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NAVAL AIR WARFARE CENTER AIRCRAFT DIVISION
PATUXENT RIVER, MARYLAND



ENGINEERING DATA REPORT

REPORT NO: NAWCADPAX/EDR-2005/13

MILDEW REMOVER FOR AIRCRAFT APPLICATIONS

by

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**El Sayed Arafat
Craig Matzdorf
Stephen Spadafora
Paul Roser
David Gauntt, Sabre Systems, Inc.
James Whitfield, NADEP Cherry Point**

1 June 2005

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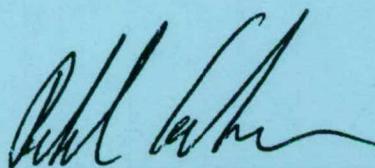
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13. SUPPLEMENTARY NOTES							
14. ABSTRACT A patented uninhibited mildew remover was developed at the Naval Air Depot, Cherry Point, North Carolina. This mildew remover passed most of the critical performance tests found in the Navy and Army's cleaner specifications MIL-PRF-885570D and ADS-61A-PRF-2002, except for the titanium total immersion corrosion and sandwich corrosion tests. A new corrosion-inhibiting version of this remover was developed which passed all of the critical test requirements. Cleaning efficiency test results were satisfactory for both the uninhibited and new corrosion-inhibiting formulations.							
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INTRODUCTION

Maintenance procedures to remove mildew growth and mildew staining from aircraft surfaces have historically required many man-hours. In addition, previously approved materials were often inadequate. The use of unauthorized cleaning solutions, such as household chlorine bleach (sodium hypochlorite), can induce corrosion damage to critical metallic surfaces. In addition, chlorine bleach causes environmental concerns. Results of fungal degradation studies (references 1 and 2) of polymeric materials used in Navy aircraft showed that the approved military cleaning procedure, based on isopropyl alcohol was ineffective. Environmental Scanning Electron Microscopy micrographs indicated that surface cleaning only removes spores from the ends of the mildew hyphae, but fragments of the hyphae remained and regrow as soon as conditions are favorable. So, even though interior surfaces appear clean, they are still contaminated with fungi. In addition, fungi appear to be able to use certain operational fluids, such as hydraulic fluid (MIL-PRF-83282) and corrosion preventive compounds as nutrients.

One study of fungal contamination on the interior surface of H-46 and H-53 rotary-wing aircraft at Naval Air Depot (NADEP) Cherry Point, North Carolina, isolated eight genera of microfungi (reference 3). The study also indicated that some corrosion on unprotected aluminum surface can be attributed to bacterial and fungal growth. One of the isolated fungi (*Aureobasidium*) from the H-53 is known to cause superficial discoloration on latex paint (reference 4). Another report indicated that one microfungus (*Cladosporium*) similar to the one found on H-53, is capable of corroding 2024 aluminum alloy panels by producing acidic metabolic products (reference 5). An additional study by Salvarezza and Videla has shown that fungi are known to thrive at the oil-water interface to produce acids that can corrode metals (reference 6).

To mitigate these issues, an uninhibited mildew remover was developed by NADEP Cherry Point personnel. This patented mildew remover formula is an aqueous solution consisting of sodium perborate (an oxidizing agent) and a nonionic detergent (reference 7). The ingredients must be mixed immediately prior to use, as the solution becomes ineffective after 24 hr. The product is applied with clean cheesecloth or a soft bristle brush to mildew growth and allowed to remain for 5 to 15 min. The surface is then cleaned thoroughly with fresh water to rinse away residue.

APPROACH

The following list of test methods from cleaner specifications MIL-PRF-85570D (reference 8) and ADS-61A-PRF-2002 (reference 9) were considered critical for product performance. The uninhibited mildew remover was evaluated to determine the effects on aircraft materials using these tests. A field test, not found in the specifications, was also performed. A brief description of each test method can be found in the "Procedures" section.

1. Sandwich Corrosion Test (ASTM F 1110-02)
2. Total Immersion Corrosion (ASTM F 483-02) and Table 1 of reference 8
3. Hydrogen Embrittlement as per ASTM F 519-97 and Table 1 of reference 8

4. Cadmium Corrosion Test (ASTM F 1111-98)
5. Effect on Painted Surfaces (ASTM F 502-02)
6. Effect on Plastics (ASTM F 484-02) reference 8, Table 1 and paragraph 4.5
7. Effect on Polyimide Wire as per reference 8, paragraph 4.5.11
8. pH Value (ASTM E 70-02)
9. Stress Corrosion on Titanium (ASTM F 945-01)
10. Sealant Adhesions, Paint Adhesion, and Adhesive Bonding (ADS-61-PRF- 2002) paragraphs 4.5.13, 4.5.17, and 4.5.18
11. Field Test

The uninhibited mildew remover was then tested in diluted concentrations to simulate rinse residues. Testing was initiated after aging the mixed product for up to 96 hr to determine the product activity period.

After completing the initial tests, the uninhibited mildew remover was found to cause corrosion in the sandwich corrosion test and the total immersion corrosion test on titanium alloy (Ti 6Al 4V). As a result, this mildew remover was modified to incorporate various corrosion inhibitors. Laboratory tests results indicated that the inhibitors significantly reduce corrosion while maintaining product performance.

Corrosion-inhibited formulations were screened using critical performance tests found in cleaner specifications (references 8 and 9). The formulations were adjusted as necessary to meet these requirements. The optimized corrosion-inhibited formulation was then retested to the critical performance tests from the two specifications above and then field tested to validate mildew remover performance.

In addition to testing the full strength mildew remover, dilutions of 50%, 25%, and 10% were tested for sandwich corrosion to simulate the consequences of incomplete rinsing. Aged samples of the mixed product were evaluated in the sandwich corrosion test to determine the window of activity of the mixed product.

Sandwich corrosion testing was performed using diluted chlorine bleach solution, Reagent Water (ASTM D 1193), Synthetic Tap Water (MIL-C-85570, paragraph 4.6.6.2), a 1.5% sodium perborate solution, and a series of perborate and surfactant solutions with various corrosion inhibitors in several concentrations. Deionized/distilled water was used as the control.

PROCEDURES

- 1. Sandwich Corrosion Test:** The sandwich corrosion test was performed in accordance with ASTM F 1110. The test was performed on four aluminum alloy coupons: anodized aluminum 2024-T3 (SAE-AMS-QQ-A-250/4), Alclad 2024 (SAE-AMS-QQ-A-250/5), anodized aluminum 7075-T6 (SAE-AMS-QQ-A-250/12), and Alclad 7075 (SAE-AMS-QQ-A-250/13). Aluminum coupons were sandwiched together with filter paper saturated with mildew remover between the coupons. The sandwiched coupons were cycled between warm dry air (100°F) and warm humid air (relative humidity 100%) for 7 days.
- 2. Total Immersion Corrosion Test:** The total immersion corrosion test was performed in accordance with ASTM F 483. The selected metal alloys were immersed in the mildew remover solution for 7 days at 100°F. The weight change of each specimen was calculated, and the specimen was examined for visual evidence of corrosion. Army representatives decided that the metal series for the total immersion corrosion test listed in reference 8 would be sufficient for their intended applications instead of Table II found in reference 9.
- 3. Hydrogen Embrittlement Test:** The hydrogen embrittlement test was performed in accordance with ASTM F 519, using type 1a (notched round bar) AISI 4340 steel specimens coated with low embrittling cadmium plating. The test was conducted using Fracture Diagnostics RSL tensile frame and consisted of applying a load equivalent to 45% of the notch fracture strength for 150 hr.
- 4. Cadmium Corrosion Test:** The cadmium corrosion test was performed in accordance with ASTM F 1111. The specimens were immersed in the mildew remover solution for 24 hr at 95°F. The maximum allowable weight change is 0.20 mg/cm²/day in accordance with MIL-PRF-85570D specification requirements.
- 5. Effect on Painted Surfaces:** The test was performed in accordance with ASTM F 502. The mildew removers were applied onto a painted panel and placed in an oven for 30 min at 100°F. The panels were rinsed with distilled water and allowed to air dry for 24 hr. The panels were examined for streaking, discoloration, blistering, and change in hardness of the finish.
- 6. Effect on Plastics:** The test was performed in accordance with ASTM F 484. The mildew remover solutions were evaluated for stress crazing of stretched acrylic plastics (type 1A) for 8 hr and showed no sign of crazing.
- 7. Effect on Polyimide Wire Insulation:** The test was performed in accordance with reference 8 requirements (paragraph 4.5.11). Polyimide wires were placed in the mildew remover solutions for 14 days at room temperature (72°F) before examining for cracks and leakage.
- 8. pH Measurement:** The pH value was determined in accordance with ASTM E 70.

9. **Stress Corrosion Test:** The stress corrosion of titanium metal was performed in accordance with ASTM F 945, Method A.

10. **Sealant Adhesion and Adhesive Bonding Tests:** The sealant adhesion test was performed in accordance with ASTM D 3167.

11. **Field Test:** The cleaning efficiency was evaluated at NADEP Cherry Point on helicopter components exhibiting mildew. Mildew removal was assessed visually using pertinent criteria determined by Cherry Point personnel. Tests were performed using both the uninhibited and corrosion-inhibited formulations to evaluate mildew removal effectiveness.

RESULTS

1. **Sandwich Corrosion Test:** The uninhibited mildew remover formulation proved to be corrosive when tested according to the ASTM F 110-02 sandwich corrosion method. The sandwich corrosion test was used to screen corrosion-inhibited formulations to address this problem and successful formulations were then tested to the other critical tests of the two specifications.

The sandwich corrosion test results are shown in tables 1 and 2 and figure 1. The original mildew remover showed surface corrosion and pitting corrosion on all coupons except anodized 7075-T6 (250/12). The distilled/deionized water did not show any corrosion on aluminum coupons except for some staining which appeared on the anodized 2024-T3 (250/4) coupons. The test was performed twice with Whatman filter paper #4 and once with Whatman Glass Microfiber. Overall performance is detailed as follows:

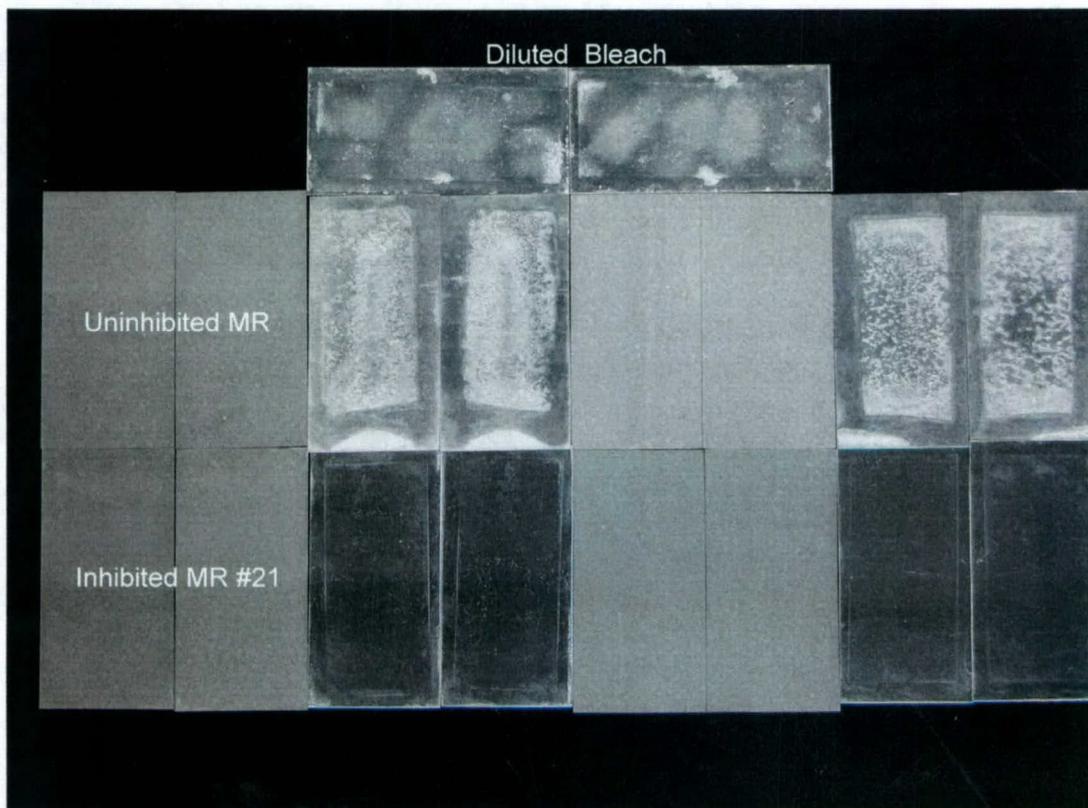
- Uninhibited mildew remover failed the sandwich corrosion test, in accordance with the requirements found in references 8 and 9.
 - a. Dilutions of the original mildew remover (50%, 25%, and 10% concentration) proved corrosive beyond the specification limits and pitting was observed.
 - b. Samples made using 24-hr old solution (uninhibited formula) were found to fail sandwich corrosion testing.
 - c. Samples made using 96-hr old solution (uninhibited formula) were found to be comparable to the deionized/distilled water control.
 - d. Samples tested at the prescribed temperature of 100°F showed more pitting than those tested at 72°F.
 - e. Samples made using synthetic tap water in place of reagent water failed with ratings of #4 for corrosion pitting.
- Corrosion-inhibited mildew remover formulation passed the sandwich corrosion test in accordance with the requirements of references 8 and 9.

Table 1: Evaluation of Uninhibited and Corrosion-Inhibited Mildew Remover in accordance with MIL-PRF-85570D (Cleaning Compounds, Aircraft Exterior)

Requirements	Specification Limits	Uninhibited Mildew Remover	Inhibited Mildew Remover
pH (ASTM E 70)	7-10	10.31- 10.48	9.98
Sandwich Corrosion Test (ASTM F 1110)	Not more than distilled water	Failed Al 250/5 Al 250/13 Al 250/4	Pass
Total Immersion Corrosion Test (ASTM F 483)	No visible corrosion mg/cm ² /day Al 7075 (250/12) 0.04 Steel 1020 (AMS 5046) 0.04 Ti 6Al 4V (AMS 9046) 0.04 Mg AZ31B (AMS4377) 0.20	mg/cm ² /day < 0.01 < 0.01 < 0.01purple color 0.02	mg/cm ² /day < 0.01 < 0.01 < 0.01 0.02
Cadmium Corrosion (ASTM F 1111)	mg/cm ² /day 0.20	< 0.01	< 0.01
Hydrogen Embrittlement (ASTM F 519 1a)	No failure to 150 hr when loaded at 45%	Pass	Pass
Effect on Plastics (ASTM F 484)	Acrylic Type A No Crazing- 8 hr Acrylic Type C No Crazing- 8 hr Polycarbonate MIL-P-83310 – 2 hr	Pass Pass Pass	Pass Pass Pass
Effect on Painted Surfaces (ASTM F 502)	No Softening > 1 Pencil Hardness	Pass	Pass
Effect on Polyimide Wire	No Dielectric Leakage No Physical Effect > Distilled Water	Pass	Pass

Table 2: Evaluation of Uninhibited and Corrosion-Inhibited Mildew Remover in accordance with ADS-61A-PRF-2002 (Army Aircraft Cleaner)

Requirements	Limits	Uninhibited Mildew Remover	Inhibited Mildew Remover
Sandwich Corrosion Test (ASTM F 1110)	Not more than distilled water	Failed Al 250/5 Al 250/13 Al 250/4	Pass
Total Immersion Corrosion Test (ASTM F-483)	No visible corrosion mg/cm ² /168 hr Al 7075 (250/12) 0.49 Steel 1020 (AMS 5046) 0.49 Ti 6Al 4V (AMS 9046) 0.35 Mg AZ31B (AMS 4377) 0.70	Pass Except Titanium (Per table 1)	Pass
Stress Corrosion	No cracks in Table II metals	Pass	Pass
Hydrogen Embrittlement (ASTM F 519 1a)	No failure to 150 hr when loaded at 45%	Pass	Pass
Effect on Plastics (ASTM F 484)	Acrylic Type A No Craziing- 8 hr Acrylic Type C No Craziing- 8 hr Polycarbonate MIL-P-83310- 2 hr	Pass Pass Pass	Pass Pass Pass
Effect on Painted Surfaces (ASTM F 502)	No Softening > 1 Pencil Hardness	Pass	Pass
Effect on Polyimide Wire	No Dielectric Leakage No Physical Effect > Distilled Water	Pass	Pass
Sealant Adhesion	100% Cohesive Failure 3.5kN/m	Primer Conforms Topcoat Failed Control and Cleaner	Primer Conforms Topcoat Failed Control and Cleaner
Adhesive Bonding	Meet or Exceed Control (Methyl Ethyl Ketone)	Primer Conforms Topcoat Failed Control and Cleaner	Primer Conforms Topcoat Failed Control and Cleaner



Al 250/4	Al 250/5	Al 250/12	Al 250/13
Anodized 2024-T3	Clad 2024-T3	Anodized 7075-T6	Clad 7075-T6

Figure 1: Sandwich Corrosion Test for Uninhibited and Corrosion-Inhibited Mildew Remover (ASTM F 1110)

2. **Total Immersion Corrosion Test:** The weight changes for the selected metal alloys are listed in table 1 using the uninhibited formulation. The selected metal alloys met the test requirements except for the Ti 6Al 4V alloy, which showed a dark purple color, as shown in figure 2. This dark purple color is an indication of the oxidation of vanadium in the alloy to vanadium oxide.

The corrosion-inhibited mildew remover formula did not yield the dark purple color on titanium and met the requirements of the total immersion corrosion test.



Figure 2: Total Immersion Corrosion Test for Titanium Alloy (Ti 6Al 4V) in Uninhibited/Corrosion-Inhibited Mildew Remover Solutions (ASTM F 483)

3. **Hydrogen Embrittlement Test:** Hydrogen embrittlement results were satisfactory on both the uninhibited and corrosion-inhibited formulations.
4. **Cadmium Corrosion Test:** Cadmium corrosion results were satisfactory on the uninhibited and corrosion-inhibited formulations tested.
5. **Effect on Painted Surfaces:** Effect on painted surfaces was satisfactory on both the uninhibited and corrosion-inhibited formulations.
6. **Effect on Plastics:** The effect on plastics was satisfactory for both uninhibited and corrosion-inhibited formulations.
7. **Effect on Polyimide Wire Insulation:** No negative effects were observed on polyimide wire insulation when subjected to either the uninhibited or corrosion-inhibited formulations.

8. **pH Measurements:** The pH results of 10.31 to 10.48 on the uninhibited mildew remover exceeded the reference 8 limit of 10.0. The corrosion-inhibited material passed this requirement with a pH of 9.98.

9. **Stress Corrosion Test:** Stress corrosion results on Ti 6Al 4V alloy were satisfactory on both the uninhibited and the corrosion-inhibited formulations.

10. **Sealant Adhesion and Adhesive Bonding Tests:** No obvious discrepancies were noted between the control (Methyl Ethyl Ketone) and both formulations tested. Clear conclusions were not possible due to low performance in both cases regarding the control and the products tested.

11. **Field Test:** The test results showed that the addition of corrosion inhibitor to the uninhibited mildew remover formula had no significant effect on the cleaning efficiency. The cleaning efficiency was satisfactory for both the uninhibited and corrosion-inhibited formulations.

DISCUSSION

Numerous corrosion inhibitors were evaluated alone or in combination with the uninhibited mildew formulation. The final formulations used in this investigation were:

1. Uninhibited Mildew Remover Formulation:
Sodium Perborate Monohydrate, 1.5%
Triton X-100 surfactant, 0.39% (or equivalent)
Reagent Water (ASTM D 1193)
2. Corrosion-Inhibited Mildew Remover Formulation # 21:
Sodium Perborate Monohydrate, 1.5%
Triton X-100 surfactant, 0.39% (or equivalent)
Reagent Water (ASTM D 1193)
Proprietary Additives, Formula #21
3. Corrosion-Inhibited (Alternate Formulation):
Sodium Perborate Monohydrate, 1.5%
Triton X-100 surfactant, 0.39% (or equivalent)
Reagent Water (ASTM D 1193)
Proprietary Additives, Formula #22

Dissolving the formulation in warm water (up to 120°F) facilitates rapid and complete solubility of ingredients, which can then be cooled to room temperature without precipitation.

The performance results of these inhibited formulas in the sandwich corrosion test have shown that some inhibitors worked for some substrates, but only two formulations passed both the requirements found in references 8 and 9. Sodium dichromate had excellent technical performance but is unacceptable due to environmental, safety, and health issues.

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CONCLUSIONS

1. The findings of this study indicate that aircraft metal corrosivity, as determined by sandwich corrosion testing, is a concern with the uninhibited sodium perborate-based mildew remover.
2. The mildew remover can be inhibited to achieve conformance with cleaner specification corrosion requirements. This inhibition can be accomplished without loss of cleaning effectiveness.
3. In fleet applications, the short exposure time and short period of activity (<96 hr) of mildew remover, both in terms of actual treatment and in frequency of applications, would tend to minimize any potential threat to the airframes involved. Inhibition provides additional insurance against potential damage from the oxidative effect on aircraft metals. These factors, taken in consideration with normal precautions (maintenance procedures and in situ protective systems including metal pretreatments and paint systems), minimize the damage potential of this product in the period between Standard Depot Level Maintenance procedures.

RECOMMENDATIONS

Based on the successful laboratory and field testing of the corrosion-inhibited mildew remover, this material (Formula #21) should be used to mitigate mildew removal issues on Navy and Marine Corps assets.

This composition is ready to be implemented by NAVAIR for removing mildew from aircraft during normal cleaning procedures. Implementation should be accompanied by issuing an authorization letter and Interim Rapid Action Change to NAVAIR 01-1A-509, Aircraft Weapons Systems Cleaning and Corrosion Control Manual. In addition, a commercial source or supplier must be developed in order to make the materials readily available for NAVAIR and other DOD users.

FUTURE WORK

Extended testing of the alternate corrosion-inhibiting formula, as a backup, should be performed to provide a second source material. This formulation also passed both the Army and Navy specifications for sandwich metal couplings; however, no other testing has been performed to date.

It is recommended that a patent disclosure be filed for the corrosion-inhibited mildew remover compositions and for their use in removing mildew on aircraft and other applications.

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8. Military Specification MIL-PRF-85570D, Cleaning Compound, Aircraft Exterior.
9. ADS-61A-PRF-2002, Army Aircraft Cleaner.

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IN REPLY REFER TO

August 5, 2008

From: Head, Industrial and Operational Chemicals Branch, Naval Air Warfare Center
Aircraft Division, Building 2188, 48066 Shaw Road Unit 5, Patuxent River, MD
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To: DTIC, Attn: Mr. Lawrence Ramserran, Suite 0944, 8725 John J. Kingman Road,
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Subj: Change of Distribution Statement

Mr. Ramserran:

This letter is in reference to the distribution statement for the Technical Report
NAWCADPAX/EDR-2005/13 entitled "Mildew Remover for Aircraft Applications".
Please replace the current distribution statement with "Distribution is Unlimited". If you
have any questions or concerns, please contact me. Thank you for your time and
assistance.

Sincerely,

A handwritten signature in black ink, reading "Kevin J. Kovaleski", is positioned above the typed name.

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