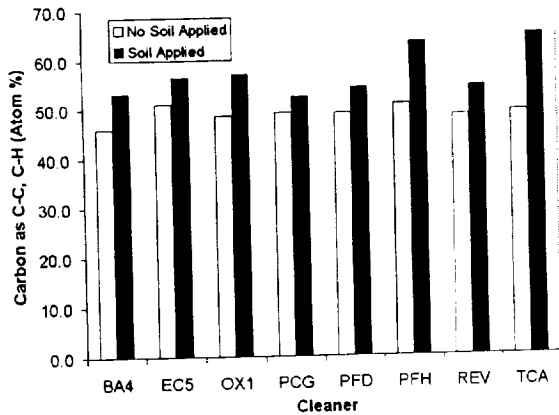


Figure 12. ESCA Hydrocarbon Levels for Solvent Wiped Painted Aluminum Substrates, With and Without HD-2 Grease Precontamination

(possibly variable) amount of its Si tag in the paint itself.

In most cases, when a cleaner exhibited lower than average cleaning efficiency in a test, that test most often involved REV or PFD. Specific cases of lower cleaning ability were: REV for vacuum putty on painted aluminum; REV for yellow tape on painted aluminum; PFD for HD-2 grease on painted steel; and PFD and REV for Celvacene grease on painted steel.

Again it must be noted that these differences are subtle, and if they occurred in isolation they could be dismissed as variability in the cleaning method. It must be noted that "out of family" cleaning performances were not observed with the same soil/cleaner (yellow tape, HD-2 grease) combinations on both painted substrates. As with the rubber cleaning, however, the data do suggest a small possibility that, while they seem to work well in most cases, REV and PFD might be slightly lower in cleaning performance. We want to emphasize that this dataset does not offer conclusive proof that any of the tested cleaners are inferior to TCA.

Miscellaneous Substrates

These substrates (with the cleaners evaluated and process soils in parentheses) include: solid propellant (BA4, Ionox, PFD, PFH, PCG, TCA/HD-2 grease, yellow tape adhesive,

hydraulic oil, dust); cork (BA1, BA4, PCG, PFD, PFH, PL4, TCA/HD-2 grease, vacuum putty, yellow tape adhesive, hydraulic oil), K5NA epoxy/cork composite (BA1, BA4, PCG, PFD, PFH, PL4, TCA/HD-2 grease, yellow tape adhesive, silicone adhesive from Teflon tape, hydraulic oil), Rencothane polyurethane (Ionox, PFD, PFH, PCG, TCA/HD-2 grease, yellow tape adhesive, hydraulic oil, dust), nylon (PFD, PFH, PCG, TCA/HD-2 grease, yellow tape adhesive, silicone adhesive from Teflon tape), cured DC90-006 RTV silicone sealant (Ionox, PFD, PFH, PCG, BA4, TCA/HD-2 grease, yellow tape adhesive, hydraulic oil, dust), cured DC93-104 silicone sealant (BA1, BA4, PFD, PFH, PCG, PL4, TCA, Ionox/HD-2 grease, uncured DC90-006 RTV, yellow tape adhesive, silicone adhesive from Teflon tape, hydraulic oil), and castable inhibitor, a liner-like material (PFD, PL4/HD-2 grease, yellow tape adhesive, hydraulic oil, dust).

With propellant, no solvent-wiped controls were analyzed, but there was one difference between cleaners that was of note. Figure 13 shows a plot of overall nitrogen and chlorine levels for samples contaminated with yellow tape and then solvent wiped. The figure shows that, for the Ionox wiped sample, the chlorine and nitrogen levels are higher than those of surfaces cleaned with the other solvents. A similar (and slightly more pronounced) difference was observed in the chlorine/nitrogen plots for HD-2 grease cleaning from propellant, with the Ionox cleaned surface again having somewhat elevated chlorine and nitrogen levels.

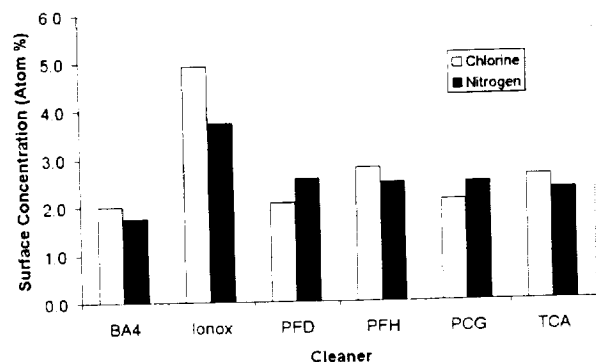


Figure 13. ESCA Chlorine and Nitrogen Levels of Solvent-Wiped Solid Propellant with Yellow Tape Adhesive Precontamination

There are three possible explanations for the different behavior of Ionox in the yellow tape and HD-2 grease. One is that the Ionox solvent simply removes the soil better. Another is that Ionox more aggressively attacks the polymeric propellant binder and exposes more of the ammonium perchlorate (AP) oxidizer. Still another, more likely explanation is that since Ionox BC is a highly polar solvent, it can leach AP out of the propellant and redeposit it in a thin layer during a wiping operation.

From the nitrogen (1s) detail scans, we can determine the ratio of nitrogen in the organically bound state (from the propellant binder) and in the ammonium ion state (from the AP oxidizer). These spectra are shown in Figure 14 for yellow tape contaminated propellant cleaned with Ionox and TCA. Clearly the Ionox-cleaned surface is enriched in the ammonium ion type of nitrogen.

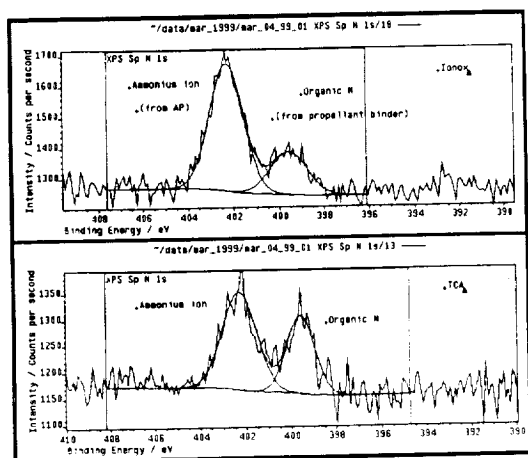


Figure 14. ESCA Detail Scans, Nitrogen (1s) Region, for Yellow Tape Adhesive Contaminated Solid Propellant Cleaned with Ionox BC and TCA

For the other process soils (hydraulic oil and dust) the tests did not indicate higher AP levels on the Ionox-cleaned samples. In the case of hydraulic oil one might surmise that it "protects" the surface from the dissolving action of the polar Ionox solvent, but in the case of dust contamination, the lack of higher AP levels on the Ionox-cleaned surfaces is a bit puzzling.

To summarize the propellant results, ESCA did not detect any definite differences in cleaning

efficiency between cleaners. Surfaces cleaned with Ionox BC may have different surface chemistry, however, due to leaching of ammonium perchlorate by this (highly polar) solvent and redeposition on the surface during wiping.

Cork substrates, as one would expect, were very difficult to clean due to their porosity. Results of a typical cleaning study (HD-2 grease) are shown in Figure 15. In addition to solvent wiped coupons, contaminated ones with only a dry wipe (labeled "none") were also analyzed.

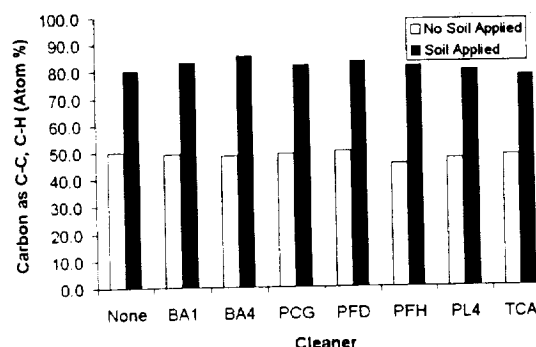


Figure 15. ESCA Hydrocarbon Levels for Solvent Wiped Cork Substrates with HD-2 Grease Precontamination

Clearly, none of the cleaners effectively remove this contaminant. In this case, from an ESCA standpoint, the cleaners perform about as well as a dry wiping cloth.

With hydraulic oil, which can soak into the cork, all of the above cleaners (except PFH, which performed surprisingly well) did a poor job of contaminant removal. Cleaning efficiencies for soils that do not soak into the cork (vacuum putty, yellow tape adhesive) were better on cork, with all cleaners being similar to TCA in performance.

Teflon tape (silicone) adhesive was not effectively removed from cork by any cleaner.

Figures 16 and 17 show typical data for hydraulic oil cleaning on epoxy-cork composite material (K5NA). All cleaners do an excellent job of removing this soil, as shown by the nitrogen levels (Figure 16, tag for the substrate)

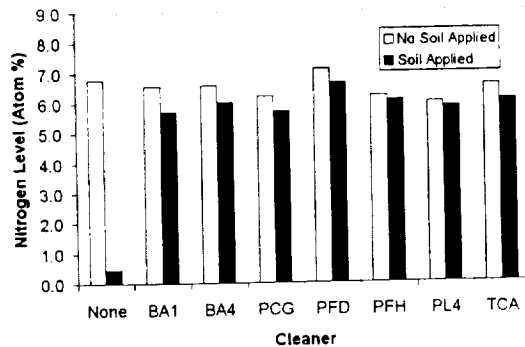


Figure 16. ESCA Nitrogen Levels of Solvent-Wiped Cork-Epoxy Composite (K5NA) With and Without Hydraulic Oil

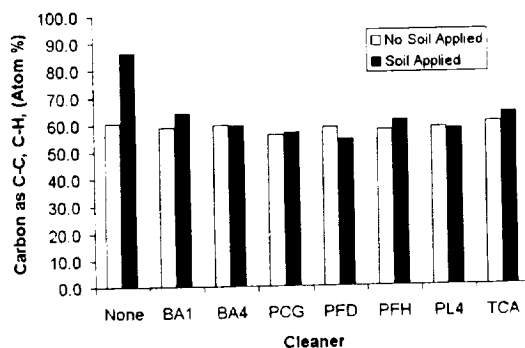


Figure 17. ESCA Hydrocarbon Levels of Solvent-Wiped Cork-Epoxy Composite (K5NA) With and Without Hydraulic Oil

and hydrocarbon levels (Figure 17, tag for the soil).

All other contaminants (HD-2 grease, yellow tape residue, etc.) except the silicone adhesive for Teflon tape were effectively removed from K5NA by the cleaners. The silicone adhesive could not be reduced below the ESCA detection limits by hand wiping alone.

With Rencothane substrates, all tested cleaners performed reasonably well for all contaminants and were as least as good as TCA. In this case, PFD seemed to outperform the other cleaners somewhat. Similarly, for nylon substrates, all cleaners removed yellow tape adhesive and HD-2 grease reasonably well. With silicone adhesive from Teflon tape, there were cleaning efficiency

issues as before, except possibly with PFH, which seemed to perform slightly better than the other cleaners.

With castable inhibitor substrates, ESCA indicated no differences between PFD and PL4 in cleaning efficiency.

For most contaminants on the RTV silicone substrates, all cleaners seemed to have excellent cleaning efficiency. For a few cases (uncured DC90-006 RTV on cured DC93-104, and silicone adhesive from Teflon tape) it was hard to tell the soil from the substrate with ESCA. With the Teflon tape adhesive a method to tell the two apart was devised from differences in the Si (2p) signatures of the two materials. As shown in Figure 18, the Teflon tape adhesive contains two chemical states of silicon -- one with a Si (2p) binding energy consistent with common silicones, and a second that is more like silica. Therefore, the amount of "silica" present on the DC93-104 surface is a measure of the amount of residual tape adhesive residue.

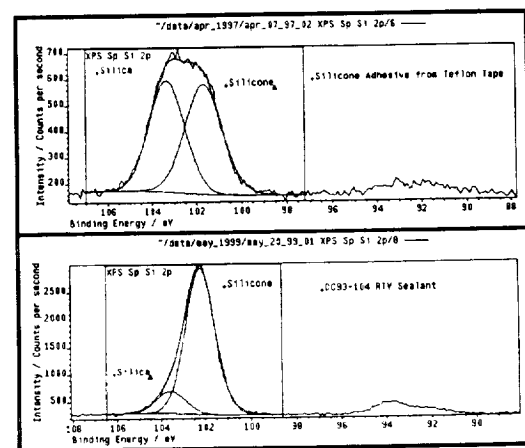


Figure 18. ESCA Detail Scans, Silicon (2p) Region, of Silicone Adhesive from Teflon Tape and DC93-104 RTV Silicone Sealant

Relative "silica" level analysis of the Teflon tape adhesive contaminated substrates is shown in the bar chart of Figure 19. (No solvent-wiped, noncontaminated control was analyzed for Ionox). The tape residues are not effectively removed by any cleaner except possibly Ionox.

As was the case with other materials, with only a few exceptions, the alternative cleaners performed at least as well as TCA for the miscellaneous substrates.

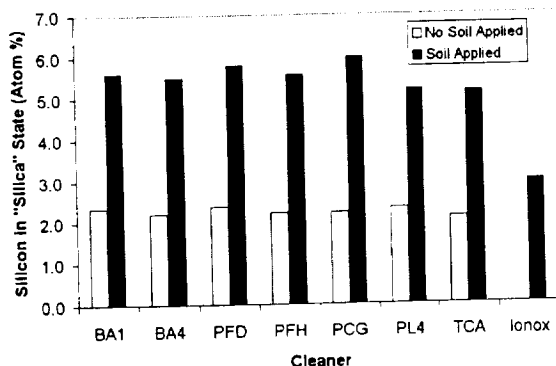


Figure 19. ESCA "Silica" Levels of Solvent Wiped DC93-104 RTV Silicone Substrates, With and Without Teflon Tape Silicone Adhesive Precontamination

Discussion

The data reported here indicate that no cleaner tested in this matrix consistently performs differently than TCA. Cleaning efficiency seems to depend more on the substrate being cleaned and the soil. Porous substrates, or those with microscopic indentations, proved to be more difficult to clean. Certain soils, notably polysulfide and RTV silicone sealants, and the silicone adhesive from Teflon tape, were very tenacious and were usually not adequately removed by any cleaner, including TCA.

Since only one replicate of each substrate/soil combination was tested, individual differences in cleaning efficiency noted in tests on a given substrate/soil combination could not always be differentiated from normal variations in the cleaning technique. In most cases, the cleaning results were nearly identical for the entire range of cleaners used on a given soil/substrate combination -- a testament to the skill and ability of the operators to produce consistent cleaning results. If a consistent difference in cleaning efficiency was observed for similar soils on multiple substrates, that was taken as an indication that it might be a real difference.

A case in point is the solvent Reveille (REV) which appeared to clean differently than TCA more often than other cleaners in the rubber and painted substrate evaluations. This also seemed

to be true, to a lesser extent, with the solvent PF Degreaser (PFD). Both of these are primarily composed of aliphatic hydrocarbons and would be expected to be less aggressive in dissolving surface contamination. Rubber specimens that were cleaned with these cleaners were less likely to perform well in bonding tests. On the other hand, in most cases outside of the rubber matrix, PFD generally performed as well as TCA. It is worth re-emphasizing that in the majority of instances PFD and REV cleaned as well as TCA and the bonding data show no difference in practical performance. These cleaners, since they are less aggressive, have the advantage of being "kinder" to the polymeric substrates. They thus may be preferable to the other cleaners in instances where attack of the polymers by absorbed solvent is an issue.

We will not engage in a detailed discussion of the complementary bonding data here. In some cases (notably natural rubber to steel bondlines in flex bearings) there were dramatic differences between cleaners in bonding performance. These differences, however, often appear to be due to differences in absorption and retention of solvents and their effect on the rubber and adhesive mechanical properties. The ESCA results strongly suggest that the differences are not caused by differences in cleaning efficiency. Even in cases where ESCA data were indicative of extremely poor cleaning efficiency (e.g. grease and oil on cork) bond data often indicated acceptable bond strengths.

The main conclusion from this study is that there are a wide variety of solvents that will clean process soils as well as TCA. The data also provide assurance that the robustness of many RSRM systems in bond tests is not concealing significant differences in cleaning performance. A cleaner that performs considerably worse than TCA but is acceptable in laboratory bonding tests is less likely to be selected with the approach we have taken here.

References

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