Solvent Substitution – PART 2
The Elimination of Flammable, RCRA and ODC Solvents for Wipe Application

by E. P. Lopez, W. E. Moddeman, J. Birkbeck, D. L. Williams, and M.G. Benkovich

[Editor's Note: All Tables and Graphs can be found in the October issue of Clean*Tech* magazine. Click here to subscribe >>]

Efforts are being made within the nuclear weapons complex (National Nuclear Security Administration) of the Department of Energy (DOE) to replace Resource Conservation and Recovery Act (RCRA) regulated solvents, (flammable, toxic, corrosive and reactive) and ozone-depleting chemicals (ODC) with more benign alternatives.

Within the National Nuclear Security Administration (NNSA) and the Department of Defense (DoD) sectors, these solvents are used for cleaning hardware during routine maintenance operations. A primary goal of this study featured in this article is to replace flammable solvents for wiping applications.

Sandia National Laboratories, the BWXT Pantex Plant, the Honeywell Kansas City Plant, and other National Nuclear Security Administration (NNSA) sites have teamed to identify suitable replacements for Resource Conservation and Recovery Act (RCRA) solvents and ozone-depleting chemicals (ODC) used in nuclear maintenance operations.

Part One of this article examined hydrofluoroether (HFE) and a hydrofluorocarbon (HFC) cleaners currently being considered as potential replacements for flammable solvents. Part Two reports on the cleaning efficacy, short-term and long-term materials compatibility, corrosion, drying times, flammability, environment, safety and health (ES&H) issues and accelerated aging studies are among the tests that are being conducted and that are used to screen candidate solvents, the traditionally used isopropyl alcohol, which serves as the baseline cleaner.

Preliminary cleaning efficacy results as determined by the contact angle indicate that isopropyl alcohol and the HFE solvent are roughly equivalent in the removal of silicone grease, fluorinated grease and a simulated fingerprint contaminant from various metal alloys. On the other hand, the MESERAN and XPS techniques indicate that in general the HFE solvent, as applied on a Kimwipe is not as effective as isopropyl alcohol. However, XPS analysis demonstrated that the HFE solvent was at least as effective as isopropyl alcohol for removing the simulated finger print contaminant when wiped with a pre-moistened cloth. This article also elaborates on the operational benefits of using the HFE and HFC cleaners.

The Results and Discussion
A. Cleaning Efficacy
Results From Goniometer/Contact Angle: An average contact angle of 62° ±4° was obtained from three 303 stainless steels samples after initial preparation with TCE and IPA. An average contact angle of 66° ±8° was obtained after contamination (with Krytox) and then wiping with IPA (Table 2). Similarly, an average contact angle of 64° ±1° was obtained for a second set of three 303 stainless steel samples and an average contact angle value of 68° ±3° was obtained after wiping with HFE-7100. The difference in contact angle was once again 4°.

In both cases, the samples were not restored back to their original condition but the relative differences in contact angle before and after cleaning regardless of which cleaner was used, was essentially the same. In some cases, the HFE-7100 solvent cleaned better than the IPA and in other cases the opposite occurred, but not to any significant extent in either case.

On the other hand, significant differences were noted when testing was performed on anodized 2024- aluminum. Neither solvent was very efficient at removing the Krytox contaminant from this particular substrate. See Table 2. This difficulty in cleaning anodized aluminum can be attributed to the high porous surface oxide produced by the anodization process [Ref. 27]. The resulting surface permits trapping of the 3 contaminants in the pores. The solvent has limited access to the contaminants in the pores and therefore light cleaning by wiping is inefficient.

Results from the MESERAN Test: MESERAN testing was performed both before applying Krytox fluorinated grease or DC-4 silicone grease and then again after wiping with IPA or HFE. The substrates included bare 2024 aluminum, bare 304L stainless steel, and passivated 304L stainless steel. Based on calibration curves developed for these specific contaminants on these specific substrates, the MESERAN slopes are converted to equivalent contamination levels.

The results for Krytox grease on bare 2024 aluminum are shown in Table 3. An average slope value of 255, which corresponds to a contamination level of >100,000 nanograms (ng/cm^2) was observed after applying the contaminant to the surface. After wiping with IPA, the average slope was 2,690, which corresponds to a contamination level of 38 ng/cm^2. Cleaning with HFE was not as efficient at removing the Krytox as cleaning with IPA, i.e., the average slope value after wiping with the HFE solvent was 1125, which corresponded to a contamination value of 5,743 ng/cm^2.

Although the average contamination value indicates a clean surface after wiping with IPA, two of the individual values within the group of five had a large amount of contaminant left on the surface and large variability as noted by the large standard deviation and percent coefficient of variance. The same trend was noted when testing 304L stainless steel, inother words, the IPA wipe (<1 ng/cm^2) was more efficient in removing the Krytox grease than the HFE wipe (5,568 ng/cm^2) (Table 4) and also for the passivated 304L stainless steel (Table 5). The vapor pressure of the HFE-7100 solvent is much higher than IPA (ca.8 times) [ref. 28].

The wiping process was performed in a fume hood. In this fume hood environment, once applied to the Kimwipe, the HFE evaporates much faster leaving the Kimwipe dry before the wiping process was completed. This may be one reason why the HFE-7100 did not clean as well as IPA. This test will be repeated using the HFE pre-moistened wipes [ref. 17] (see Experimental XPS section) since it appears that the HFE evaporation rate from the cloth wipe is reduced.

The results for the DC-4 silicone grease on bare 2024 aluminum are shown in Table 6. An average slope value of 106, which corresponds to a contamination level of >100,000 ng/cm^2, was observed after applying the contaminant to the surface. After wiping with IPA, the average slope was 2602, which corresponds to a contamination level of 63 ng/cm^2. No comparison can be made to the HFE since testing has not been completed.

Wiping DC-4 silicone grease from bare 304L stainless steel (Table 7) and passivated 304L stainless steel (Table 8) had similar results as the aluminum surface. The contamination levels detected were <1 ng/cm^2 for bare 304L stainless steel and 67 ng for passivated 304L stainless steel. Operator variability was not as evident with the DC-4 silicone grease as it was with the Krytox grease on bare 2024 aluminum.

Results from XPS- Low Resolution Scans: The XPS scan on the methanol cleaned baseline disc revealed that the surface had elements characteristic of the aluminum 6061 alloy, such as Al, Si, Mg, Cu, Zn and Fe, and an oxide of aluminum that was roughly 1 to 2 nm thick. These elements are part of the original metal alloy [ref. 27] and the oxidizable elements migrate to the surface during machining of the alloy disc.

The XPS scan of the 4 µg of dust sebum emulsion that was applied to the methanol-cleaned disc, consisted primarily of carbon and oxygen, as expected with the application of 40 superimposed fingerprints.

Upon wiping with HFE-7100, the carbon signal decreased and the oxygen and aluminum signals increased as the number of solvent wipes increased. Finally, a light rubbing with the HFE reduces the carbon level to very close to that observed on the original ultrasonically cleaned metal. Table 9 summarizes the average atomic % noted on each sample with the associated standard deviation and the number of analyses.

A second sample of the ultrasonically cleaned aluminum 6061 was contaminated with dust sebum emulsion. This sample was wiped with IPA moistened Kimwipes and the carbon decreased and correspondingly the oxygen and aluminum increased after 3 wipes and even more after 6 wipes. The removal of the emulsion is more effective when using a Kimwipe saturated with IPA than one saturated with HFE, as seen in Table 9.

The experiment was repeated by wiping a third sample with a cloth wiper pre-moistened with HFE-7100, and repeated again with a second pre-moistened wiper. The carbon significantly decreased and the oxygen and aluminum greatly increased. The data in Table 9 show that 2 wipes with the HFE-7100 pre-moistened cloth wiper are nearly as effective as 3 wipes with an IPA saturated Kimwipe. The HFE-7100 is a more volatile solvent than IPA by almost 8 times [ref. 28].

Kimwipes (Kimberly-Clark) have an open weave, which facilitates rapid evaporation of the solvents. It was noted that the bulk of the HFE solvent had evaporated before the wiping of the substrate with the Kimwipe even began. However, the thicker tighter weave of the cloth wipe retains more of the solvent longer so that it is available to actually clean. The cloth is made of semi-soft polyester fibers with a high surface area that are interwoven to form interlocking loops. This construction retains the very volatile HFE as well as provides strength and resilience during the wiping process.

High Resolution Scans: The effect on the passive oxide film of the aluminum 6061 substrate by the contamination with the dust sebum emulsion and by contact with the various solvent treatments was determined from the high resolution XPS scans (Figure 1). It was concluded that neither the deposit of the emulsion nor the contact of either of the two solvents affected the native aluminum oxide film on the aluminum 6061 surface.

Cleaning Results of LASER-induced fluorescence (LIF) spectroscop: In addition to the LIF spectra of the dust sebum emulsion on the aluminum 6061 substrate, spectra were also recorded from the aluminum 6061 disc ultrasonically cleaned with methanol and on contaminated aluminum 6061 discs after 3 wipes with the HFE pre-moistened cloth wipers. The ultrasonically cleaned aluminum 6061 disc showed a flat baseline as expected, while the dust sebum emulsion sample showed a very large triangular fluorescence emission.

The wavelength region was integrated from 800 nm to 1000 nm, and the results of the integrated signal are summarized in Table 10. It is clear that the fluorescent signal is very strong for dust sebum emulsion (~730,000 counts). Since the numbers of counts are directly proportional to the amount of material that is fluorescing [ref. 18], it appears that about 80% of the emulsion is removed by the first few wipes with the HFE pre-moistened cloth wiper.

B. Sandwich Corrosion Test Results

The relative corrosion rating for the metal alloys per ASTM F1110-90 are listed in Table 11. The bare aluminum 7075 alloy and the bare aluminum 6061 alloy exhibited an average corrosion rating of 4 and 3 respectively when exposed to deionized water. A rating of 4 corresponds to extensive corrosion exhibited on 25% or more of the total surface area and a rating of 3 corresponds to moderate corrosion on 10 to 25% of the surface area exposed. The remaining alloy types indicated very slight to no visible corrosion regardless of the exposure to deionized water, IPA or the HFE solvents.

An example of a bare aluminum 7075 panel before and after exposure to deionized water is shown in Figure 2. In previous studies, microanalyses identified the residue as aluminum hydroxide. This type of residue is typically found in oxidized and hydrated aluminum samples and is a major material in many kinds of corroded aluminum [ref 16]. An example of beryllium after exposure to deionized water is shown in Figure 3. This sample was assigned a corrosion rating of 3 (Table 11).

C. Immersion Corrosion Test Results

Immersion corrosion tests were performed on the following alloys: aluminum 2024, anodized aluminum 2024, alodined aluminum 2024, aluminum 7075, aluminum 6061, 304L stainless steel, passivated 304 L stainless steel, 303 stainless steel, titanium 6Al-4V, and beryllium. No corrosion effects were observed after immersion of any of the alloys in either IPA or HFE for a period of 24 hours at 100°F. The evaluations included a combination of weight change measurements and a visual qualitative determination of change.

D. Materials Compatibility Test – Polymeric Materials

None of the materials that were tested in IPA or HFE for either time period (2 or 5 minutes) exhibited any significant permanent weight change. Furthermore, there were no detectable visual changes such as discoloration, swelling, dissolution or texture change. Examples of materials that were tested include polyurethane, polyimides, compression pads, polyesters and other polymers.

E. Compatibility of High Explosives, Potting Compounds and Adhesives

Differential scanning calorimetry and chemical reactivity tests were performed on a variety of high explosives, such as PETN. Basically, the effect on the stability of the explosives when in contact with the HFE was negligible and the solvent passed the test. No DSC or CR tests have yet been done with IPA as the solvent. With respect to cure inhibition, adhesives such as Halathane 883, Epon 828/Versamid 140 and Adhesive 934 were tested. Similarly, potting compounds such as DC 93-122 and Silastic RTV-732 were also tested. There were no reactions observed with HFE, nor with Vertrel HFC. However, tests have not yet been done with IPA as the solvent.

F. Non-volatile residue comparison between HFE and IPA

The residue weight obtained after evaporation of 1 liter of solvent of HFE was 1.1 mg/liter. The residue weight obtained for IPA from a flame tamer was 18.0 mg/liter. Due to flammability concerns associated with the use of IPA, it is required to be housed in a container known as a “flame tamer”. While the container addresses safety concerns, it also contributes to the overall residue content. A sample of the residue from the IPA was submitted for Direct Insertion Probe Mass Spectroscopy. The major contaminant identified was bis-ethylhexylphthalate, which most likely was leached from the O-Ring that seals the flame tamer container. Note that HFE is nonflammable and therefore is not required to be dispensed from a flame tamer. Evaporation of the HFE produced insufficient non-volatile residue for analysis.

G. Worker Safety – Air Monitoring

Two personal-exposure monitoring tests were performed. One involved wiping for 15 minutes with HFE and the other was based on a 105-minute test using a spray box that contained 5 gallons of HFE. The wiping test did not detect any HFE vapors in either the breathing zone nor in the area monitored. The measurements, which contributed to the Time Weighted Average (TWA) calculation in ppm over an 8-hour period, were collected from the 105-minute spray box study as well as the wipe test. These data are summarized in Table 12. The three 8 Hour TWA for exposure to HFE are well below the EPA proposed limit of 750 ppm and the more restrictive NNSA action level of 375 ppm. The 8 Hour TWA for IPA is 400 ppm and the more restrictive NNSA action level is 200 ppm. The spray box test involving 5 gallons of HFE is an extreme over-test. Therefore, the exposure of personnel to HFE vapors during any wiping or rubbing application is not a worker safety issue.

Summary and Conclusions

Cleaning hardware during routine maintenance operations has historically been accomplished with RCRA-regulated or ODC solvents within the NNSA. In an effort to curtail the use of these toxic and flammable solvents for wipe applications, a study is currently underway to identify and qualify a more benign alternative or alternatives. The primary goal is to systematically reduce flammable and combustible solvents used in proximity to and in nuclear explosive operations through solvent elimination, minimization or substitution. Although this paper is part of an on-going study, some preliminary tests using a variety of qualification criteria on HFE-7100, a hydrofluoroether solvent, were performed and the data compared to IPA.

Contact angle measurements indicated that the two solvents (IPA and HFE) were roughly equivalent in the removal of the three contaminants (DC-4 silicone grease, dust sebum and Krytox). The efficacy testing involving the three contaminants have not yet been completed for the XPS or the MESERAN. To date, preliminary cleaning efficacy results for these two techniques indicate that in general the HFE solvent, *as applied on a Kimwipe*, is not as effective as IPA for the removal of these contaminants from various metal alloys.

On the other hand, the three analytical methods did not always correlate. Furthermore, XPS analysis demonstrated that the HFE solvent *was as least as effective as IPA* for removing dust sebum emulsion if 1) a rubbing back and forth motion is used with the moistened Kimwipe or 2) an HFE pre-moistened cloth was used to wipe in lieu of a moistened Kimwipe. Specifically, the lint-free cloth impregnated with the HFE solvent, is more effective than a Kimwipe, because the solvent probably remains much longer in the pores of the fibers and because the fibers assist in lifting the dust sebum emulsion from the scratches and machining marks on the metal surface.

In all cases, wiping or rubbing with a Kimwipe or cloth wipe containing either solvent did not affect the passive oxide film on any of the aluminum 6061 samples. The XPS cleaning efficacy was also followed by another spectroscopic technique, LASER-induced fluorescence. This data revealed that >80% of the dust sebum emulsion was removed by just one wipe with the HFE pre-moistened cloth wipe.

All of the ASTM sandwich and immersion corrosion tests with either IPA or HFE on the 10 different metal alloy substrates showed no signs of pitting, etching or other evidence of corrosion. As part of these tests, a control was performed using deionized water as a solvent. Bare aluminum 7075 and bare beryllium did, however, show signs of moderate corrosion (10-25%) when tested with the deionized water.

No deleterious effects were noted for polymeric materials immersed in either IPA or the HFE solvent. The test criteria included weight, tactile and appearance changes and the total immersion represented a severe over-test scenario. High explosives compatibility using DSC and CR tests showed no reactions with either the IPA or HFE to the various explosives. Similarly, no cure inhibition reactions were noted for HFE on any of the adhesives or potting compounds.

Because this is a wipe application, the amount and type of residue after the solvent evaporates is of particular concern. The HFE solvent contained 1.1 mg/liter of non-volatile residue whereas IPA from a flame tamer contained 18.0 mg/liter.

The eight-hour TWA for HFE is well below the detection limit for wiping applications. Therefore, the exposure of personnel to HFE vapors during any wiping or rubbing application is not a worker safety issue. Future work will include the completion of these tests as well as the expanded use of cloth wipes and investigation of HFE-71IPA.

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About the Authors
E. P. Lopez is from Sandia National Labs, W. E. Moddeman, J. Birkbeck, and D. L. Williams are from BWXT Pantex, (Amarillo), and M. G. Benkovich is from Honeywell, (Kansas City). Author’s Note: Sandia is a multiprogram laboratory operated by

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