Development of Environmentally Compliant Cleaners
For Replacement of P-D-680 Solvent

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ABSTRACT

Federal Specification P-D-680 solvents have historically been used for general cleaning to remove oil and grease from aircraft and engine components and from ground support equipment. The San Joaquin Valley Air Pollution Control District imposed restrictions limiting the use of solvents with Volatile Organic Compound (VOC) content to 50 g/L or less for immersion cleaning processes. To meet the new regulation requirements, multiple efforts were initiated to identify alternative replacements for P-D-680. One approach focused on aqueous-based replacements for cleaners to be used in parts washers and steam cleaners. Another approach focused on non-aqueous based replacements, such as exempt solvents and recycled P-D-680 solvent.

The Parts Washer Cleaners and Cabinet Spray Specification, MIL-C-29602, was revised to improve the quality and effectiveness of products qualified to the specification and to address deficiencies that hinder use of aqueous parts washers as alternatives to P-D-680 solvent.
Steam cleaning equipment has been used by avionics cleaning facilities in accordance with NAVAIR 16-1-540. The testing indicated that the corrosion inhibitor and detergent additives did not meet the corrosion limits of SAE AMS-C-22542 (Cleaning Compound, High Pressure Cleaner).

P-D-680 solvent was recycled using *System One* equipment at NADEP Cherry Point, which reduced waste disposal. The results of testing indicated that the recycled cleaner is as effective as the fresh solvent control.

Commercially available solvent cleaners were evaluated for cleaning capability. The data indicated that none of the tested products meet the new regulation requirements. An effort is in progress to develop a new cleaner to meet the new regulations.

Keywords: Solvents, Cleaners, Recycling P-D-680, Steam Cleaner, Parts Washer

INTRODUCTION

P-D-680 solvent, commonly called Stoddard Solvent or mineral spirits, contains petroleum fractions which are complex mixtures of mostly aliphatic hydrocarbons, but which may contain some aromatics and olefinics. Cold solvent cleaning of aircraft components is performed at organizational, intermediate and depot level and usually takes the form of either spray sinks or batch loaded dip tanks. Historically, the primary solvent used for these applications has been P-D-680 Type II, which has a VOC content of more than 750 grams per liter (g/L). Alternative processes are immersion cleaning with cold or hot water-based products, heated high-pressure spray washers using water-based products, and exempt solvent cleaning. However, water-based processes are often ineffective on heavy soils and can result in flash rusting of steel components.

The San Joaquin Valley Unified Air Pollution Control District (APCD) Rule 4662 (1), limits VOC content of immersion cleaning solvents to 50 g/L or requires airtight cleaning systems. This ruling impacts multiple naval aviation cleaning operations.

Military specification MIL-C-29602 (2) establishes the requirements for materials used in parts washers and spray cabinets to clean aircraft components. The current specification contains several deficiencies relative to test protocols for corrosion, hydrogen embrittlement (HE), cleaning efficiency, and hard water stability. Additionally, the HE testing did not incorporate Ion Vapor Deposited Aluminum (IVD AL), which is an alternate coating to cadmium (Cd) plating for high strength steel aircraft components. Proposed revision MIL-PRF-29602A will address the cited deficiencies and will incorporate an oil separation test and universal solution maintenance instructions.

Steam cleaning equipment has been used by avionics cleaning facilities in accordance with NAVAIR 16-1-540 (3). However, the application of this equipment to general cleaning of aircraft alloys needed to be studied in more detail, including corrosion testing on a range of alloys at the use temperatures involved.

Steam cleaning models are tabletop steam generators (either intermittent or continuous, depending on the model) connected to a hand-held nozzle. When directed at a component, the steam jet can displace most soils. The hot part then dries quickly leaving the soil deposited on absorbent materials underneath the part. A detergent was added to help suspend soils and minimize redeposition. A corrosion inhibitor was added for subsequent rinsing of surfaces that must be free of any detergent residue.

NADEP Cherry Point evaluated *System One*, a cleaning unit that incorporates a solvent distillation unit, in its hydraulic transmission shops. The objective of testing recycled P-D-680 was to monitor the level of the chemical constituents of the recycled solvent and to test for its effectiveness and compatibility.

EXPERIMENTS AND RESULTS

A. Parts Washers Specification Revision (MIL-C-29602)

The currently qualified products were diluted to the manufacturer's recommended concentration and tested in accordance with the proposed revision. Testing included total immersion corrosion, hydrogen embrittlement, cleaning efficiency, hard water stability, and oil separation. Universal solution maintenance instructions based on an acid-base titration protocol were developed to facilitate maintenance of the solutions, regardless of the source of the qualified product.

I. Total Immersion Corrosion Test

Total immersion corrosion testing was performed on all metals and alloys listed in Table I. Bare corrosion specimens were polished with 240-grit aluminum oxide. Coated and bare specimens were cleaned and exposed as specified in ASTM-F483 (4), except that the cleaning solutions were heated to 160 ±2 °F prior to and during the test. After 24 hours, the panels were removed, cleaned, and weighed in accordance to ASTM-F483. The weight loss of each specimen was calculated, and the specimens were examined for visual evidence of corrosion.

The results of the total immersion corrosion test for the qualified products have shown that all products have met the new requirements. The revised specification states that the cleaning compound shall cause neither visual corrosion nor an average weight change of any specimen greater than that shown in table I.

Table I. Total Immersion Corrosion Limits

Metal	Revised Corrosion Limit mg/cm^2/24 hours
Al 2024 bare	0.04
Al 2024 anod	0.04
Steel 1020	0.04
Cu	0.10
Mg	0.20
Hastalloy X	0.04
SS 410	0.04
Cd plate	0.20
Ti	0.04

II. **Hydrogen embrittlement Test**: Hydrogen embrittlement requirements were changed to include the testing of IVD AL coated steel and to incorporate the use of the automated Rising Step Load (RSL) test equipment.

The hydrogen embrittlement test was performed in accordance with ASTM-F519 (5), using type 1a (notched round bar) AISI 4340 steel specimens coated with Cd plating or IVD AL. The test was conducted using Fracture Diagnostics RSL tensile frame. The protocol consisted of applying a load equivalent to 45 percent of the notch fracture strength (NFS) for 24 hours, after which the loading was stepped at a rate of 5 percent of the NFS each hour until failure.

Cadmium plated specimens were prepared in accordance with ASTM F519, treatment B, without the supplemental conversion coating. The specimens were baked in accordance with ASTM-F519.

The hydrogen embrittlement test results on Cd plated steel specimens demonstrated that all qualified products met the specification requirements and passed the test with 90% or higher fracture strength failure.

Two types of IVD AL specimens were used in the study. The first series was prepared in accordance with MIL-DTL-83488D (6), Class 1, Type I, except as follows. Specimens were not grit blasted prior to vapor deposition; specimens were not burnished following deposition; and no conversion coating was applied. The second series was prepared in accordance with MIL-DTL-83488D Class 2, Type II. The specimens were grit blasted prior to deposition, but not burnished following deposition.

Each specimen was masked so that only plated surfaces were exposed to fresh cleaning solution at 160^{o}F for 30 minutes. Four specimens for each coating were individually exposed, immediately dried, and then immediately tested for embrittlement.

The data indicate that all qualified products failed the test on the IVD AL Class 1, Type I plated specimens. The revised specification states that failure is indicated if a specimen fractures at less than 85 percent of the notch fracture strength for the Rising Step Load method (RSL).

The hydrogen embrittlement test on IVD AL Class2, Type II, has not been completed due to the inconsistency of specimens' characteristics. The results and the conclusion of the test will be reported upon completion of the study.

III. **Cleaning Efficiency Test:** The cleaning efficiency test was revised to use more reproducible soils and to make use of more suitable coupons and rinsing methods.

Each cleaning compound was prepared with synthetic hard water (Appendix A). Two soils (Alox 2028 and MIL-G-21164 molybdenum disulfide grease, Appendix B) were used to measure the cleaning efficiency. Three coupons of each soil were prepared for each product evaluated. The test coupons were manufactured from aluminum, 0.25 by 1.0 by 4.0 inches with a 0.0625 inch deep rectangular depression 0.75 by 2.75 inches, located 0.375 inches from one end. Prior to a soil application, the coupons were cleaned with acetone, dried, baked at 221 $\pm$5 °F for 5 minutes, cooled, and weighed to the nearest 0.1 milligram (mg).

The test coupons were loaded (using a clean acid brush) by brushing the bottom of the depression with a test soil to give a uniform film. The Alox 2028 panels were conditioned at 221 ^{o}F for one hour, air-cooled to room temperature and weighed. The MIL-G-21164 panels were weighed without conditioning.

Five hundred milliliters (500 mls) of the cleaning solution and a magnetic stirring bar (0.375 by 2 inches) were placed in a 600-ml beaker and heated at 160 $\pm$5 °F using a stirrer/hot plate. The stirring speed was adjusted to 500 revolutions per minute (rpm). Once the temperature was stabilized, three coupons of the same soil were clamped to the inside wall of the beaker so that the soiled depression was fully immersed. After a 10-

minute exposure, the soiled coupons were rinsed as follows. The beaker containing Alox 2028 coupons was drained and immediately placed under flowing cold tap water for one minute without impinging on the soiled areas. The MIL-G-21164 soiled coupons were removed from the beaker and immediately rinsed under a 4-liter/minute water stream from a laboratory faucet with a serrated tip; test coupons were held 10-12 inches from the faucet tip at 45^{o} to the stream flow.

The coupons were dried for 5 minutes at 221 $\pm$ 5 ^{o}F, cooled and weighed. The cleaning efficiency result for each of the two soils was the average of three test coupons. Cleaning efficiency (CE) was calculated as follows:

$$\textbf{CE (\%)} = (W_2 - W_3) / (W_2 - W_1) \times 100$$

Where: W1 = initial mass of test coupon
W2 = mass of coupon after soil loading
W3 = mass of coupon after cleaning, rinsing and drying

The results of the cleaning efficiency test demonstrated that all qualified products have successfully met the requirements. The revised specification states that cleaning compounds shall remove at least 95% of Alox soil and 75% of molybdenum disulfide grease.

IV. Hard Water Stability Test

Two hundred mls of the cleaner solution were prepared by mixing concentrated cleaner solution with synthetic hard water according to the manufacturer's recommended concentration and placed in a 250-ml polymethylpentene (PMP) container. The container was shaken vigorously for 15 seconds, heated in an oven at 160 °F for two hours, and allowed to stand undisturbed for 16 hours at room temperature. The filtrate solution was tested for corrosivity on SAE-AMS-A-250/4 aluminum test panels as specified in the total immersion corrosion test.

The results of the hard water stability test demonstrated that all products have met the specification requirements. The revised specification requires that the cleaning compound shall not cause any corrosion of SAE-AMS-A-250/4 aluminum in excess of that allowed in Table I.

V. Oil separation Test

Ten mls of hydraulic fluid (MIL-PRF-83282) were added to 90 mls of diluted cleaner solution in a 100-ml graduated cylinder. The cylinder was heated in an oven at 160 ºF for one hour. The cylinder was removed from the oven, shaken vigorously for 10 seconds, and allowed to stand at room temperature for one hour. The volume of the top oil layer was measured and recorded.

The oil separation test results demonstrated that all qualified products have met the specification requirements. The specification requirement states that the oil layer shall be no less than 9 and no more than 13 milliliters.

VI. Universal Solution Maintenance Kit

A solution test kit was developed to aid in the maintenance of the parts washer cleaning solution by replenishment with the concentrated cleaning compound. The kit consists of graduated cylinders, plastic flasks, and dropper bottles of phenolphthalein indicator and 1.0 N sulfuric acid solution. A chart for each product can be established by titrating a series of freshly diluted cleaner solutions (ranging either side of the manufacturer's recommended dilution) with drops of sulfuric acid solution and phenolphthalein as an indicator. Using the chart and a sample's titration result, the concentration of the sample (indicated concentration) can be determined. To calculate the makeup volume of cleaner to add to the tank, the indicated concentration is subtracted from the desired concentration (manufacturer's recommended dilution). The result is then multiplied by the volume of the tank.

(Desired concentration – indicated concentration) oz/gal X (Tank Volume) gal = oz Concentrate to add

If the total of all makeup additions is more than the amount of cleaner initially charged to the tank, the tank should be dumped, cleaned and recharged with fresh cleaner and water.

B. Steam Cleaner System

To assess cleaning effectiveness, both the detergent and the corrosion inhibitor solutions were first tested for cleaning against distilled water in a 295-psi system. In this test, panels soiled with MIL-G-21164 molybdenum disulfide grease were cleaned for 2 minutes at a one-inch standoff distance. To assess corrosivity, both the detergent and the inhibitor solutions were subjected to the corrosion tests contained in SAE AMS-C-22542 (7) with the required alloys and with additional engine alloys. Both solutions were further tested using the full range of alloys in a 24-hour immersion test at 190°F per ASTM F483 and in a sandwich corrosion test per ASTM F1110 (8).

I. Cleaning Efficiency Test: To assess cleaning effectiveness, both the detergent and inhibitor solutions were first tested for cleaning against distilled water in a 295-psi steam cleaner system. In this test, panels were soiled with MIL-G-21164 molybdenum disulfide grease and cleaned for 2 minutes at a one-inch standoff distance. Aluminum panels were cleaned, dried and weighed (W1) before soiling with grease soil. The soiled panels were dried in an oven at 105 °C for one hour, air-cooled to room temperature, and reweighed (W2). The panels were cleaned by the steam cleaner system technique using distilled water, detergent and inhibitor additives. The panels were dried in an oven at 105 °C for one hour, air-cooled at room temperature, and weighed (W3). The cleaning efficiency (CE) was calculated as follows:

$$\%CE = (W2-W3)/(W2-W1) \times 100$$

Cleaning efficiency test results on MIL-G-21164 grease demonstrated that neither the detergent nor the inhibitor additive enhanced the cleaning effectiveness of the steam cleaner unit.

II. Corrosivity: To assess corrosivity, both detergent and inhibitor solutions were subjected to the corrosion test contained in SAE AMS-C-22542 (steam cleaning compound) with the required alloys and with additional engine alloys. In this test, the cleaned panels were partially immersed in 6% cleaner solution and heated at 205 °F for one hour. The panels were removed, cleaned with distilled water, rinsed with absolute alcohol and examined for evidence of attack, oxidation, or discoloration.

Corrosivity test results in accordance with SAE AMS-C-22542 demonstrated staining on the bare aluminum, 410 stainless steel, and copper panels in both detergent and inhibitor additive solutions. Corrosion spots were detected on 1020 steel panels in the vapor phase of both additive solutions.

III. Total Immersion Corrosion Test: The detergent, inhibitor solutions and distilled water were further tested using the full range of alloys in a 24-hour immersion test at 190°F per ASTM F483.

The total immersion corrosion test results for the detergent, the inhibitor and distilled water demonstrated corrosion on 2024 bare aluminum, 2024 anodized aluminum, and 7075 clad aluminum panels in all solutions (detergent, inhibitor, and distilled water). In addition, corrosion was detected on 1020 steel panels in distilled water.

IV. Sandwich Corrosion Test: A sandwich corrosion test was performed on the detergent and inhibitor additives in distilled water per ASTM F1110.

The results of the sandwich corrosion test for the detergent and inhibitor solutions produced a slight stain in the inhibitor solution for 7075 anodized aluminum panels.

In the search for a potential corrosion inhibitor for these conditions, a corrosion inhibitor was identified and tested for corrosion resistance. The inhibitor was diluted at 0.1%, 3.0%, and 7.0% in distilled water and tested for corrosion resistance by the total immersion corrosion test method per ASTM F483 and the sandwich corrosion test per ASTM F1110.

The corrosion test results for the selected inhibitor have shown that only the diluted solution at 0.1 % exhibited corrosion resistance; the other two dilutions exhibited corrosion on 1020 steel, 2024 anodized aluminum, and magnesium panels.

C. Evaluation of Recycled P-D-680 Solvent

Samples for used, fresh and recycled P-D-680 solvents were tested for effectiveness and compatibility. The effectiveness and compatibility of the three solvents were determined by testing for cleaning efficiency, corrosivity, acidity, nonvolatile contents, flash point, and GC/MS chemical analysis.

I. Cleaning efficiency test: The cleaning efficiency test was performed on all samples by immersing and removing the soiled panels in the solvent at a rate of 20 cycles per minute. Panels were soiled with MIL-G-21164 molybdenum disulfide grease with 10**%** Raven 1040 carbon black (Appendix B). The data indicated that there is no significant difference between the used and the recycled solvents compared to the control fresh solvent.

II. Nonvolatile content: The nonvolatile contents in all solvents were measured according to the ASTM-D1353 (9). The data indicated that the fresh and the recycled solvents had no residue and the used solvent showed only 0.04% residue.

III. Acidity Test: The acidity test was performed on all solvents according to the ASTM-D-847 (10). The data indicated that the used solvent shows a slight change in the acidity compared to the fresh and recycled solvents.

IV. Corrosion Test: The total immersion corrosion test was performed on all samples according to the ASTM-F-483. The test was performed only on magnesium (Mg) metal panels. The data indicated that the weight change in all samples was less than the MIL-PRF-680 (11) requirements limit (0.07 mg/cm2/24hrs).

V. Flash point: The Pensky-Martens apparatus was used to measure the flash point of the three solvents according to the ASTM-D-56 (12). The flash points of the three solvents met the MIL-PRF-680 specification limit of 140F for Type II.

VI. GC/MS Chemical Analysis: Gas Chromatography/Mass Spectrometer (GC/MS) technique was used to monitor the level of volatile and semi-volatile contents among the three solvents (used, fresh, and recycled). GC/MS analysis showed that the used and recycled solvents contain additional hydrocarbon derivatives compared to the control solvent.

CONCLUSIONS

Parts Washer Specification

Parts washer cleaners are known to be effective, environmentally friendly, low cost alternatives, and will help reduce dependence on petroleum solvents. Parts washer cleaning has been successful for cleaning many aircraft parts but is not appropriate for all components, such as wheel bearings where trapped water can cause a serious corrosion problem. Disposal of the hazardous waste generated from the parts washer is an additional concern of using the system.

A draft specification revision (MIL-PRF-29602A) has been prepared and is awaiting confirmation of the embrittlement characteristics of the qualified products. The changes that have been proposed are described below.

- The hydrogen embrittlement test was revised to include ion vapor deposited aluminum (IVD AL) plated steel specimens and to allow the use of the more rapid rising step load (RSL) testing using automated equipment.
- The corrosion test was revised to include total immersion corrosion test to replace stock loss method.
- An oil separation test was added to ensure effective oil separation from the solution tank.
- A solution maintenance kit was introduced to maintain the cleaning solutions by replenishment with the concentrated cleaning compound.
- The current QPL will be updated according to the proposed revised specification.

Steam Cleaner System

The testing revealed that the detergent and inhibitor solutions did not meet the corrosion limits of SAE AMS-C-22542. Subsequent testing per ASTM F483 showed both detergent and inhibitor to be corrosive to aluminum but not to steel or other alloys. In this test, distilled water was also corrosive to aluminum and steel, as was expected. The inhibitor solution exhibited a slight stain in the sandwich corrosion test but this result would not be considered to have failed.

The use of Monacor 4000 is recommended as an inhibitor for distilled water. Excellent immersion and sandwich corrosion test results were achieved at a concentration of 0.10 weight percent.

Evaluation of Recycled P-D-680 Solvent

The results of the performance testing and chemical analysis of used, fresh, and recycled solvents indicated that the recycled solvent is as effective as the control solvent.

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REFERENCES

(1) Clean Air Act, San Joaquin Valley APCD Rule 4662, May 1999.
(2) MIL-C-29602, Cleaning compounds for parts washers and spray cabinets, 01 August 1999.
(3) NAVAIR 16-1-540, NAVAIR Manual for Avionic Corrosion Control
(4) ASTM F 483-98, Standard test method for total immersion corrosion test for aircraft maintenance chemicals, 10 October 1998.
(5) ASTM F519, Standard test method for mechanical hydrogen embrittlement evaluation of plating processes and service environments, 10 May 1997.
(6) MIL-DTL-83488D, Coating, Aluminum, High purity, 1 April, 1999.

(7) AMS-C-22542, Cleaning compound, high pressure cleaner, 5 May, 2002.
(8) ASTM F1110, Standard test method for sandwich corrosion test, 8 October, 2002.
(9) ASTM-D1353, Standard test method for nonvolatile matter in volatile solvents for use in paint, varnish, lacquer, and related products, 10 December 2002.
(10) ASTM-D847, Standard test method for acidity of Benzene, Toluene, Xylene, solvent Naphtha, and similar Industrial Aromatic Hydrocarbons, 10 January 1996.
(11) MIL-PRF-680, Performance Specification for degreasing solvent, 13 December 1999.
(12) ASTM-D56, Standard test method for flash point by Tag Closed Cup Tester, 6 October, 2002.

Appendix. A: Preparation of synthetic hard water

Synthetic hard water solution was prepared by dissolving 0.20 ±0.005 gram of analytical reagent grade calcium acetate, Ca $(C_2H_3O_2)_2 \bullet H_2O$, and 0.14 ±0.005 gram of analytical reagent grade magnesium sulfate, $MgSO_2 \bullet 7H_2O$, in one liter of boiled distilled water.

Appendix. B: Preparation of grease soil

Molybdenum disulfide grease soil was prepared by blending 50 grams of Raven 1040 carbon black (Columbia Carbon Company or equal) and 500 grams of MIL-G-21164 grease with a mechanical grease worker for 15 minutes. Alox 2028 (available from Alox Corporation, Niagara Falls, NY) was used as received.