

## **Solvent Substitution – PART 1**

### ***The Elimination of Flammable, RCRA and ODC Solvents for Wipe Application***

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In recent years, efforts have been 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 examines two cleaners including a hydrofluoroether (HFE) and a hydrofluorocarbon (HFC) currently being considered as potential replacements for flammable solvents. 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. Part two, appearing in the October issue features the results, which are compared to 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 Objectives**

The primary goal is to systematically reduce the usage of flammable solvents (principally isopropyl alcohol) used in proximity to and in nuclear explosive operations through a risk-cost benefit assessment of solvent and combustible material elimination, minimization or substitution.

The cost benefits to all programs at BWXT Pantex Plant by removing a flammable solvent, such as isopropyl alcohol (IPA), would include (1) the savings of significant process time if the requirements for task exhaust, bonding and dry times were lifted due to the use of nonflammable solvents, (2) other operational efficiencies, such as the use of facilities that are not currently available for weapons work due to the absence of task exhaust, could be optimized if the requirement was removed, (3) waste disposal costs could be reduced for both the NNSA/BWXT Pantex Plant and the DoD since the waste generated has the potential of not being categorized as hazardous or mixed, and most importantly (4) safety would be greatly enhanced, i.e., the elimination of flammable solvents would remove the fuel component necessary to support a fire.

As mandated by NNSA [Ref.1], the BWXT Pantex Plant is currently in the process of implementing a two-stage approach that will eliminate the use of RCRA (especially flammable) and ODC solvents in one pilot program. The first stage is to reduce the number of cleaning steps where these solvents are used, and the second stage is to

substitute a non-flammable/non-combustible solvent, where it is not possible to eliminate solvent use, or implement an alternative cleaning process. To date, most of the Freon TF (CFC-113), methyl ethyl ketone and 1,1,1 trichloroethane in the pilot program have been eliminated, primarily by replacement with IPA. Although BWXT Pantex Plant is in the process of eliminating several cleaning steps where IPA is used, complete elimination is impossible. Therefore, a nonflammable alternate solvent(s) must be found.

Up until now, one candidate solvent HFE-7100 hydrofluoroether, [Ref. 2], has been extensively studied as a potential replacement. Future testing will include Vertrel® XF hydrofluorocarbon solvent (HFC) [Ref. 3].

HFE-7100 is an inseparable mixture of methoxynanofluorobutane and methoxynanofluoroisobutane. Vertrel XF is a decafluoropentane. Isopropyl alcohol is the principal baseline solvent in this study.

The solvents were evaluated not only for their inability to support combustion, but on other criteria that include: ES&H issues, e.g. toxicity, ozone depletion potential, global warming potential etc.; cleaning efficacy; corrosion of metal alloys; materials compatibility of polymers; nonvolatile residue; high explosive compatibility; cure inhibition of polymers; and short-term/long-term compatibility concerns.

Three contaminants were evaluated on several metal substrates. The three contaminants included Krytox [Ref. 4] fluorinated grease, Dow Corning 4 silicone grease [Ref. 5] and dust sebum emulsion (a simulated fingerprint oil) [Ref. 6]. The contaminants selected were a representative cross-section of those found on weapon surfaces.

## The Tests

### A. Solvent Properties

A comparison of some of the physical properties of HFE-7100, Vertrel XF, and IPA are shown in Table 1.

**Table 1: Solvent Properties**

Solvent Properties	IPA	HFE-7100	Vertrel® XF
Boiling Point @ 760 mmHg	82°C	61°C	55°C
Vapor Pressure	96 mm Hg at 25°C	202 mm Hg at 25° C	226 mm Hg at 25° C
Flash Point	54 °C	None	None
Time Weighted Average (8hr.)	400 ppm	750 ppm	200 ppm
Global Warming Potential		320 (lb equivalent CO <sub>2</sub> )	1300 (lb equivalent CO <sub>2</sub> )
Ozone Depletion Potential	0	0	0

### B. Cleaning Efficacy

Four methods were used to determine cleanliness levels: a Goniometer/Contact Angle instrument, the MESERAN, X-ray photoelectron spectroscopy and LASER-induced fluorescence (LIF) spectroscopy.

A *Goniometer/Contact Angle* instrument manufactured by Advanced Surface Technology Inc. (Video Contact Angle System, Model 2500) was used to determine relative 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 qualitative measure of surface wettability [Ref. 7]. In general, the cleaner the surface is of organic contamination, the lower the contact angle measurement.

Substrates were 1.5 inch diameter metal discs that were ¼ inch thick and machined to a 16 rms finish. The six metal alloys exposed to the contaminants were 2024-aluminum, anodized 2024-aluminum, alodined-2024 aluminum, 304 L stainless steel, passivated 304 L stainless steel, and 303 stainless steel. Following machining, they were vapor degreased in trichloroethylene (TCE) for three minutes followed by an IPA rinse and then flushed with dry nitrogen to create a uniform initial substrate surface.

The contaminants were applied as follows. For the dust sebum, approximately four micrograms of the simulated fingerprint oil were deposited and spread over the center of each disc. The dust sebum emulsion consists primarily of organic acids, paraffin, and oils [Ref. 4]. Because a fingerprint weighs ca. 0.1 micrograms, each deposit corresponds to 40 superimposed fingerprints.

The Krytox fluorinated grease and the DC-4 silicone grease were each deposited by squirting a small blob on a disc and then lightly spreading the contaminant across the entire surface of the disc. The applications of these two contaminants were operator dependent, although the operators tried to be consistent. After the contaminant was applied to the disc, the samples were allowed to dry for 30 minutes before being wiped clean and the contact angle measured.

The contaminants were removed by wiping with either HFE-7100 or IPA using a Kimwipe impregnated with roughly 5-10 ml of solvent. One wipe consists of applying a light pressure with the middle and forefingers on the wiper and dragging it across the surface of the metal disc. A second wipe consists of using a fresh wipe impregnated also with ca. 5-10 ml of solvent etc. In some cases, up to six wipes were necessary to remove the contaminant from the surface, regardless of the type of solvent used. Removal of the three contaminants from the six metal substrates was evaluated by the contact angle method. Replicates of three samples per condition were performed.

The *MESERAN* (Measurement and Evaluation of Surfaces by Evaporative Rate ANalysis) provided a second technique for determining cleanliness. The characterization is done by depositing a chemical detector onto the test surface and then observing the rate at which the chemical detector disappears [Ref. 8-14]. The chemical detector covers approximately one cm<sup>2</sup> on the surface being tested. When testing samples that were contaminated with DC-4 silicone grease, the detector consisted of tridecane C-14 radiochemical dissolved in methylene chloride. When testing samples that were contaminated with Krytox fluorinated grease, the detector consisted of tridecane C-14 radiochemical dissolved in CFC-113. The rate at which the radiochemical evaporates is a function of the amount of residue on the surface.

The samples were prepared, contaminated and cleaned as they were for the contact angle. Removal of the three contaminants from the six metal substrates was evaluated by the *MESERAN* method. Replicates of five samples per condition were performed.

*X-ray photoelectron spectroscopy* (XPS) is the third technique for evaluating cleaning efficacy [Ref. 15], and compliments the contact angle and *MESERAN* data. It determines the elemental makeup of the surface and the quantity of the contaminants present. Kratos Analytical manufactured the AXIS Ultra model XPS which is fitted with an automated stage that allows for unattended operation while analyzing several areas on one sample. XPS scans were taken in three different manners: (1) overall low resolution to identify the elements of the surface; (2) individual element low resolution scans to obtain the surface composition in atomic%; and (3) individual element high resolution scans to monitor the surface chemistry of the metal substrate-contaminant-cleaning solvent interactions.

In this part of the study, aluminum 6061 was used as the substrate, and the

removal of dust sebum emulsion (contaminant) evaluated. The substrate was ultrasonically cleaned in methanol for 5 minutes and used as a baseline. Then, 4  $\mu\text{g}$  of the emulsion was spread over 0.5  $\text{in}^2$  of the substrate. And finally, the emulsion was removed by wiping with either HFE-7100 or IPA solvents using two different wipers. One technique used a Kimwipe impregnated with roughly 10 ml of solvent, and the second, a cloth wiper [Ref. 16], that was pre-moistened with 30 ml of the HFE-7100 solvent. The discs were cleaned in a manner consistent with the previous two analytical methods.

*LASER-induced fluorescence* (LIF) spectroscopy was the fourth technique employed for evaluating cleaning efficacy [Ref. 17]. A portable Raman spectrometer (Model R2001) from Ocean Optics Inc. consisting of a LASER light source utilizing a wavelength of 785 nm, a 7-optical fiber probe bundle, and a diode array spectrometer that detects the red-shifted scattered light, was used. The samples consisted of the 6061-aluminum alloy discs and were prepared, contaminated and cleaned in the same manner as those for the XPS analysis.

An attempt was made to record Raman spectra from the dust sebum emulsion with little success due to the large fluorescence signal produced by the impinging LASER. Therefore, no spectroscopic information was obtained, but the LIF signal proved quite sensitive to the presence of the dust sebum emulsion. The fluorescence signal, generated by the 785 nm excitation, was integrated from 800 to 1000 nm for the control and was compared to the signals of the cleaned substrates.

### **C. Corrosion of Metal Alloys**

In addition to the cleaning efficacy of the solvents, it is important to know that the solvent does not react with or corrode the substrate. Therefore, corrosion tests were conducted that included the Sandwich Corrosion Test per ASTM F1110-90 [Ref. 18], and the Immersion Corrosion Test per ASTM F483-98 [Ref. 19].

The Sandwich Corrosion Test is a comparative accelerated aging test used to determine the corrosiveness of cleaners, in other words, solvents, generally on aluminum alloys. In this case, the study was expanded to include 304 L stainless steel, passivated 304 L stainless steel, 303 stainless steel, titanium 6A14V and beryllium as well as 7075-aluminum, 2024-aluminum, anodized 2024-aluminum, alodined 2024-aluminum, and 6061-aluminum. These metal samples (2" X 4" X 0.04") were machined to a 16 rms finish and were then cleaned with mineral spirits and methyl ethyl ketone. The beryllium samples were cleaned with methanol.

Briefly, the sandwiches are created by placing a filter paper saturated with a candidate solvent between two plates of the same alloy. The sandwiches (replicates of three per condition) are cycled between warm air at ambient relative humidity (100°F, 30-60% RH) and warm, humid air (100°F, 95-100% RH) for five days and then left in the warm humid air environment over the weekend, for a total of 168 hours of exposure.

After the entire cycle is completed, the samples are inspected with the naked eye and then with 10X magnification to determine whether corrosion has occurred. A relative corrosion severity rating system is used to numerically rank the results. Only the surfaces that were in contact with the saturated filter paper are compared. Any corrosion at the edge of the sandwich is disregarded per ASTM F1110-90 [ref. 18]. Any corrosion in excess of that shown by the control group is cause for rejection per the ASTM standard definition.

The Immersion Corrosion Test determines the corrosiveness of the solvents on metals under conditions of total immersion by a combination of weight change measurements and a visual qualitative inspection. The metals were the same as those in the sandwich corrosion tests.

The procedure is as follows: 1) three replicate samples of each alloy are pre-cleaned with mineral spirits and methyl ethyl ketone, 2) the samples are weighed to the nearest 0.1 mg prior to immersion, 3) the samples are immersed in the solvent for a 24-hour period at 100°F, 4) at the end of the 24-hour period, the samples are

removed from the solvent and reweighed and inspected (for discoloration, dulling etching, presence of growth, pitting, presence of selective or localized attack, etc.), and compared to the control sample.

#### ***D. Materials Compatibility Test – Polymeric Materials***

Compatibility is the chemical property of materials to coexist without adverse reaction for an acceptable period of time [Ref. 20]. Compatibility tests on polymeric materials were performed to evaluate the long-term effects of the solvent on the polymers in the event of an inadvertent spill. This compatibility test consists of a minimum two-minute immersion of representative polymers in either HFE or IPA [Ref. 15].

The polymeric samples were tested in the as-received condition. No pre-test cleaning or conditioning was done. In an effort to over-stress the solvent-polymer compatibilities, a 5-minute immersion was done in some cases. Weight and visual analyses (discoloration, swelling, dissolution, texture change, etc.) of the materials were recorded before and after immersion.

#### ***E. Compatibility of High Explosives, Potting Compounds and Adhesives***

Compatibility tests are performed on weapons to satisfy the requirement that no material that is deleterious to the quality or the stockpile life of a weapon shall be used to treat or be placed in contact with a high explosive part [Ref. 21]. The DOE Explosives Safety manual states, "before mixing new explosives with other materials, the compatibility and stability of the explosive with the new materials should be determined" [Ref. 22]. The stability of an explosive in contact with inert materials can be determined by Differential Scanning Calorimetry (DSC) and the Chemical Reactivity Test (CRT) [Ref. 23]. Therefore, both DSC and CR tests were performed on LX-10, RX-03-BB, and XTX 8003 explosives with the HFE-7100 solvent.

Cure inhibition testing is performed to ensure that no material used will inhibit the cure of potting compounds or adhesives [Ref. 24]. This test is especially important for solvents in order to ensure that no residue is left that will inhibit the cure of the polymers. Cure inhibition determinations were performed according to BWXT Pantex Operations and Inspection Manual 7-9972 Issue E [Ref. 24] on the following materials: 1) Epon 828/Versamid 140, 2) Epon 828/Versamid 125, 3) Epon 828/Curing Agent U, 4) Halathane 73-18, 5) Adhesive 934, 6) Halathane 883, 7) Epoxy Epoweld 8173, 8) Explostix 473, 9) APC 3.8, 10) APC 10.0, 11) Silastic RTV 732 and 12) DC 93-122 Potting Compound.

#### ***F. Non-Volatile Residue Comparison Between HFE and IPA***

A conventional gravimetric method per ASTM D 2109-96A [Ref. 25], for halogenated organic solvents was used to determine the non-volatile residue (NVR) of IPA and HFE-7100. The procedure is as follows: (1) dry a platinum or high-silica content glass evaporating dish in an oven at 221°F and cool in a desiccator until a constant weight is obtained, (2) rinse and fill a clean one-liter class A volumetric flask to the mark with the solvent, (3) invert the flask and the dish and place them together so that the dish is exposed to a constant heat source of approximately 212°F, (4) allow all the solvent to evaporate, (5) place the dish and contents in an oven at 221°F for one hour, cool in desiccator, reweigh the dish and contents and (6) calculate the NVR in parts per million (ppm).

#### ***G. Worker Safety***

Two air-monitoring tests were performed to determine the toxicity effects of HFE-7100 on the worker. A Breathing Zone pump equipped with a carbon filter was used to capture the solvent vapors. The solvent was extracted from the carbon filters and analyzed by liquid chromatography [ref. 15]. The first air-monitoring test was the breathing zone (BZ), which monitors a 2-foot radius around the head and shoulders of the worker. The BZ results are typically used to determine the exposure limits.

The second test was area monitoring, which monitors how vapors spread out to different areas. These tests were conducted during normal wiping operations, i.e. during cleaning steps of the pilot program processes. These wiping operations are

normally performed within a 15-minute period.

**Editor's Note**

*Next month in Part 2 of Solvent Substitution, The Elimination of Flammable, RCRA and ODC Solvents for Wipe Application the authors discuss the results and their conclusions.*

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