SURFACE QUALITY IMPACT OF REPLACING VAPOR DEGREASERS WITH AQUEOUS IMMERSION SYSTEMS

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**Title:** SURFACE QUALITY IMPACT OF REPLACING VAPOR DEGREASERS WITH AQUEOUS IMMERSION SYSTEMS

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**Abstract:**
With effective vapor-degreasing solvents environmentally suspect, other methods of cleaning metal surfaces must be used. Aqueous immersion cleaning, currently the preferred method for intermediate, lighter-duty cleaning, is a promising alternative for precleaning and degreasing. Alkaline cleaners are the principal aqueous cleaner group and represent the most workable, broad substitute for vapor degreasers. The efficiencies of aqueous immersion degreasing and vapor degreasing for removing contaminants from an aluminum surface are compared. Intentionally soiled, artificially weathered 7075 aluminum panels are degreased and then either anodized or chemically conversion coated. The quantity and composition of the contaminant is determined after the cleaning. The performance of the coating is then ascertained and correlated with the contaminant history. The degreasing system is shown to have no effect on the performance of anodized or chemically conversion-coated aluminum surfaces. Performance is assessed in terms of resistance to both corrosion and abrasion and on the integrity of the oxide coating. The subsequent light-duty immersion cleaning and pickling removes any soil that survives the degreasing. Very little contamination survives the light-duty cleaning.

**Subject Terms:** Vapor-degreasing, aqueous immersion systems, metal surfaces
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INTRODUCTION

A variety of coatings are applied to metals to increase corrosion resistance, hardness, wear resistance, and the aesthetic qualities of the surface. Prior to the application of the coating, the metal undergoes a series of preparation treatments which may include grinding, brightening, degreasing, cleaning, pickling, etching, and de-smutting. With the residual microsoils having the most significant effect on the condition of the subsequent coatings (Cohen, 1987), the degreasing is one of the more important preparation treatments (EPA, 1994b).

Vapor degreasing has been one of the preferred processes used to clean metals prior to coating. In this process, a solvent is heated to its boiling point, generating substantial vapor which contacts soiled parts suspended above the liquid surface as shown in Figure 1. Solvent condensing on the parts dissolves the soil, and the liquid/soil mixture falls back down into the boiling solvent. The contaminants usually have higher boiling points than the solvent so the vapor itself remains relatively pure. Figure 2 shows a second major advantage of vapor degreasing: the part dries rapidly when removed from the solvent-saturated atmosphere. There were approximately 24,500 vapor degreasers operating in the United States in 1992 (EPA, 1995).

Traditionally, chlorinated hydrocarbon solvents have been used in vapor degreasers because they are very effective and nonflammable cleaners (EPA, 1994a). The solvents most commonly used were CFC-113, trichloroethylene (TCE), perchloroethylene (PERC), methylene chloride (METH), and 1,1,1-trichloroethane (TCA). However, TCE, PERC, and METH are toxic and are suspected carcinogens. In addition, TCE is photochemically reactive; its vapor contributes to the formation of smog. In the early 1970s, these solvents began to be replaced by, primarily, CFC-113 and TCA. Cleaning efficiencies are comparable, and both have a lower toxicity and a much lower photochemical reactivity (Bird and Donahue, 1993).

Then in the late 1970s, some chlorofluorocarbons were found to undergo chemical changes in the upper atmosphere that result in the destruction of stratospheric ozone. This discovery led to the Montreal Protocol on "Substances that Deplete the Ozone Layer," signed in 1987 by 45 nations including the United States. Agreements were made to restrict the production and use of ozone-depleting chemicals (EPA, 1994a). The Montreal Protocol and its subsequent amendments provided the catalyst to amend the U.S. Clean Air Act, setting deadlines for phasing out ozone-depleting chemicals in the United States. The production of Class I ozone-layer-depleting substances, which includes both CFC-113 and TCA, was banned in the U.S. beginning January 1, 1996.

With all five effective vapor-degreasing solvents now environmentally suspect, other methods of cleaning metal surfaces must be used. The selection promises to be abundant. Some tested alternatives have been commercially available for a number of years, for example, aqueous, semiaqueous, and hydrocarbon immersion processes (Wang and Merchant, 1993). The development of other technologies, such as supercritical CO₂ processes (Rancourt, 1994; Rancourt and Messer, 1994) is being accelerated.
Aqueous Cleaning Systems

Aqueous immersion cleaning is currently the preferred method for intermediate, lighter-duty cleaning and is a promising alternative for precleaning and degreasing (Weltman and Evanoff, 1991). Aqueous cleaners may be broadly defined as cleaning solutions made of water plus chemical additives such as surfactants, builders, corrosion inhibitors, and antioxidants (Bernett and Krebs, 1990). They are non-ozone depleting and usually nontoxic. Most aqueous cleaners have very low volatility, and most are biodegradable. The soiled part is immersed in the cleaner as shown in Figure 3. Thus, these cleaners have the disadvantage of losing their effectiveness as the bath becomes contaminated. Drying problems are inherent with certain parts (Woodrow, et al., 1995). Regardless, a recent survey suggests that aqueous cleaning is technologically feasible in 80 to 90 percent of all metal cleaning applications (D'Ruiz, 1991).

Aqueous cleaners are commercially available in many compositions and may also be custom formulated for particular applications. These cleaners can be grouped into three categories: emulsion, acidic, and alkaline (ASM, 1982). Each has its specific applications. Emulsion cleaners have problems with disposal of spent emulsions and the strict VOC emission regulations imposed on them (D'Ruiz, 1991). Emulsion cleaners are less thorough than alkaline cleaners (ASM, 1982). In general, broad application of acidic cleaners is unlikely due to limitations on the use of acid on metal substrates. Acid cleaners will etch aluminum and other nonferrous metals. Alkaline cleaners are the principal aqueous cleaner group and represent the most workable, broad substitute for vapor degreasers (Evanoff, 1990).

Finishing a Metal Surface

Preparation of a metal surface for plating is a critical operation because maximum adhesion of the coating to the substrate is the major requirement for quality work (ASM, 1982), and adhesion depends on both the elimination of surface contamination to better induce a metallurgical bond and the generation of a completely active surface to initiate plating. Adequate preparation requires a long series of steps, such as:

1. Degreasing with a solvent or aqueous cleaner
2. Intermediate cleaning with an alkaline cleaner
3. Electrocleaning to remove the last traces of contaminants
4. Acid treatment to remove light oxide films formed during previous cleaning stages and to microetch the surface
5. Anodic de-smutting to remove any carbon smut formed during acid treatment
6. Aluminum is normally anodized prior to plating

The preparation stages vary, depending on the substrate and the type of plating, but in all plating operations, the final product is far removed from the degreasing. Figure 4 is a
photograph of a typical industrial metal finishing shop showing the various processing tanks lined up side by side.

Preparation of an aluminum surface for anodic or chemical conversion coatings is less stringent than the preparation of a surface for plating, and therefore, the degreasing step is more critical to the quality of the final product. The solvent/aqueous degreasing of aluminum is normally followed only by immersion in a dilute alkaline cleaner and one or more stages of pickling to remove surface oxides, although pickling removes up to 0.0003 inch of surface metal.

Anodizing is the electrochemical conversion of the aluminum surface to its oxide while the metal is the anode in an electrolytic cell. The primary purpose of the process is to increase corrosion resistance by providing a barrier to corrosants. The anodic coating also enhances subsequent electroplating (ASM, 1982). Type II sulfuric acid anodizing produces a coating with a thickness of 0.00015 to 0.00025 inch. Pores in a Type II coating are sealed by immersion in a dichromate solution.

Chemical conversion coatings are adherent surface layers of low solubility oxide, phosphate, or chromate compounds produced by the reaction of suitable reagents with the aluminum surface (ASM, 1982). Conversion coatings are formed by a chemical oxidation-reduction reaction at the surface of the metal. This reaction involves the removal of 0.00001 to 0.0001 inch of surface metal. Conversion-coated surfaces are thinner and weaker than anodized surfaces, and would be more affected by surviving surface contamination.

PREVIOUS TESTS FOR CLEANER EFFICIENCY

Since the Montreal Protocol was signed, numerous tests have been conducted to evaluate the cleaning efficiency of different alkaline aqueous degreasers. These tests ranged in comprehensiveness from the efforts at several small shops, in which a single cleaner was evaluated, to the work contracted by the Air Force to EG&G Idaho, Inc. (Wikoff, et al., 1989), which included testing the efficiency of 163 different cleaners. A few cleaners were tested by several investigators. For example, the cleaning efficiency of Brulin 815 GD was appraised by most aerospace companies. The cleaning efficiencies of the Turco products were included in tests conducted by many of the military facilities. Many tests of metal cleaners were never published in the open literature. Hundreds of commercially available aqueous cleaners have never been independently tested.

A key to any such test is the ability to determine metal surface cleanliness. There have been a number of methods used, ranging from a simple wiping test, where the metal surface was wiped to see if any contaminant remained, to the measurement and analysis of the electrons emitted from a soiled metal surface illuminated with an ultraviolet (UV) light. The water break (ASM, 1982; Spring, 1974; Cohen, 1987) and weight change methods (Tam, et al., 1993) are probably the most widely used. Other methods include:

1. Visual inspection (ASTM, 1994a)
2. Wiping (ASM, 1982; Spring, 1974; Cohen, 1987)
3. Black (UV) light inspection (ASTM, 1994a)
4. Adhesive bonding strength (Woodrow, et al., 1995)
5. Fluorescent particles (Hill, et al., 1994; ASM, 1982)
6. Mist test (Spring, 1974)  
8. Surface energy (Jones, 1985)  
11. Ultrasonic extraction (Monroe, 1994)  
12. Contact angle (ASTM, 1994b; Spring, 1974)  
13. Scanning electron microscope (Paciej, et al., 1993)  
14. Optically stimulated electron emissions (Chawla, 1990)  
15. Infrared specular reflectance (Williams and Jones, 1993)  
17. Evaporative rate (Anderson, et al., 1968)  
18. Radioisotope tracers (ASM, 1982)  
20. Laser profilometry (Paciej, et al., 1993)  

Table 1 is a partial but representative summary of cleaner efficiency tests that have been conducted. Several of these tests are of particular interest. Among the earliest were the cleaner evaluations conducted at the Gaseous Diffusion Plant in Paducah, Kentucky (Gunn, 1988) on intentionally soiled, unweathered Monel, copper, steel, aluminum and bronze panels. These tests are noteworthy because the cleaning efficiencies of eight different aqueous cleaners were directly compared to efficiencies obtained using both TCE and TCA vapor degreasers. Laboratory scale vapor degreasers were employed. Cleanliness was determined by estimating the surface energy of the metal (Jones, 1985). The ten cleaners were compared statistically; one of the aqueous cleaners was found to be the best multipurpose degreaser.

The EG&G tests (Wikoff, et al., 1989) are notable because of their comprehensiveness. A matrix involving 163 different cleaners, 5 different soils, and 16 different metal panels was employed. The panels were weathered by heating them to 100°C for 1 hour. Both aqueous and nonaqueous cleaners were tested. Cleanliness obtained by immersion in TCA was used as a baseline. Cleanliness was evaluated by measuring weight loss (Tam, et al., 1993). Approximately forty solvents passed the cleaning test with wax the most difficult soil to remove. The mechanisms for stirring the cleaner were another parameter of interest although the results were inconclusive.

Simply measuring the mass of the soils removed from an unfinished surface by a particular cleaner or cleaning system, however, ignores the usual purpose of the cleaning. Only a few of the cleaner efficiency tests previously conducted used the performance of the surface finish as the criterion for evaluating degreasing efficiency, and the evaluation was often limited to adhesion properties or the ability to survive in a salt fog chamber (ASTM, 1994c).

The cleaning tests at General Dynamics/Fort Worth (Weltman and Evanoff, 1991) included a study of the effects of aqueous degreasers on unweathered 2024 aluminum surfaces that had been anodized or chemically conversion coated. The coated panels were immersed in four different cleaners and compared with results when TCE vapor degreasing was employed. Corrosion resistance to salt spray was the criterion, 336 hours for the anodized panels and 168
hours for the conversion-coated panels. The aluminum was cleaned after the coating was applied. The quality of the coating was then evaluated. One of the immersion cleaners failed.

If the performance of the surface coating is the primary variable in determining the efficiency of a degreasing system, all steps between the degreasing and the coating must also be retained for the study to have validity. For example, if the coating is only applied after a deoxidation step, then the test specimens must also be deoxidized.

Lockheed Missile and Space Center conducted a series of tests in which the corrosion resistance of unweathered 7075 and 2024 aluminum panels cleaned in a TCA vapor degreaser were compared with surfaces immersed in different alkaline aqueous degreasers. The contaminant was a mixture of kerosene, Tap Magic, Microcut, Alumicut, and Dykem Steel Blue. Following the degreasing step, the TCA-cleaned surfaces were visually clean while the panels immersed in the aqueous cleaners showed some residue. However, based on nonvolatile residue measurements (Allen, et al., 1993), the aqueous degreased panels were cleaner. The panels were then anodized or chromate conversion coated following normal procedures. Corrosion resistance was tested by placing the aluminum panels in a salt spray chamber for a minimum of 336 hours. There were no failures in any of the anodized panels. Several of the conversion-coated 2024 panels failed, including one vapor degreased panel.

Most metal cleaning tests used panels rather than actual parts. The reason is economics; the use of enough actual parts to make the tests statistically valid would be too expensive. The use of panels is tantamount to stipulating that surface cleanliness is judged on how well an accessible surface is cleaned. Success with hard-to-clean areas such as odd-shaped tubing, sandwich welds, and honeycombs is not included, although these areas are successfully cleaned using vapor degreasers.

One exception was the tests conducted at Lockheed Fort Worth (Woodrow, et al., 1995) comparing an aqueous alkaline cleaner with TCE vapor degreasing. Five sections of chemically conversion-coated aluminum honeycomb core and composite skins used in the F-16 aircraft were cut out and used as test specimens. Following normal procedure, after the degreasing, these sections were subjected to two stages of deoxidation. Adhesive bonding was the criterion for evaluating surface cleanliness; shear and tension loads were applied to skins bonded to the honeycomb. The performance of the coating was then evaluated by placing the parts in a salt fog chamber for 30 days. Results of the tests indicated that the method of degreasing had no adverse effect on the cleanliness or corrosion resistance of the parts.

To date, no attempt has been made to link the performance of the surface finish with the composition of the contaminant not removed by a particular degreaser.

TEST PROCEDURE

The work presented in this report is a comparison of the effects (if any) of different degreasing systems on the performance of an anodized or chemically conversion-coated aluminum surface. Intentionally soiled, artificially weathered aluminum panels were degreased and then coated. The quantity and composition of the contaminant was determined after the cleaning. The performance of the coating was then ascertained and correlated with the contaminant history.
Figures 5 and 6 are schematics showing the cleaning/coating processes. The different cleanliness and surface performance analyses and the steps after which they were conducted are also included in these figures. Appendix A describes the tests in detail. The composition of the soils was analyzed using plasma spectroscopy. The quantity and composition of the soils remaining on the panels after each step of the cleaning and coating were determined using infrared spectroscopy. The panel surfaces were also examined with optical microscopes. In addition to corrosion and abrasion tests, the integrity of the coated panels was evaluated using electrochemical examination. Appendixes B and C discuss in detail the cleanliness tests and the tests used for evaluating surface performance, respectively. Simple water break free tests were applied after the degreasing stages.

One hundred 7075 aluminum test panels were cut, soiled, weathered, cleaned, and anodized or chemically conversion coated using the facilities and personnel of McDonnell-Douglas Aerospace, St. Louis, Missouri. Metal cleaning and surface finishing procedures and specifications adhered to at McDonnell-Douglas were retained.

An early major decision was whether the contaminants should be applied individually or mixed together. Several standard metal-cleaning efficiency tests consider a mixture of contaminants to be the most difficult to remove (FST, 1994). Previous tests were about equally divided.

The panels used for these tests were intentionally soiled with a mixture of equal volumes of four common lubricants considered by McDonnell-Douglas to be the most difficult to remove: Safety Draw 700, Cimflo #20, CRC Soft Seal, and Titan Lube #1129. Safety Draw 700 and Cimflo #20 are aluminum stretch-forming lubricants. CRC Soft Seal is a door release agent and Titan Lube #1129 is a titanium tube-bending lubricant. CRC Soft Seal and Titan Lube #1129, although not used for aluminum parts fabrication, are very plentiful in aerospace shops and often show up on these parts. Material Safety Data Sheets of all four lubricants are provided in Appendix D.

Actual parts are often not cleaned immediately after they are soiled. A soil applied to a metal and immediately dunked in a cleaner is many times easier to remove than that same soil applied to a metal that was subsequently subjected to fabricating operations such as forming, drawing, stamping, cutting, welding, or rolling (Scislowski, 1990).

Forming of an aluminum part was simulated by applying 2,000 psi to the panels in a laboratory press and then heating them in a circulating air oven at 150°F for 2 hours. The panels were stored uncovered on shelves in the cleaning shop for 3 weeks, allowing the contaminant to dry, before degreasing and finishing.

Three different degreasing processes were compared: cleaning with fresh Brulin 815 GD (an alkaline aqueous cleaner in common use in the aerospace industry), cleaning with used Brulin 815 GD, and TCE vapor degreasing, which was used as the baseline. Cleaning with fresh Brulin was conducted in a small tank in a laboratory environment. Degreasing with the used Brulin and with TCE vapor was accomplished using currently active industrial-sized systems at McDonnell-Douglas. The Brulin in the McDonnell-Douglas shop was 3 weeks old when the test panels were cleaned.

Often, as there was for this study, there is a delay between the degreasing and the application of the finish. Therefore, the first step in the finishing sequence was a light-duty cleaning by immersing the parts in a dilute solution of the alkaline cleaner Turco 4215 NC-LT to
remove dust, inks, and light oils that have recontaminated the aluminum parts. A Material Safety Data Sheet of this cleaner is provided in Appendix D. Surface oxides and some surface metal were then removed by two stages of pickling in a dilute nitric acid solution. The panels were rinsed in tap water after each step.

Finally, an anodized coating was applied to half of the panels, applying 18 volts DC for 25 minutes, meeting the requirements specified in MIL-A-8625 for Type II, Class 1 sulfuric acid anodizing. The surfaces were dichromate sealed by immersion in a potassium-dichromate solution. The other half of the panels were chemically conversion coated, immersing the panels in a solution of the reagent Iridite 14-2 for 3 minutes, meeting the requirements specified in MIL-C-5541.

RESULTS

It was immediately apparent through visual examination that the vapor degreaser was not removing all of the contamination. A light, but easily visible, film remained on the aluminum surfaces. The Brulin cleaned panels, by comparison, were visually clean. Figures 7 and 8 are 1.75X and 4X photographs, respectively, comparing the vapor-degreased and Brulin cleaned panel surfaces with a soiled surface. Note in Figure 7(b), the vapor-degreased panel, that the section on which the 2,000-psi “forming” pressure was applied is more soiled than the surrounding metal, evidence that working a soiled surface exacerbates the cleaning problem.

ICP Analyses of Contaminants

The Supersoil, the individual components of the Supersoil, and the fresh and used Brulin cleaner solutions were analyzed by inductively coupled plasma emission spectroscopy (ICP). The only elements detected in significant concentrations in the Supersoil were boron at approximately 650 ppm from the Safety Draw 700, and sodium at 100 ppm, also from the Safety Draw.

In the fresh Brulin solution, sodium, potassium, and phosphorous were detected in concentrations greater than 20,000 mg/L. Silicon was also found at approximately 1,500 mg/L, with a smaller amount of nickel at 130 mg/L. Analysis of the used Brulin revealed similar concentrations of the above, plus lower concentrations of calcium, magnesium, and zinc. These latter metals could be coming from the tap water used to dilute the Brulin solutions and/or the cleaning tanks. A discussion of ICP theory and analysis techniques is included in Appendix B.

FTIR Cleanliness Analyses

Fifty-six circular (0.5-inch-diameter) samples were cut from the aluminum test panels. The locations of the cuts were selected so that a number of the samples came from panel sections where pressure was applied. All samples were analyzed by Fourier transform infrared spectroscopy (FTIR) using a Biorad FTS-60 instrument and a diffuse-reflectance sampling device. A cleaned 0.5-inch circular disc from an unsoiled panel was used as the background to subtract out any peaks intrinsic to the panels themselves. A detailed description of FTIR theory, the analysis procedures followed, and the results are included in Appendix B.
Eight samples were cut from the “as-received” panels (not soiled, cleaned, or finished). The peaks (areas of increased energy absorbency by the material) in the FTIR spectra are weak but consistently located at approximately 2,920 and 2,850 cm\(^{-1}\) (wave numbers) and at 1,592, 1,378 and 948 cm\(^{-1}\), as shown in Figure 9. This indicates that there is some kind of hydrocarbon contaminant on the “as-received” panels. However, the spectra peaks are too weak to allow the contaminant to be classified or identified. (Hydrocarbon peaks appear consistently at 3,000 to 2,800 cm\(^{-1}\) in the FTIR spectra of thousands of organic materials containing CH\(_3\) and CH\(_2\) chemical groups.)

Twelve samples were cut from panels purposely soiled with Supersoil, the blend of four metal lubrication compounds (panels not cleaned or finished). All spectra for these panels match the spectrum of the Supersoil blend itself. Compare Figures 10 and 11. No data trend is evident between the samples with the soil pressed into the panels and the samples with the uncompressed soil.

Twelve samples were taken from panels that were soiled with the lubricant mixture then cleaned in the TCE vapor degreaser (panels not finished). Figure 12 shows the typical FTIR spectrum of a vapor-degreased panel. Several peaks match those of the “as-received” panels: 2,922, 2,850, 1,590, 944 cm\(^{-1}\) with a peak at 1,450 rather than 1,378 cm\(^{-1}\). However, the hydrocarbon peaks are stronger (stronger absorbency related to presence of more hydrocarbon) in the vapor-degreased spectra. These observations suggest that components of the Supersoil may still be on the surfaces of these panels. Hydrocarbon peaks in the spectra of the vapor-degreased panels occur at 2,922 and 2,850 cm\(^{-1}\), indicating the presence of CH\(_2\) rather than CH\(_3\) (2,960 and 2,870 cm\(^{-1}\)).

Examining the spectra of the four components of the Supersoil, Figures 13 through 16, the Safety Draw and Soft Seal spectra have primarily CH\(_2\) absorbency rather than CH\(_3\) absorbency. Titanlube and Cimflo spectra have both CH\(_2\) and CH\(_3\) absorbency of similar intensities. This would suggest that the vapor degreaser did not remove all the Safety Draw and/or the Soft Seal from the contaminated panels. No trend is evident between the panel samples with pressed soil versus those with uncompressed soil.

Twelve samples were taken from panels that were contaminated with Supersoil, then cleaned using fresh Brulin 815 GD (panels not finished). Figure 17 shows a typical spectrum. The few visible peaks are questionable (at noise level). Hydrocarbon peaks are absent. The only “peak-like” absorbencies are at approximately 1,595 and 945 cm\(^{-1}\). The spectra of these samples are the “cleanest” (lack of peaks) of all the spectra analyzed. It appears as though the fresh Brulin successfully cleaned these panels. No trend is evident between the panel samples with pressed soil and those with uncompressed soil.

Finally, 12 samples were taken from panels that were soiled with the Supersoil then cleaned with used Brulin. Based on the FTIR spectra, for example Figure 18, the samples are soiled with some unknown contaminant. Hydrocarbon peaks are not visible. The combination of peaks at approximately 1,350, 1,203, 1,170, 1,111, and 1,088 cm\(^{-1}\) do not completely correlate with the spectra of the Supersoil components or the spectrum of fresh Brulin (Figure 19). The contaminant could be from something in the used Brulin, since these peaks are not visible in the spectra of the samples cleaned with fresh Brulin. FTIR was run on the used Brulin solutions received from the tanks where the panels were washed. The spectra initially appeared the same as that of fresh Brulin; no significant presence of foreign contamination was visible. Upon computer subtraction of peak data points of the fresh Brulin spectrum from the used Brulin spectrum, a few unique peaks were revealed but still did not entirely match the peak locations of
the panel spectra. The panel peaks are too weak to classify or identify. Again, no trend is evident between the panel samples with pressed soil and those with unpressed soil.

**Water Break Cleanliness Analyses**

All of the degreased panels were tested for water break. The tests were conducted following the light-duty immersion cleaning in Turco 4215 NC-LT as illustrated in Figures 5 and 6. All of the panels passed this test.

**Resistance of Surface to Abrasion**

Three soiled, anodized panels that had been degreased in TCE vapor, three panels degreased in clean Brulin 815 GD, and three degreased in used Brulin were selected for testing resistance to abrasion. The test panels were sheared off 4 inches from their bottom edge and a 1/4-inch hole punched in the center for attachment to the abrader. A Model 503 Taber Abraser was employed. Rubbing wear is produced by rotating the sample on a vertical axis while in contact with two weighted abrasive wheels. A detailed description of the procedures followed and the complete tabulated results are included in Appendix C.

The surface wear index was defined as the weight loss in milligrams per 1,000 cycles of abrasion while applying a 500-gram load. Weight loss and wear index differences within each panel-type set were as great or greater than differences between panel types. Furthermore, the percentage of difference between all test panels, regardless of type, was within the specified precision for testing panels of the same type within a single laboratory per ASTM D 4060. Therefore, no discernible difference was found in the abrasion resistance of the coating developed subsequent to the different cleaning methods.

**Resistance of Surface to Corrosion**

Four soiled conversion-coated panels that had been degreased in TCE vapor, four panels degreased in clean Brulin 815 GD, and four degreased in used Brulin were selected for testing resistance to corrosion. Analogous anodized panels were also selected. The panels were placed in a salt spray (fog) testing apparatus supported by a rack slotted to hold the panel at 20 degrees from the vertical. The panels were inspected weekly for any evidence of corrosion. Photographs of the apparatus and the test panels are included in Appendix C.

After 4 weeks of exposure, all panels, including the conversion-coated panels, exhibited no more than a single pit which could not be tied to original defects. However, the conversion-coated panels did experience corrosion at the panel identification stamps which was not observed on the anodized panels. The typical appearance of these stress-corrosion cracks is shown in Figure 20. These cracks were observed on all the conversion-coated panels and no difference could be established between panels subjected to the different cleaning processes.

**Integrity of Coating**

Cathodic breakdown behavior was evaluated through potentiostatic polarization of a portion of the surface of the anodized panels. The surface was held at a fixed potential, relative
to a saturated calomel reference electrode (SCE), by potentiostatic circuitry controlling the application of current from a platinum counter electrode. By monitoring this current, the resistive nature of the anodizing oxide film was measured. With breakdown there was a corresponding increase in current. Tests were run at various potentials cathodic to the unperturbed potential to determine the polarization value required for breakdown in a 1,200-second timespan. The circuitry and test apparatus are described in Appendix C.

Figures 21 through 26 are potentiostatic polarization plots for tests on two panels from each of the three cleaning procedures. Each figure shows two plots for polarization at two different potentials (and two separate locations) bracketing breakdown for the panel designated. Breakdown was arbitrarily defined as an increase in absolute current greater than 5 μA/cm² in 200 seconds. Results for panels subjected to the same cleaning process were very similar, attesting to the repeatability of the method. Results for panels subjected to the different cleaning processes were also very similar. In all cases, only a slight increase in current density was measured at -1.4 volts relative to SCE, while at -1.5 volts, breakdown occurred at similar rates. No discernible difference in the cathodic polarization behavior was found.

STATISTICAL VALIDITY OF SAMPLE SIZE

The tests used to ascertain cleanliness were qualitative. A numerical deviation of the results and subsequent calculation of the number of samples required to make the tests statistically valid was, therefore, not possible. To be safe, 12 samples degreased in each of the three systems were analyzed for surface contamination using FTIR. Every one of the 90 soiled panels was tested for contamination using the water break free method.

The tests to evaluate surface performance produced numerical results; or could have. In the salt fog tests, no distinguishable “events” ever occurred. In the tests for coating integrity, all results were essentially the same. So, instead, the necessary number of samples was acquired from military specifications.

Two samples are required by MIL-A-8625 to be tested for abrasion resistance. Three anodized panels for each cleaning system were tested. Regardless, the percentage of difference in weight loss between any of the test panels was well within the specified precision of the method as specified in ASTM D 4060.

Five samples are required by MIL-A-8625 to be exposed for 2 weeks in a salt fog chamber to test for corrosion resistance. Four panels for each cleaner/finish combination were tested for 4 weeks. No pits were formed on any of the samples after 4 weeks, and additional corrosion testing of samples was canceled.

Two samples are required by MIL-STD-105 when testing the continuity of the coating. Ten samples for each cleaner/anodized surface combination were tested for cathodic breakdown.
CONCLUSIONS

The following conclusions were made:

1. **The degreasing system has no effect on the performance of anodized or chemically conversion-coated 7075 aluminum surfaces.** Performance is assessed in terms of resistance to both corrosion and abrasion and on the integrity of the oxide coating. The subsequent light-duty immersion cleaning and pickling removes any soil that survives the degreasing. Very little contamination survives the light-duty cleaning.

2. **The aluminum surfaces degreased in a Brulin 815 GD solution are cleaner than surfaces degreased in TCE vapor.** Also, fresh Brulin cleans the aluminum more efficiently than used Brulin. Cleanliness is assessed as the contamination remaining on the metal surface, determined both visually and qualitatively.

3. **Soiled surfaces subjected to high pressures and temperatures, such as would occur during forming operations, are more difficult to clean.** This was easily apparent upon visual examination of the TCE-cleaned panels, although FTIR analyses could not detect a difference in the contamination of pressed and unpressed surfaces.

4. **The contamination remaining on the TCE vapor-degreased surfaces was primarily Safety Draw 700 and CRC Soft Seal.** The Cimflo #20 and Titan Lube #1129 were cleaned off the panels.

There are caveats to these conclusions. The aluminum panels were soiled with specific forming lubricants. Furthermore, the used aqueous cleaner was only 3 weeks old, eliminating, for example, the problem of extracting an immersed part through a floating contaminant. Regardless, the pickling, which removes some of the surface metal, would be expected to eliminate any but the most severe remaining contamination.

REFERENCES


<table>
<thead>
<tr>
<th>Investigator</th>
<th>Date &amp; Sponsor</th>
<th>No. of Cleaners</th>
<th>No. of Aqueous Alkaline Cleaners</th>
<th>Soil</th>
<th>Metals</th>
<th>Coupons</th>
<th>Cleanliness Tests</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>Paducah Gaseous Diffusion Plant, KY</td>
<td>1988</td>
<td>8</td>
<td>3</td>
<td>Wax, carbonized oil/xylene mixture, hydraulic fluid/carbon mixture, molybdenum sulfide/carbon mixture</td>
<td>Copper, nickel, various aluminum, carbon steel, stainless steel, Monel, inconel, titanium, magnesium, waspalloy</td>
<td>Yes</td>
<td>Weight change</td>
<td>Gunn, 1988</td>
<td>Blue Gold, Tivaclean, Chem-Crest 200 are aqueous cleaners tested</td>
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<td>Boeing, Seattle, WA</td>
<td>1990</td>
<td>50</td>
<td>5</td>
<td>2014 aluminum</td>
<td>Soiled coupons baked at 100°C</td>
<td>Water break, GC/MS analysis of TCA rinse, visual, black light</td>
<td>Unpublished (J.T. Snyder)</td>
<td>Compared with TCA vapor degreaser</td>
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<tr>
<td>Lockheed Missile and Space, Sunnyvale, CA</td>
<td>1990</td>
<td>6</td>
<td>“Fish” oil, mineral oil, glycerine, machining oil, layout dye, aluminum mill stamps</td>
<td>Water break, UV light, Nielsen method</td>
<td>Weltman and Evanoff, 1991</td>
<td>4 cleaners selected for final tests; also corrosion tests</td>
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<td>Martin Marietta, Astronautics Group, Denver, CO</td>
<td>1991</td>
<td>46</td>
<td>4</td>
<td>Forming oils, greases, waxes, inks, mill marks, fines, particulates</td>
<td>Aluminum anodized or conversion coated</td>
<td>Yes, heated at 75°F for 72 hrs.</td>
<td>Unpublished (C. Fong)</td>
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<td>General Dynamics, Fort Worth, TX</td>
<td>1991</td>
<td>4</td>
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Table 1. Aqueous Immersion Cleaner Efficiency Tests
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<tr>
<th>Investigator</th>
<th>Date &amp; Sponsor</th>
<th>No. of Cleaners</th>
<th>No. of Aqueous Alkaline Cleaners</th>
<th>Soil</th>
<th>Metals</th>
<th>Coupons</th>
<th>Cleanliness Tests</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>Naval Aviation Depot, North Island, San Diego, CA</td>
<td>1992</td>
<td>8</td>
<td>8</td>
<td>2 aircraft greases, spray preservatives, activated carbon</td>
<td>Aluminum</td>
<td>Coupons welded to tubes</td>
<td>Visual, weight change, water break</td>
<td>Unpublished (T.R. Woods)</td>
<td>TCE used as reference</td>
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<td>Naval Weapons Station, Concord, CA</td>
<td>1994</td>
<td>43</td>
<td></td>
<td></td>
<td>Aluminum, magnesium, titanium, steel</td>
<td>Yes</td>
<td>Infrared spectrometric residue, weight loss</td>
<td>Unpublished (Kelvin Tse)</td>
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<td>Battelle, Columbus, OH</td>
<td>1994, EPA</td>
<td>1</td>
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<td></td>
<td></td>
<td>Yes</td>
<td>Water break</td>
<td>Preliminary report (Abraham Chen)</td>
<td>Primarily a solvent regeneration test, only Brulin 815GD tested</td>
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<td>Mare Island Naval Shipyard, CA</td>
<td>1994, Naval Sea Systems Command, Arlington, VA</td>
<td>4</td>
<td></td>
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<td></td>
<td></td>
<td>Black light (UV)</td>
<td>Antin, 1994, 1995</td>
<td>Also compatibility &amp; corrosion tests</td>
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<td>Corpus Christi Army Depot, TX</td>
<td>1994</td>
<td>29</td>
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<td>Aluminum, titanium</td>
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<td>Water break, residue by weight</td>
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<td>Kennedy Space Center Houston, TX</td>
<td>1994</td>
<td></td>
<td></td>
<td>Different types of grease</td>
<td></td>
<td></td>
<td>NVR</td>
<td>Littlefield, 1994</td>
<td>Brulin 815GD tested</td>
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<td>Thiokol Corp. Washatch, UT</td>
<td>1994</td>
<td>2</td>
<td>2</td>
<td>Cosmoline 1104, Rust Veto</td>
<td>Steel</td>
<td>Coupons bonded together</td>
<td>NVR, black light, water break</td>
<td>Keen, 1994</td>
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<td>Research Triangle Institute Research Triangle Park, NC</td>
<td>1994/EPA</td>
<td>Several, including water</td>
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<td>Steel</td>
<td>No, parts were used</td>
<td>Visual, weight change</td>
<td>Monroe, 1994</td>
<td>Compared with TCE vapor degreasing</td>
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<td>Lockheed, Fort Worth, TX</td>
<td>1995</td>
<td>2</td>
<td>1</td>
<td>Not intentionally soiled</td>
<td>Aluminum</td>
<td>No, skins, honeycomb cores</td>
<td>Adhesive bonding</td>
<td>Woodrow, et al., 1995</td>
<td>Parts coated prior to cleaning, salt fog tests for corrosion also conducted</td>
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<tr>
<td>Lockheed Martin, Denver, CO</td>
<td>1995</td>
<td>6</td>
<td></td>
<td></td>
<td>2014 aluminum</td>
<td></td>
<td></td>
<td>Weland, 1995</td>
<td>Compared with TCA vapor degreasing, conversion coating evaluated using salt fog</td>
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<td>Sandia National Labs Albuquerque, NM</td>
<td>1995</td>
<td>8</td>
<td>8</td>
<td>Machining lubricants</td>
<td>Copper, aluminum</td>
<td>Yes</td>
<td>Contact angle, spectroscopy, evaporation rate</td>
<td>Lopez, 1995</td>
<td>Compared with TCE vapor degreasing, Brulin 815GD was cleaner of choice</td>
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Figure 1. Soiled aluminum panels lowered into TCE vapor degreaser.

Figure 2. Clean panels dry immediately when removed from vapor atmosphere.
Figure 3. Soiled panels lowered into aqueous immersion cleaner.

Figure 4. Typical industrial metal finishing tanks.
Figure 5. Procedures followed to evaluate surface performance of anodized aluminum test panels.
Figure 6. Procedures followed to evaluate surface performance of chemical conversion-coated aluminum test panels.
(a) Panel soiled and weathered but not cleaned.

(b) Panel soiled, weathered, and TCE vapor degreased.

Figure 7. Visual comparison of aluminum surface cleaning system efficiencies, 1.75X magnification.
(c) Panel soiled, weathered, and degreased in used Brulin 815GD.

Figure 7. Continued.
(a) Panel soiled and weathered but not cleaned.

(b) Panel soiled, weathered, and TCE vapor degreased.

Figure 8. Visual comparison of aluminum surface cleaning system efficiencies, 4X magnification.
(c) Panel soiled, weathered, and degreased in used Brulin 815GD.

Figure 8. Continued.
Figure 9. Typical FTIR spectra of panels before Supersoil was applied.
Figure 10. Typical FTIR spectrum of panels after Supersoil was applied.
Figure 12. Typical FTIR spectra of soil panels after TCE vapor degreasing.
Figure 15. FTIR spectrum of CRC Soft Seal.
Figure 16. FTIR spectrum of Titan Lube #1129.
Figure 17. Typical FTIR spectra of soil panels after degreasing with fresh Brulin 815 GD.
Figure 18. Typical FTIR spectra of soiled panels after degreasing with used Brulin 815 GD.
Figure 19. FTIR spectrum of Brulin 815 GD.
Figure 20. Stress corrosion cracks around ID stamp of conversion-coated panels exposed to 4 weeks of salt fog.
Figure 21. Cathodic breakdown behavior of vapor-degreased panel VS8.

Figure 22. Cathodic breakdown behavior of vapor-degreased panel VS9.
Figure 23. Cathodic breakdown behavior of panel AL9 cleaned in fresh Brulin 815 GD.

Figure 24. Cathodic breakdown behavior of panel AL10 cleaned in fresh Brulin 815 GD.
Figure 25. Cathodic breakdown behavior of panel AS9 cleaned in used Brulin 815 GD.

Figure 26. Cathodic breakdown behavior of panel AS10 cleaned in used Brulin 815 GD.
Appendix A

PROCEDURES FOR CLEANING, ANODIZING, AND CHEMICAL CONVERSION COATING OF ALUMINUM PANELS

by

G.D. Anguiano

The steps followed to prepare, clean, and finish the surfaces of the aluminum test panels are listed below. Material Safety Data Sheets of the chemicals used in this study are provided as Appendix D. Both the cleaning and surface finishing were done at McDonnell-Douglas Aerospace, St. Louis, Missouri.

1. Fifty test panels each at 4.5 by 10 by 0.032 inches and another fifty test panels at 3 by 10 by 0.032 inches were cut from a 30 ft² section of 7075-T6, 0.032-inch-thick aluminum sheet.

2. The fifty 4.5- by 10-inch test panels were marked for identification as follows: fifteen with AL1 through AL15, fifteen with AS1 through AS15, fifteen with VS1 through VS15, and five with no ID markings. The ID mark was stamped on the top edge (4.5-inch dimension) with steel dies. Figure A-1 is a closeup of the panels showing the ID marking.

3. The fifty 3- by 10-inch test panels were marked in the same manner: fifteen with AL1 through AL15, fifteen with AS1 through AS15, fifteen with VS1 through VS15, and five with no ID markings. The ID mark was also located on the top edge (3-inch dimension).

4. One hundred nylon clean room bags were acquired, each bag just large enough to hold a single test panel.

5. Three 3- by 10-inch and three 4.5- by 10-inch test panels, with no ID markings, were put in clean bags, one test panel per bag, and saved for future analyses.

6. Four lubricants were acquired to use as contaminants:

   (a) 1 quart of Safety Draw 700, an aluminum stretch-forming lubricant

   (b) 1 quart of Cimflo #20, also an aluminum stretch-forming lubricant

   (c) 1 quart of Titanlube No. 1129, a titanium tube-bending lubricant but a common contaminant of aluminum parts

   (d) 1 quart of CRC Soft Seal, a mold-release agent

A-1
7. A "super soil" was prepared by mixing equal volumes of Safety Draw 700, Cimflo #20, Titanlube No. 1129, and CRC Soft Seal. The mixture was blended thoroughly. (A 2-ounce sample of each lubricant and 2 ounces of the "super soil" were saved for future analyses.)

8. One side (the side with the ID markings) of the forty-seven remaining 4.5- by 10-inch test panels and forty-seven 3- by 10-inch test panels were then contaminated with the "super soil." The mixture was applied by hand, being consistent in both the direction of application and the quantity of this soil.

9. On the contaminated side of every contaminated panel, at the bottom and center of the panel (location of ID markings is considered the top), forming stresses were simulated by placing them in a small press and applying a 2,000-pound force over a 1-inch-square area for at least 5 seconds as shown on Figure A-2.

10. Forming procedures were further simulated by heating all 94 contaminated test panels in a circulating air oven at 150°F for 2 hours. The panels were placed flat on a sheet of clean kraft paper as shown on Figure A-3.
Figure A-2. Forming stresses simulated by placing panels in a laboratory press.

11. Finally, all 94 contaminated test panels were stored in a shop environment for 3 weeks, undisturbed but uncovered. Figure A-4 shows the panels stored in the shop area.

12. Two 4.5- by 10-inch and two 3- by 10-inch contaminated and aged test panels, those with no ID markings, were put in separate nylon bags and saved for future analyses.

13. A fresh solution of Brulin 815 GD (15 percent Brulin and 85 percent tap water) was prepared in a laboratory aqueous degreasing tank. Figure A-5 shows the tank used for this part of the tests. This solution was heated to 150°F and agitation set at its maximum value. The agitation is still only moderate as shown on Figure A-6.

14. Fifteen of the 4.5- by 10-inch test panels, labeled AL1 through AL15, were cleaned for 15 minutes in this laboratory-prepared solution of Brulin 815 GD. Figure A-7 shows the panels secured for immersion in the laboratory-scale aqueous cleaning tank. The panels were rinsed for 2 minutes in a tap water tank and inspected for cleanliness, using the water break free test. All panels passed this test. The panels were dried, wrapped in clean dry kraft paper, and delivered for anodizing.
Figure A-3. Panels “weathered” by heating them in a circulating air oven for 2 hours at 150°F.

Figure A-4. Soiled panels stored in open shop area for three weeks before degreasing.
Figure A-5. Laboratory tank used for immersion degreasing with fresh aqueous cleaner.

Figure A-6. Agitation of cleaner in laboratory degreasing tank.
15. Test panels AL11 through AL15 were placed in the nylon bags and stored for future analyses. A quart of used Brulin 815 GD from these tests was also saved.

16. The used Brulin 815 GD from this laboratory aqueous degreasing tank was drained, rinsed out, and refilled with a fresh 15 percent Brulin solution to prepare for the conversion-coating tests. The solution was again heated to 150°F with agitation set to its maximum.

17. The fifteen 4.5- by 10-inch test panels labeled VS1 through VS15 and fifteen 3- by 10-inch test panels also labeled VS1 through VS15 were vapor degreased with trichloroethylene (TCE). Figure A-8 is an external view of the vapor degreaser. Figure A-9 shows the panels immersed in the TCE vapor.

18. The cleaned panels were inspected for cleanliness by applying water break free. All panels passed this test. After drying, panels VS1 through VS10 (both 4.5- and 3-inch panels) were wrapped in clean dry kraft paper and delivered for anodizing or conversion coating. Test panels VS11 through VS15 (both sizes) were stored in nylon bags, one panel per bag, for future analyses.

19. The fifteen 4.5- by 10-inch panels and fifteen 3- by 10-inch panels labeled AS1 through AS15 were cleaned for 15 minutes in an industrial-scale system using a 20 percent solution of the aqueous degreaser Brulin 815 GD. The Brulin was about 3 weeks old. The solution was maintained at 150°F with agitation. The racked panels were lowered into the tank as shown in Figure A-10. The agitation was much greater than the agitation of the cleaner in the laboratory tank. The panels were rinsed for 2 minutes in a tap-water tank and inspected for cleanliness using the water break free test. All panels passed this test. After drying, test panels AS1 through AS10 (both 4.5-inch and 3-inch panels) were wrapped in clean dry kraft paper and delivered for anodizing or conversion coating.

20. Test panels AL11 through AL15 (both sizes) were placed in the nylon bags and stored for future analyses. A quart of used Brulin 815 GD from these tests was saved.

21. Fifteen of the 3- by 10-inch test panels, labeled AL1 through AL15, were cleaned for 15 minutes in the fresh laboratory-prepared solution of Brulin 815 GD. The panels were rinsed for 2 minutes in a tank filled with tap water and inspected for cleanliness using the water break free test. All panels passed this test. The panels were dried, and panels AL1 through AL10 wrapped in clean dry kraft paper and delivered for chemical-conversion coating.

22. Test panels AL11 through AL15 were placed in the nylon bags and stored for future analyses. One quart of used Brulin 815 GD from these tests was saved.
Figure A-7. Panels secured for immersion degreasing in laboratory cleaning tank.

Figure A-8. External view of TCE vapor degreaser.
Figure A-9. Panels are immersed in TCE vapor.

Figure A-10. Racked panels are lowered into industrial-sized tank for immersion aqueous degreasing.
23. The thirty 4.5- by 10-inch test panels to be anodized, AL1 through AL10, AS1 through AS10, and VS1 through VS10, and the thirty 3- by 10-inch test panels to be conversion coated, also designated AL1 through AL10, AS1 through AS10, and VS1 through VS10, were prepared for finishing by first immersing them in a 5 percent solution of the alkaline cleaner Turco 4215 NC-LT for 10 minutes. The existing surface oxides were then removed by pickling in a 50 percent nitric acid solution for 4-1/2 minutes (9-1/2 minutes for the panels to be anodized) and in a dilute solution of the deoxidizer Amchem 7/17 for another 3 minutes. The panels were rinsed in ordinary tap water after each step. The process tanks were arranged in order (Figure A-11) and the rack containing the panels was simply moved from tank to tank (Figure A-12).

24. The thirty 4.5- by 10-inch test panels labeled AL1 through AL10, AS1 through AS10, and VS1 through VS10 were anodized, applying 18 volts DC for 25 minutes, meeting the requirements specified in MIL-A-8625 for Type II, Class 1 sulfuric acid anodizing. The surfaces were dichromate sealed by immersion in a 5 percent potassium dichromate solution for 15 minutes.

25. The 4.5-inch-wide test panels, labeled AL1 through AL10, AS1 through AS10, and VS1 through VS10, after being anodized, were placed in nylon clean bags, one test panel per bag, for future analyses.

26. The thirty 3- by 10-inch test panels labeled AL1 through AL10, AS1 through AS10, and VS1 through VS10 were chemically conversion coated, immersing the panels in a 1 percent solution of the reagent Iridite 14-2 for 3 minutes, meeting the requirements specified in MIL-C-5541. Figure A-13 shows the conversion-coated panels immediately after removal from the reagent tank.

27. The 3-inch-wide test panels, labeled AL1 through AL10, AS1 through AS10, and VS1 through VS10, after being conversion coated, were placed in nylon clean bags, one test panel per bag, for future analyses.
Figure A-11. Cleaning, deoxidizing, rinsing, and anodizing tanks arranged in order.

Figure A-12. Rack containing the panels to be anodized was simply moved from tank to tank.
Figure A-13. Conversion-coated panels immediately after removal from the reagent tank.
Appendix B

ANALYSIS OF PANEL SURFACE CLEANLINESS

by

Theresa A. Hoffard

FTIR ANALYSIS

FTIR Theory

Fourier transform infrared spectroscopy (FTIR) is an analytical method that uses infrared radiation to characterize and quantify organic (and some inorganic) materials. The infrared portion of the electromagnetic spectrum covers a wavelength range of 0.75 to 1,000 micrometers. The mid-infrared region of 2.5 to 25 micrometers, or wave numbers of 4,000 to 400 cm$^{-1}$, is the most useful region for IR analytical spectroscopy. Wave numbers (cm$^{-1}$) are proportional to frequency and are calculated as inverse wavelengths.

At the molecular level, an organic substance absorbs infrared energy and undergoes vibrations at discrete frequencies according to its unique chemical makeup. A graph of the energy absorbed (absorbency) versus the infrared frequency (wave numbers) is the absorption “spectrum” of that material. Different chemical functional groups produce unique absorption patterns so that, for a pure compound, the spectrum becomes a “fingerprint” for identification. For unknown materials or mixtures such as paints, a spectrum may classify the material as being from a particular chemical family, e.g., urethane versus epoxy for a paint material. However, it might not provide enough information to identify the pure components.

In the FTIR spectrophotometer, a material is placed in a sample compartment of the instrument. It is hit with a beam of infrared energy, usually covering the mid-infrared frequency range. For gases and transparent or translucent liquids and solids, the beam passes through the sample, is attenuated by sample absorption, then travels to the detector. For opaque solids, the beam is reflected off the sample and guided to the detector with a series of mirrors (and sometimes with special refractive crystals). Diffuse reflectance is an FTIR sampling method for solid or semisolid materials that uses mirrors.

A device inside the instrument called a Michelson interferometer uses a “beamsplitter” and both a fixed and a moving mirror to “modulate” the infrared beam. The infrared beam is “split” by the beamsplitter into two beams, one to the fixed mirror, and one to the moving mirror. The two beams are reflected back from the mirrors to the beamsplitter where they recombine constructively or destructively, depending on the position of the moving mirror. The optical path difference between the beam coming from the fixed mirror and the beam coming from the moving mirror is called “retardation.” The modulated beam then travels to the sample compartment and on to the detector. At the detector, the raw electrical signal is called an interferogram.

FTIR employs a Class II He Ne (helium neon) laser. The laser is not the source of the infrared radiation. Rather, it generates a reference signal for the computer: measuring the
retardation of the recombined infrared beam and acting as an internal clock. This clock allows the FTIR computer to convert the interferogram signal at the detector into an absorption spectrum. The computer uses a set of mathematical operations for this, primarily the Fourier transform.

**FTIR Analysis Techniques**

The following FTIR analysis techniques were considered during the project:

1. **EPA Method 413.2 for analysis of the Brulin cleaning solutions**

   Several solutions of Brulin 815 GD used to clean the panels were received for analysis. They were to be analyzed according to EPA method 413.2, a method using Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) to extract oil and grease from aqueous solutions for analysis by FTIR. The FTIR instrument scans for hydrocarbons (indicating presence of grease or related materials) in the extract. The method was attempted but abandoned due to the following:

   (a) Supersoil is not completely soluble in Freon-113, and so the extraction efficiency is questionable. (Solubility of Supersoil was tested in several solvents including Freon-113.)

   (b) The Brulin is a detergent and its components are designed to be compatible both with water and organic materials. The Brulin itself appeared to be partially extracting into the Freon. (An extract from fresh Brulin was found to contain hydrocarbons even in the absence of Supersoil contaminant.)

   (c) The manufacturer has designed Brulin in such a way that many oils and greases will not dissolve in the Brulin, but instead rise to the top of the solution where they can be skimmed. Visible small lumps of Supersoil material were clinging to the upper walls of the plastic sampling containers of used Brulin, meaning the soil is not miscible with the Brulin.

2. **FTIR solvent analysis of test panel contaminants by Soxhlet extraction or solvent-wipe**

   Contaminants on the test panels were to be extracted into solvent and analyzed by FTIR, utilizing portions of EPA Methods 413.2, and 3540B Soxhlet Extraction. This procedure was not attempted due to the following:

   (a) Solubility tests on Supersoil show it is not soluble in the solvents used to extract the material from test panel samples.

   (b) The amount of contaminant left on the cleaned test panels was so small that a prohibitively large sample of the panel would be needed to extract a sufficient quantity of contaminant for analysis.
3. Diffuse reflectance FTIR on the test panels -

Panel analysis was successfully accomplished by direct analysis of the metal panels using FTIR reflectance spectroscopy. Metal discs cut from panels were analyzed in a diffuse reflectance sampling device (nondestructive test). The results, although not strictly quantitative, do show an overall trend in the degree of panel soiling.

Reference Supersoil components were placed on metal discs (volatiles allowed to evaporate) and analyzed in the same manner as the test panels. The Brulin solutions were run by gently drying samples in an oven to remove water, placing the remaining residue on metal discs, and analyzing as above.

Results of FTIR Analyses

Table B-1 presents the tabular data for each panel tested plus comments on the data. Circular (0.5-inch-diameter) samples numbered 1 to 56 were cut from the aluminum test panels. The samples were analyzed by FTIR (Fourier transform infrared spectroscopy) using a Biorad FTS-60 and a diffuse-reflectance sampling device. A cleaned 0.5-inch circular disc (from an unsoiled panel) was used as the background to subtract any peaks intrinsic to the panels themselves. The origin of the samples (i.e., which samples were from which panels) was not revealed to the analyst until after the samples had been run and the spectra (output data) analyzed. The results are as follows (see the accompanying chart):

1. Samples 1 through 8 were taken from the as-received panels (not soiled, cleaned, anodized, or coated). What peaks did show up in the FTIR spectra are very weak but are consistently located at approximately 2,920 and 2,850 cm\(^{-1}\) (CH\(_2\) hydrocarbon peaks) and at 1,592, 1,378, and 948 cm\(^{-1}\). Samples 2, 7, and 8 did not have visible hydrocarbon peaks. This indicates that there is some kind of hydrocarbon contaminant on most of the as-received panels. However, the spectral peaks are too weak to allow the contaminant to be classified or identified. Hydrocarbon peaks appear from 3,000 to 2,800 cm\(^{-1}\) in the spectra of many thousands of different organic materials.

2. Samples 9 through 20 were taken from the soiled panels (not cleaned, anodized, or coated). These samples were purposely soiled with Supersoil, a blend of four metal-lubricating compounds. All of the FTIR spectra for samples 9 through 20 match the spectrum of the Supersoil blend itself. No trend is evident between the samples with the soil pressed onto the panels and those samples with unpressed soil.

3. Samples 21 through 32 were taken from panels that were soiled with Supersoil, then cleaned using a vapor degreasing method. The FTIR spectra peaks are very weak. However, several peaks match those of the as-received panels - 2,920, 2,850, 1,590, and 944, indicating that the original contamination present on the panels was not successfully removed. The hydrocarbon peaks are stronger (related to the presence of more hydrocarbon) in the spectra of samples 21 through 32, and a peak at
approximately 1,450 appears for most of the samples. These observations indicate that components of Supersoil may be left on the surfaces of these panels. No trend is evident between the panel samples with pressed soil versus those with unpressed soil.

4. Samples 33 through 44 were taken from panels that were soiled with Supersoil, then cleaned using fresh Brulin 815 GD, an aqueous cleaner. What peaks can be seen are extremely weak and are questionable (at noise level). Hydrocarbon peaks at the typical locations are not visible and the only other peak-like absorbencies are at approximately 1,595 and 945. The spectra of samples 33 through 44 are the cleanest (least number of peaks) of all the spectra analyzed. No trend is evident between the panel samples with pressed soil versus those with unpressed soil.

5. Samples 45 through 56 were taken from panels that were soiled with Supersoil then cleaned with used Brulin. According to the samples’ FTIR spectra, the samples are soiled with some unknown contaminant (although hydrocarbon peaks are not visible). The combination of peaks at approximately 1,350, 1,203, 1,170, 1,111, and 1,088 do not completely correlate with the spectra of Supersoil components or the spectrum of fresh Brulin. Samples 47, 48, and 49 do not show 1,203 to 1,088 peaks. The peaks are too weak to definitively classify or identify. No trend is evident between the panel samples with pressed soil versus those with unpressed soil.

6. FTIR was run on fresh Brulin, as well as used Brulin solutions received from the tanks where the panels were washed. The individual spectra of the used versus fresh Brulin appear the same. A computer subtraction of the fresh Brulin spectrum from the used Brulin spectrum was performed. Several small unique peaks in the subtracted Brulin spectrum are visible, but do not completely correlate to the spectra peaks of panel samples 45 through 56.

Conclusions

As expected, the panels soiled with Supersoil, but not cleaned or finished, all produced strong FTIR spectra matching the spectrum of the reference sample of Supersoil.

The as-received panels represent the test panels before any intentional soiling, cleaning, or finishing was performed. The FTIR data indicate that there is a small amount of contamination on the surfaces of these panels. The as-received panels were stored in individual plastic bags upon arrival at NFESC and were not handled with bare hands or exposed to other atmospheric contaminants. Thus, the contamination occurred before arrival at NFESC. The contaminants could be a number of things: fingerprints, dust from the atmosphere, residue from the cutting process, etc.

The FTIR data for the vapor-degreased panels showed the most contamination of any of the panels tested. There is clearly and visibly contamination on the surfaces of these panels beyond the as-received contaminants. The trichloroethylene (TCE) vapor degreaser appears NOT to have performed as well as the aqueous Brulin cleaner to remove the Supersoil. Although not definitive, the location of the hydrocarbon peaks in the FTIR data suggests that of the four
components making up the Supersoil, the Safety Draw and/or Soft Seal components are the most likely to be left behind on the panel surfaces.

The FTIR data for the panels cleaned with fresh Brulin show very little or no contamination. The fresh Brulin appears to have cleaned the panels more thoroughly than either the TCE degreaser or the used Brulin.

The FTIR data for the panels cleaned with used Brulin show some slight contamination which appears to be different than as-received contamination. The used Brulin may have carried contamination from its previous use and imparted it to the test panel surfaces, or an unidentified remnant of Supersoil may be left on these panels. The subtraction spectrum of the used Brulin minus the clean Brulin revealed only a few unique peaks which do not completely match the spectra of panel samples 45 through 56. The weakness of the panel spectra peaks makes it impossible to tell whether the subtracted peaks are being produced from the same contaminant that is on the surfaces of panel samples 45 through 56.

Positive identification of contaminants on the cleaned and as-received panels is not feasible due to the extremely small amounts present, resulting in very weak FTIR spectra.

ICP-EI ANALYSIS

ICP Theory

Inductively coupled plasma emission spectroscopy (ICP) is an analytical method which uses argon "plasma" to quantitatively detect metals and other elements in aqueous (and some non-aqueous) solutions. Some types of solid samples may be analyzed using acid digestion and extraction of the metals into solution.

Emission spectroscopy is based upon the phenomenon that atoms and ions of elements, when energetically excited, emit electromagnetic radiation at discrete wavelengths. When these atoms or ions are excited, the outermost electrons undergo energy transitions back to the ground state and emit photons of ultraviolet, visible, and near-infrared radiation.

An ICP instrument contains a quartz torch tube through which argon gas flows. Plasma formation, the ionization of the argon, is initiated by a spark. Surrounding the torch is an argon-cooled coil powered by a radio-frequency generator. The coil produces a fluctuating magnetic field which inductively causes ions and electrons of the argon plasma to flow in a specific path.

Sample solutions are aspirated, converted to aerosols, and injected into the plasma. The elements in the solution atomize and ionize in the plasma. The extreme heat of the plasma serves to excite the elements. Each excited element emits radiation at a series of discrete wavelengths unique for that element. A photomultiplier tube is used to detect the emissions and produce a signal which is converted by the ICP computer into an emission "spectrum." The emission counts are mathematically converted to the element's concentration in solution. Generally, one wavelength per element (usually in the visible or near UV range) is chosen by the ICP operator to determine concentration for that element.
ICP Analysis Techniques

The components of Supersoil were analyzed by ICP. They were treated as "soils" and digested by EPA Method 3050A. Method 3040 was not used since the components are not completely soluble in the required organic solvents. The digested soils were analyzed according to Method 6010A in aqueous solution. Over twenty metals were checked, some of which are not listed in these methods.

The fresh Brulin cleaner solution was also analyzed by ICP. The samples were diluted, acidified, and run according to Method 6010A. Used Brulin solution was likewise analyzed.

It was originally planned that the contaminants on the metal panels would be analyzed by ICP. The panels were to be solvent wiped or Soxhlet extracted and the residue in solvent analyzed. However, the Supersoil was found to be insoluble in the solvents used to perform these methods (insoluble in water as well). Also, the very low concentrations of contaminants on the panels would have dictated that a large sample of each panel be required for the analyses. There was not enough of each panel to go around between the ICP test and the other tests (FTIR, salt-fog, X-ray, etc.). Digestion of metal samples into aqueous solution for ICP would have caused the aluminum itself to digest, interfering with the accuracy of an ICP analysis.

Results of ICP Analysis

The only elements present in significant concentrations in the Supersoil were boron from the Safety Draw component at approximately 650 ppm and sodium at 100 ppm (also from the Safety Draw).

In the fresh Brulin, sodium, potassium, and phosphorous were present in concentrations greater than 20,000 mg/L. Compounds containing sodium, potassium, or phosphorous are common ingredients in detergents. Silicon was also found at approximately 1,500 mg/L, with a smaller amount of nickel at 130 mg/L. Analysis of the used Brulin revealed similar concentrations of the above, plus lower concentrations of calcium, magnesium, and zinc. These latter metals could be coming from the tap water used to dilute the Brulin solutions and/or the tanks.

Conclusions

Since ICP was not feasible for the analysis of the panel samples, no conclusions can be drawn comparing the panel contaminants to the materials applied to the panels (Brulin and Supersoil).

Future X-ray fluorescence analysis may be used to reveal the presence of elements on the panel surfaces corresponding to Supersoil and Brulin elements. No contaminant extraction or digestion is required for this method.
BIBLIOGRAPHY


Environmental Protection Agency (1986). Dissolution procedure for oils, greases, or waxes, method 3040. SW-846 Test Methods for Evaluating Solid Waste, Ch. 3.2, Rev 0, 1986.


<table>
<thead>
<tr>
<th>Panel</th>
<th>FTIR Sample No.</th>
<th>Soil Pressed (P)</th>
<th>Cleaning Status</th>
<th>*Peaks at 3,000-2,800 cm⁻¹</th>
<th>Other Peaks</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-A</td>
<td>1</td>
<td>As received</td>
<td>Barely Visible</td>
<td>1,592, 1,378, 948 + broad hump at 3,454</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2-A</td>
<td>2</td>
<td>As received</td>
<td>Not Visible</td>
<td>1,600, 1,374, 948 + broad hump at 3,531</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1-A</td>
<td>3</td>
<td>As received</td>
<td>Barely Visible</td>
<td>1,600, 1,383, 948 + broad hump at 3,444</td>
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<td></td>
</tr>
<tr>
<td>B2-A</td>
<td>4</td>
<td>As received</td>
<td>Barely Visible</td>
<td>1,593, 1,371, 948 + broad hump at 3,522</td>
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</tr>
<tr>
<td>C1-C</td>
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<td>As received</td>
<td>Barely Visible</td>
<td>1,595, 1,389, 948 + broad hump at 3,450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2-C</td>
<td>6</td>
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<td>1,592, 1,378, 943 + broad hump at 3,457</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1-C</td>
<td>7</td>
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<td>1,601, 1,372, 943 - no hump</td>
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<td></td>
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<tr>
<td>D2-C</td>
<td>8</td>
<td>As received</td>
<td>Not Visible</td>
<td>1,372 and 945 - no hump</td>
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<tr>
<td>E1</td>
<td>9</td>
<td>P</td>
<td>Applied soil</td>
<td>Strong 0.8 A.</td>
<td>All peaks match Supersoil spectrum</td>
<td></td>
</tr>
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<td>10</td>
<td>Applied soil</td>
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<td>E3</td>
<td>11</td>
<td>Applied soil</td>
<td>Strong 1.2 A.</td>
<td></td>
<td></td>
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<td>F1</td>
<td>12</td>
<td>P</td>
<td>Applied soil</td>
<td>Strong 0.9 A.</td>
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<td></td>
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<tr>
<td>F2</td>
<td>13</td>
<td>Applied soil</td>
<td>Strong 0.5 A.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>14</td>
<td>Applied soil</td>
<td>Strong 0.7 A.</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>G1</td>
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<td>P</td>
<td>Applied soil</td>
<td>Strong 0.7 A.</td>
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<td>16</td>
<td>Applied soil</td>
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<td></td>
<td></td>
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<td>G3</td>
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<td>Applied soil</td>
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<td>H1</td>
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<td>P</td>
<td>Applied soil</td>
<td>Strong 0.6 A.</td>
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<td></td>
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</tr>
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<td>H3</td>
<td>20</td>
<td>Applied soil</td>
<td>Strong 0.7 A.</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>I-VS11-1</td>
<td>21</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Barely visible</td>
<td>1,596 and 942</td>
<td></td>
</tr>
<tr>
<td>I-VS11-2</td>
<td>22</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,590, 1,450, 942, 745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J-VS12-1</td>
<td>23</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,590, 1,448, 941, 745</td>
<td></td>
</tr>
<tr>
<td>J-VS12-2</td>
<td>24</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,590, 1,448, 941, 850, 745</td>
<td></td>
<td></td>
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<tr>
<td>K-VS13-1</td>
<td>25</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,590, 1,448, 942, 752</td>
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<td>K-VS13-2</td>
<td>26</td>
<td>Vapor degreased</td>
<td>Barely visible</td>
<td>1,585, 1,445, 944</td>
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<td></td>
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<tr>
<td>L-VS11-1</td>
<td>27</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Barely visible</td>
<td>1,585, 1,460, 941, 850</td>
<td>Most peaks extremely weak and noisy.</td>
</tr>
<tr>
<td>L-VS11-2</td>
<td>28</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,593, 1,446, 944, 745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-VS12-1</td>
<td>29</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Barely visible</td>
<td>1,590, 1,443, 944, 850</td>
<td>1,590 and 945 peaks match peaks of &quot;as-received&quot; panels. (The 745 is just a tiny bump.) Impossible to identify contamination since spectra are so weak.</td>
</tr>
<tr>
<td>M-VS12-2</td>
<td>30</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,590, 1,445, 944, 850, 745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-VS13-1</td>
<td>31</td>
<td>P</td>
<td>Vapor degreased</td>
<td>Weak but visible</td>
<td>1,594, 1,448, 941, 745</td>
<td>Best guess is that the vapor degreaser has removed some (but not all) of the Supersoil and has left some original contamination behind as well. Hydrocarbon peaks are stronger than in the &quot;as-received&quot; spectra indicating more than original contamination is present.</td>
</tr>
<tr>
<td>N-VS13-2</td>
<td>32</td>
<td>Vapor degreased</td>
<td>Barely visible</td>
<td>1,595, 1,448, 945, 745</td>
<td></td>
<td></td>
</tr>
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</table>

(Continued)
Table B-1. (Continued)

<table>
<thead>
<tr>
<th>Panel</th>
<th>FTIR Sample No.</th>
<th>Soil Pressed (P)</th>
<th>Cleaning Status</th>
<th>*Peaks at 3,000-2,800 cm⁻¹</th>
<th>Other Peaks</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-AL11-1</td>
<td>33</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny 945</td>
<td></td>
<td>Peaks extremely weak and noisy, almost not visible. Looks as though the fresh Brulin is superior to the vapor degreaser. Appears as though the Brulin has cleaned off the Super-soil and at least some of the original contamination.</td>
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<tr>
<td>O-AL11-2</td>
<td>34</td>
<td></td>
<td>Fresh Brulin</td>
<td>Tiny 944</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-AL12-1</td>
<td>35</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny at 1,597, 949</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-AL12-2</td>
<td>36</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>&quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q-AL13-1</td>
<td>37</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>&quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q-AL13-2</td>
<td>38</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>&quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-AL11-1</td>
<td>39</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny at 1,590, 947</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-AL11-2</td>
<td>40</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny 947</td>
<td></td>
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<tr>
<td>S-AL12-1</td>
<td>41</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny at 1,596, 943</td>
<td></td>
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<tr>
<td>S-AL12-2</td>
<td>42</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny at 1,589, 940</td>
<td></td>
<td></td>
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<tr>
<td>T-AL13-1</td>
<td>43</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny 945</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-AL13-2</td>
<td>44</td>
<td>P</td>
<td>Fresh Brulin</td>
<td>Tiny at 1,599, 941</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-AS11-1</td>
<td>45</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,595, 1,350, 1,208, 1,170, 1,103, 1,080, 938, 830</td>
<td></td>
<td>Samples 47, 48, 49 appear as clean as samples 33-44. All other samples appear to be contaminated with something. The combination of peaks at 1,350, 1,203, 1,170, 1,111, and 1,088 do not exactly match the Super-soil components or the fresh Brulin spectra. The contaminant could be from the used Brulin solution (spectra of panels washed in fresh Brulin did not show the above combination of peaks).</td>
</tr>
<tr>
<td>U-AS11-2</td>
<td>46</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,345, 1,208, 1,170, 1,111, 941, 842</td>
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<td></td>
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<tr>
<td>V-AS12-1</td>
<td>47</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,590, 1,387, 943</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-AS12-2</td>
<td>48</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,597, 1,354, 939</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-AS13-1</td>
<td>49</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,591, 941</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-AS13-2</td>
<td>50</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,342, 1,203, 1,092, 947, 845</td>
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<td></td>
</tr>
<tr>
<td>Y-AS11-1</td>
<td>51</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,599, 1,203, 1,137, 1,085, 942</td>
<td></td>
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</tr>
<tr>
<td>Y-AS11-2</td>
<td>52</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,345, 1,197, 1,120, 1,088, 941, 843</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z-AS12-1</td>
<td>53</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,591, 1,213, 1,165, 1,079, 941, 845</td>
<td></td>
<td>Peaks may be too weak to classify what the contamination is.</td>
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<td>Z-AS12-2</td>
<td>54</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,364, 1,130, 1,091, 943, 848</td>
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<td></td>
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<tr>
<td>AA-AS13-1</td>
<td>55</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,597, 1,348, 1,143, 946</td>
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<td></td>
</tr>
<tr>
<td>AA-AS13-2</td>
<td>56</td>
<td>P</td>
<td>Used Brulin</td>
<td>1,355, 1,170, 945</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Indicates presence of aliphatic hydrocarbons (found in most greases, oils, and similar compounds).
Appendix C

ANALYSES OF PANEL SURFACE PERFORMANCE

by

D.R. Polly

ABRASION RESISTANCE

Abrasion resistance was evaluated in accordance with Method 6192.1 of FED-STD-141C which is specified by MIL-A-8625F: Anodic Coatings, for Aluminum and Aluminum Alloys. A Model 503 Taber abraser was employed. Rubbing wear is produced by the abraser by rotating the sample on a vertical axis while in contact with two weighted abrasive wheels as shown on Figure C-1.

Figure C-1. Aluminum panel being tested in the abraser.

Sample Preparation

Three soiled anodized panels that had been degreased in TCE vapor, three panels degreased in clean Brulin 815 GD, and three degreased in used Brulin were selected to test for resistance to abrasion. The sealed test panels were sheared off 4 inches from their bottom edge. A 1/4-inch hole was punched in center of the bottom portion for attachment to the abrader. The plastic wrap was removed just prior to testing.
Anodized Coating

Abrasion tests on anodized panels were conducted using CS-17 abrading wheels and a 500-gram load. In trial runs with this configuration, wear through the anodizing was accomplished in approximately 4,000 cycles. A standard of 2,000 cycles was used for comparison testing to ensure weight loss measurements were not affected by abrasion of the substrate. Before each test, the wheels were refaced by running S-11 discs for 50 cycles. The vacuum suction regulator was set to 80 for the duration of the tests.

The results are summarized in Table C-1. The wear index was calculated as the loss in weight in milligrams per 1,000 cycles of abrasion. Weight loss and wear index differences within each panel type set were as great or greater than differences between panel types. Furthermore, the percent difference in weight loss between any of the test panels, regardless of the cleaning method, was well within the specified precision of the method for testing of panels of the same type within a single laboratory per ASTM D 4060. Therefore, no discernible difference was found in the abrasion resistance of the coating developed subsequent to the different cleaning methods.

Table C-1. Results of Abrasion Resistance Tests on Anodized Panels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>Weight Loss (g)</th>
<th>Wear Index</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS5-A</td>
<td>23.94458</td>
<td>0.01028</td>
<td>5.14</td>
<td></td>
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<tr>
<td></td>
<td>23.93430</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>VS6-A</td>
<td>24.33749</td>
<td>0.01020</td>
<td>5.11</td>
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<td></td>
<td>24.32727</td>
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<td></td>
<td></td>
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<td>VS7-A</td>
<td>24.49241</td>
<td>0.00983</td>
<td>4.92</td>
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<td></td>
<td>24.48258</td>
<td></td>
<td></td>
<td></td>
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<td>AL7-A</td>
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<td>5.09</td>
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<tr>
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<td>24.63815</td>
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<td>4.70</td>
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<tr>
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<td>4.66</td>
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<td>24.59937</td>
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<td></td>
<td>24.54571</td>
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<td></td>
<td>5.24</td>
</tr>
</tbody>
</table>
Conversion Coating

Although conversion coatings are not intended to impart any abrasion or wear resistance, an attempt was made to get some information concerning surface “adhesion” of the conversion coating. However, even with a very mild abrasive wheel (CS-10F) and very small load (50 gram), wear through the coating was accomplished in less than 10 cycles. There was no measurable weight loss to 0.01 mg. Therefore, no useful performance comparisons could be made.

CATHODIC BREAKDOWN TEST

Numerous accelerated electrochemical tests have been employed for testing surface coatings with various degrees of success. Reportedly (Ref 1), good correlation between cathodic breakdown and longer term performance of anodized coatings has been found. A modified version of an aircraft industry breakdown test (Ref 2) was employed for investigating possible differences in the anodized coating due to the different cleaning processes.

Test Procedure

Cathodic breakdown behavior was evaluated through potentiostatic polarization of a portion of the surface of test panels from each cleaning process. The surface was held at a fixed potential relative to a saturated calomel reference electrode (SCE) by potentiostatic circuitry (Figure C-2) controlling the application of current from a platinum counter electrode. By monitoring this current, the resistive nature of the anodizing oxide film was measured. With breakdown there was a corresponding increase in current. Tests were run at various potentials cathodic to the unperturbed potential to determine the polarization value required for breakdown in a 1,200-second timespan.

Test Fixture

The test apparatus shown in Figure C-3 was employed for containment of the electrolyte. A Plexiglas cylinder with an “O”-ring seal on the lower rim was clamped to the surface. The sealed area was then submerged in electrolyte consisting of 10 mL of a 5 percent solution of sodium chloride. The area of the submerged surface was 11.40 cm².
Figure C-2. Cathodic breakdown test circuitry.

Figure C-3. Cathodic breakdown test fixture.
Polarization Plots

Figures 21 through 26 in the main body of this report are potentiostatic polarization plots for tests on two panels from each of the three cleaning procedures. Each graph shows two plots for polarization at two different potentials (and two separate locations) bracketing breakdown for the panel designated. Breakdown was arbitrarily defined as an increase in absolute current greater than \(5 \mu A/cm^2\) in 200 seconds. Results for panels subjected to the same cleaning process were very similar, attesting to the repeatability of the method. Results for panels subjected to the different cleaning processes were also very similar. In all cases only a slight increase in current density was measured at -1.4 volts relative to SCE while at -1.5 volts breakdown occurred at similar rates. No discernible difference in the cathodic polarization behavior was found.

CORROSION RESISTANCE

Corrosion resistance was evaluated by testing in accordance with ASTM B117, Operating Salt Spray (Fog) Testing Apparatus, which is specified by MIL-A-8625F, Anodic Coatings for Aluminum Alloys.

Test Procedure

Four soiled conversion-coated panels that had been degreased in TCE vapor, four panels degreased in clean Brulin 815 GD, and four degreased in used Brulin were selected to test for resistance to corrosion. Analogous anodized panels were also selected. Specimens were removed from their sealed wrapping and placed into the fog chamber as shown in Figure C-4. The panels were supported by an FRP rack slotted to hold the panel at 20 degrees from the vertical. Panels were oriented with the identification marked surface facing up. The identification marked end was placed in the slots so that there would be no contact with the pressure treated area at the opposite end of the panel. Panels were inspected weekly for any evidence of corrosion.

Figure C-5 is a photograph taken at 2 weeks (336 hours) of exposure. After this exposure period, which is specified by MIL-A-8625, no corrosion other than that associated with defects due to anodizing electrode contact, scratches, or edge effects was observed on any of the conversion-coated or anodized panels. Testing was continued to determine if longer-term exposure might reveal differences in performance. Figures C-6 and C-7 are photographs of the panels taken at 3 and 4 weeks of exposure, respectively. After 4 weeks of exposure, all panels including the conversion-coated panels exhibited no more than a single pit which could not be tied to original defects. However, the conversion-coated panels did experience corrosion at the panel identification stamps which was not observed on the anodized panels. These cracks were observed on all the conversion-coated panels. No difference could be established between panels subjected to the different cleaning processes.
REFERENCES


Figure C-4. Salt fog chamber with test panels inside.
Figure C-5. Conversion-coated (on the left) and anodized panels after 2 weeks of exposure to salt fog.
Figure C-6. Conversion-coated and anodized panels after 3 weeks of exposure to salt fog.
Figure C-7. Conversion-coated (top) and anodized panels after 4 weeks of exposure to salt fog.
Appendix D

MATERIAL SAFETY DATA SHEETS
OF CLEANERS AND CHEMICALS USED IN THIS STUDY

Enclosed in this appendix are excerpts of Material Safety Data Sheets summarizing the ingredients and physical and chemical properties of the aqueous degreaser used in these analyses,

Brulin 815 GD

the four soils,

Safety Draw 700
Cimflo 20
TitanLube No. 1129
CRC Soft Seal

the alkaline light-duty cleaner,

Turco 4215 NC-LT

the deoxidizers,

Parker Amchem Deoxidizer 7
Parker Amchem Deoxidizer 17

and the chemical conversion coating reagent,

Iridite 14-2.
BRULIN 815 GD

IDENTIFICATION
Brulin & Company, Inc.
P.O. Box 270
Indianapolis, IN 46206-0270
(317) 923-3211

West Coast Factory
Richmond, CA

Southeastern Factory
Tampa, FL

24-Hour Emergency Number (317) 923-3233
CHEMTREC 1-800-424-9300

Identity (as listed on label): FORMULA 815GD
HMIS Hazard Ratings: Health: 1, Flammability: 0, Reactivity: 0

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
This product contains no hazardous chemical substances at 1.0% or more listed in 29 CFR 1910 Subpart Z or ACGIH Threshold Limit Values. Also, this product contains no carcinogens at 0.1% or more listed in NTP Annual Report on Carcinogens, IARC Monographs, or 29 CFR 1910 Subpart Z.

PHYSICAL/CHEMICAL CHARACTERISTICS
Boiling Point: 212°F
Vapor Pressure (mm Hg): Approx. 17 @ 68°F
Vapor Density (Air = 1): Approx. 0.6
Solubility in Water: Complete
Appearance and Odor: Blue green, mild odor
Specific Gravity (H₂O = 1) 1.075
Melting Point: Approx. 30°F
Evaporation Rate (Water = 1): 1.0
SAFETY DRAW 700

IDENTIFICATION
Safety Draw 700
Castrol Industrial Inc.
1001 West 31st Street
Downers Grove, IL 60515-1280

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
Contains no ingredients now known to be hazardous as defined by OSHA 29 CFR 1910.1000

PHYSICAL/CHEMICAL CHARACTERISTICS
Appearance and Odor: Opaque milky white emulsion; bland odor
Boiling Point: 211.89°F (99.94°C)
Melting Point: NA
Specific Gravity (H₂O = 1): 0.97
Vapor Pressure: NA
Vapor Density (Air = 1): NA
Evaporation Rate (Butyl Acetate = 1): <1
% Volatiles by Volume: 70-90
VOC: 000.00 g/L 00.000 lbs/gal (VCC not yet determined for this product)
Solubility in H₂O: Miscible
pH as is: 7.4-8.4
pH (Dilute): 7.9-8.3 @4%
CIMFLO 20

IDENTIFICATION
CIMFLO 20
Products Division
Cincinnati Milacron Marketing Co.
4701 Marburg Avenue
Cincinnati, OH 45209

Emergency Telephone: (513) 841-8181
Information Telephone: 1-800-On-2-Time
(800-662-8463)

Product Code(s): 201
Generic Name: Oil-based metal forming fluid

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
This product has been determined to be nonhazardous in accordance with 29 CFR 1900.1200(d) (hazard determination). Further composition information may be made available to health professionals as provided in the standard.

PHYSICAL/CHEMICAL CHARACTERISTICS
Boiling Point: NA
Specific Gravity: 0.915
Vapor Pressure (mm Hg): NA
Melting Point: NA
Vapor Density: NA
Evaporation Rate: NA
Solubility in Water: NA
Appearance/Odor: Clear/chemical
pH: NA
TITAN LUBE NO. 1129

IDENTIFICATION
Buckeye Lubricants
20801 Salisbury Rd.
Bedford, OH 44146

Phone (216) 581-3600
FAX (216) 581-2734

Chemical name and synonyms: NA
Chemical Family: NA
Other Product Info: Proprietary formulation
Emergency Phone: (216) 581-3600

Health: 1
Flammability: 1
Reactivity: 0
Protection: C

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
None.

PHYSICAL/CHEMICAL CHARACTERISTICS
Boiling Point (F): ND
Melting Point (F): NA
pH: NA
Vapor Density (Air = 1): <1.0
Vapor Pressure (mm Hg): ND
Evaporation Rate (BuAc = 1): ND
% Volatile (by volume): ND
Specific Gravity (H₂O = 1): 0.889
Solubility in Water: Insoluble
Appearance and Odor: Very thick, pale yellow liquid
CRC SOFT SEAL

IDENTIFICATION
CRC Heavy Film Soft Seal
CRC Chemical USA
885 Louis Drive
Warminster, PA 18974
(215) 674-4300

Formula: Aerosol

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
Volatile: 79%
- Mineral Spirits: 200 TLV (units)
- Methylene Chloride: 200 TLV (units)
- 1,1,1-Trichloroethane: 350 TLV (units)
- Isobutane-Propane: 1,000 TLV (units)
Nonvolatile: 21%

PHYSICAL/CHEMICAL CHARACTERISTICS
Boiling Point (°F): 130°F
Vapor Pressure (mm Hg): 40-45, Aerosol psig @70°F
Solubility in Water: Negligible
Appearance and Odor: A dark transparent film
Specific Gravity: 1.016
TURCO 4215 NC-LT

IDENTIFICATION
TURCO Products, Inc.
Division of Elf Atochem North America
2375 State Road
Cornwells Heights, PA 19020
Emergency Phone: (202) 483-7616 (800) 424-9300
Information Phone: (215) 245-3128

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
NOTE: This product and/or the container it is packaged in may contain components, or trace components, known to the State of California to cause cancer, reproductive damage, or birth defects.

The following ingredients are defined to be hazardous per 29 CFR 1910-1200:

<table>
<thead>
<tr>
<th>NAME (CAS)</th>
<th>CERCLA RQ</th>
<th>RCRA NO</th>
<th>SARA REPORTABLE</th>
<th>%</th>
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<tr>
<td>Nonylphenoxypoly (Ethyleneoxy) Ethanol (9016-45-9)</td>
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<td>Not listed</td>
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<td>ACGIH TLV: Not established</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>OSHA PEL: Not established</td>
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<td></td>
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<td>Alkyl Polyoxyalkylene Glycol Ether (68154-97-2)</td>
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<td>Not listed</td>
<td>No</td>
<td>&lt;5</td>
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<td>Diethylene Glycol Monobutyl Ether (112-34-5)</td>
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<td>Not listed</td>
<td>Yes</td>
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<td>Sodium Tetraborate, Pentahydrate (1303-96-4)</td>
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<td>Not listed</td>
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<td>OSHA PEL: 10 mg/m³</td>
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<td>OSHA PEL: Not established</td>
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<tr>
<td>Sodium Silico Flouride (16893-85-9)</td>
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<td>OSHA PEL: 2.5 mg/m³ (F)</td>
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<td>Sodium Tripolyphosphate (7758-29-4)</td>
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<td>Not listed</td>
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<td>35</td>
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</table>
This MSDS complies with the community right-to-know laws of certain states, including Pennsylvania and New Jersey.

Carcinogens: None (as defined in 29 CFR 1910-1200, Appendix A (1)).

DOT Information Proper Shipping Name: Not regulated by DOT in normal ground transportation in containers of 100 gallons or less.

**PHYSICAL/CHEMICAL CHARACTERISTICS**
- Boiling Point: NA
- Vapor Density (Air = 1): NA
- Volatile: NA
- Solubility in Water: Appreciable
- Appearance and Odor: White free flowing powder; mild odor
- Specific Gravity: NA
- Evaporation Rate (BuAc = 1): NA
- pH: 3% in solution 10.0
PARKER AMCHEM DEOXIDIZER 7

IDENTIFICATION
Parker Amchem
Henkel Corporation
32100 Stephenson Highway
Madison Heights, MI 48071

Product Trade Name: Deoxidizer 7 Make-Up
DOT Proper Shipping Name: Oxidizer, corrosive, solid, N.O.S. (contains potassium nitrate and sodium bifluoride), NA9194.
DOT Hazard Classification: Oxidizer and corrosive
Technical Contact (Name): Product Acceptance Office
Telephone: (313) 583-9300
Emergency Telephone: 1-517-263-9430

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

<table>
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<tr>
<th>MATERIAL</th>
<th>CAS NO.</th>
<th>CONTENTS (% WT/WT)</th>
<th>HAZARD</th>
<th>TLV/PEL</th>
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</thead>
<tbody>
<tr>
<td>+Potassium Dichromate</td>
<td>7778-50-9</td>
<td>&gt;60</td>
<td>Carcinogen, IARC, NTP, Corrosive</td>
<td>0.05 mg/m³ as Cr</td>
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<tr>
<td>Potassium Nitrate</td>
<td>7757-79-1</td>
<td>10-30</td>
<td>Oxidizer</td>
<td>None</td>
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<tr>
<td>Sodium Bifluoride</td>
<td>1333-83-1</td>
<td>1-10</td>
<td>Corrosive</td>
<td>2.5 mg/m³ as F</td>
</tr>
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</table>

This product contains a chemical (+) subject to the reporting requirements of Section 313, Title III of SARA, Part 372.

PHYSICAL/CHEMICAL CHARACTERISTICS
Appearance: Orange powder
Solubility in Water: Complete
Odor: Bland
Specific Gravity: NA
pH of Concentrate: NA
Boiling Point (°F): NA
Other: None
PARKER AMCHEM DEOXIDIZER 17

IDENTIFICATION
Parker Amchem
Henkel Corporation
32100 Stephenson Highway
Madison Heights, MI 48071

Product Trade Name: Deoxidizer 17 Replenisher
Technical Contact: Regulatory Affairs Department
Telephone: (810) 583-9300
Emergency Telephone: (800) 424-9300

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

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<th>PEL/OSHA</th>
<th>% WEIGHT</th>
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<td>*Potassium Dichromate</td>
<td>07778-50-9</td>
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<td>See below</td>
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<tr>
<td>Sodium Bifluoride</td>
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<td>2.5 mg/m³</td>
<td>10 - 30</td>
</tr>
<tr>
<td>Potassium Ferricyanide</td>
<td>13746-66-2</td>
<td>None</td>
<td>None</td>
<td>1 - 10</td>
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</table>

*Refer to Section XII
Chromium compounds, water soluble: TLV = 0.05 mg/m³.
Chromic acid and chromates: PEL = C 0.1 mg/m³.

**TLV/PEL = 2.5 mg/m³ for fluorides, as F.

Emergency Overview: Orange powder. Contact causes eye and skin burns. Carcinogen - contains chromic acid.

PHYSICAL/CHEMICAL CHARACTERISTICS
Appearance and Odor: Orange-red powder; no odor.
Specific Gravity: NA
Boiling Point °F (°C): NA
Evaporation Rate: NA
pH: NA
Vapor Density (Air = 1): NA
Solubility in Water: Appreciable
Vapor Pressure: NA
VOC: NA
IRIDITE 14-2

IDENTIFICATION
Iridite 14-2
MacDermid Inc.
245 Freight Street
Waterbury, CT 06702
Telephone: (203) 575-5700
Emergency Telephone: CHEMTREC (800) 424-9300

Product Code: 78659
Chemical Family: Acid
Formula: Proprietary Mixture
HMIS Rating: Health: 3, Flammability: 0, Reactivity: 1
(0 = Insignificant, 1 = Slight, 2 = Moderate, 3 = High, 4 = Extreme)

HAZARDOUS INGREDIENTS/IDENTITY INFORMATION
MacDermid Inc. has identified the following chemical ingredient(s) as hazardous:

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>CAS NO.</th>
<th>BY WEIGHT %</th>
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<td>Chromic Acid</td>
<td>1333-82-0</td>
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PHYSICAL/CHEMICAL CHARACTERISTICS
Density: Not determined
Specific Gravity: Not determined
Freezing Point: Not determined
Vapor Pressure: Not determined
Chemical Oxygen Demand (COD): Not determined
Solubility in Water: Moderate solubility
Color/Odor: Red, odorless
Form: Solid
pH: Not determined
Flash Point: Not determined
Volatile %: Not determined

Note: These physical properties are typical values for this product.
DISTRIBUTION LIST

AFCEE / MAXWELL, BROOKS AFB TX; AFCEE / PPD, BROOKS AFB TX
AFIT / DEV, WRIGHT-PATTERSON AFB OH
AGMC/EM / COLSON, NEWARK AFB OH
AMARC/LABC / WILSON, DAVIS MONTTHAN AFB AZ
ANNISTON ARMY DEPOT / SDSAN-DEL-EMD, ANNISTON AL
APCD / FRESNO CA; GOLETA CA; SAN DIEGO CA
AQMD / SACRAMENTO CA; DIAMOND BAR CA
ARMY ARDEC / PIRROTTA, PICATINNY NJ
ARMY CRREL / ISKANDAR, HANOVER NH
ARMY ENGRG DIV / ED-SY, HUNTSVILLE AL
BAAQMD / CONTROL OFFICER, SAN FRANCISCO CA
BARRON / LAFAYETTE CA
BOEING DEFENSE AND SPACE GROUP / GROSHART, SEATTLE WA; OSBORNE, SEATTLE WA
BROOKS AFB / CODE HSC-YAQ, SAN ANTONIO TX
BRULIN AND CO INC / ZUPAN, INDIANAPOLIS IN
CAL AIR RESOURCE BOARD / SACRAMENTO CA
CALEPA / GARZA, SACRAMENTO CA; LODER, SACRAMENTO CA; LUAN, SACRAMENTO CA;
CHEMICAL SOLUTIONS INC / MILLE, LIVERMORE CA
CNO / CODE N451H, ARLINGTON VA
COMSUBPAC / CODE 44A1, PEARL HARBOR HI
CONCURRENT TECH CORP / JOHNSTOWN PA
CORPUS CHRISTI ARMY DEPOT / GAWENIS, CORPUS CHRISTI TX; SDSCC-M (MS-58), CORPUS CHRISTI TX
DEFENSE DEPOT OGDEN / FACILITY ENGINEER, OGDEN UT
DLA / BEDDOES, ALEXANDRIA VA; COFFIE, ALEXANDRIA VA
FLT AIR CARIBBEAN / N09003, FPO AA
HQ AFMC/ENX / BLACK, WRIGHT PATTEN AFB OH; HERRING, WRIGHT PATTEN AFB OH; MONROE, WRIGHT PATTEN AFB OH
HQAMC / NAPOLITANO, ALEXANDRIA VA; VERDONIK, ALEXANDRIA VA
INLAND TECH CORP / HALAR, TACOMA WA
JACOBS ENGR GROUP / CALLAHAN, PASADENA CA
JOINT DEPOT / SMITH, DAYTON OH
LETTERKENNY ARMY DEPOT / SDSLE-EN, CHAMBERSBURG PA
LLNL / MELTZER, LIVERMORE CA
LOCKHEED FORT WORTH CO / BARNES, FORT WORTH TX; PHILLIPS, FORT WORTH TX; WOODROW, FORT WORTH TX
LOCKHEED/MARTIN MISSILES AND SPACE / CAMAHORT, SUNNYVALE CA
MCAS / ENVIRONMENTAL AFFAIRS, CHERRY POINT NC
MCAS CHERRY POINT / CODE 35450, CHERRY POINT NC
MCLB / CODE 88-4, ALBANY GA; CODE 883 (RIVERS), ALBANY GA; CODE 883 (WOODWARD), ALBANY GA
MONTEREY BAY UNIFIED APCD / MONTEREY CA
NAB NORFOLK / N61463, NORFOLK VA
NAS JACKSONVILLE / CODE 0015, JACKSONVILLE FL; CODE 340, JACKSONVILLE FL; CODE 343, JACKSONVILLE FL; N09607, JACKSONVILLE FL
USNF JAPAN / N57006, FPO AP
USNF KOREA / N62894, APO AP
USNF MARIANAS / N57043, FPO AP
VCAPCD / VENTURA CA
WATER POLLUTION PLANT / MUKHAR, SAN JOSE CA
WR-ALC/TIEAC / (GIBBS), ROBINS AFB GA