Electroactive Materials

as Smart Corrosion-Inhibiting Coatings for the Replacement of Hexavalent Chromium

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Most military coatings on aluminum alloys utilize hexavalent chromium (Cr(VI)) conversion coating (CCC), a Cr(VI) primer followed by a topcoat (non-Cr(VI)). Cr(VI) is a well-known corrosion inhibitor. However, Cr(VI) is a carcinogen and regulations regarding its use and disposal are under constant scrutiny. The Department of Defense (DoD) must comply with current and future regulations regarding the use and disposal of Cr(VI) from the Environmental Protection Agency (EPA) and the U.S. Occupational Safety and Health Administration (OSHA). Currently, there is no non-Cr(VI) pretreatment/primer system which can provide corrosion protection as well as a Cr(VI) military coating. A new "smart coating" system is needed that can provide "on-demand" corrosion protection and adhesion without the environmental liabilities of Cr(VI). The Naval Air Warfare Center Weapons Division (NAWCWD) in cooperation with its military partner Wright Patterson Air Force Base (WPAFB) and research partner the University of Dayton Research Institute (UDRI) have developed and tested a non-Cr(VI) pretreatment for use with a qualified non-Cr(VI) primer and standard topcoat for a total non-Cr(VI) paint system. This pretreatment system utilizes an electroactive polymer (EAP), poly(2,5-bis-(N-methyl-N-hexylamino) phenylene vinylene) (BAM-PPV), to provide protection on aluminum alloys in accelerated weathering tests. BAM-PPV has completed preliminary field testing by WPAFB on non-critical military hardware as the pretreatment coating.

INTRODUCTION

The aerospace industry and the DoD currently use chromate conversion coatings (CCC) and hexavalent chromium (CrVI)-based primers to inhibit corrosion on aluminum alloys.[1-3] In addition to their corrosion-inhibiting properties, Cr(VI)-based coatings provide excellent paint adhesion to the metal surface and between the primer and topcoat. These coatings are applied via spraying onto both aluminum and steel substrates. Several recent studies have shown that unreacted Cr(VI) in both the pretreatment and primer provide corrosion protection via a "self-healing" mechanism, where the Cr(VI) migrates to the damage site and provides corrosion protection.[4-6] However, Cr(VI) is a known carcinogen and is highly regulated by the EPA and OSHA.[7,8]

Any viable alternative to Cr(VI) coatings must meet or exceed the adhesion and corrosion-inhibiting performance of current Cr(VI) military coatings. Ideally, these alternative coatings must be able to passivate the metal surface.[9] Over the past several decades, EAPs have received considerable interest as corrosion-inhibiting coatings.[10-13] Most of these studies have focused on polyaniline (PANI) applied

This paper was presented at the 2010 American Coatings Conference, April 14–16, 2010, in Charlotte, NC.

as a primer onto steel substrates. More recent studies have focused on PANI and derivatives of PANI as replacements for Cr(VI) pretreatment applications. BAM-PPV coated onto aluminum alloys has also shown corrosion inhibition in simulated seawater and exposure to neutral salt fog spray.[14-16] There have been numerous reports that have described the versatility of EAPs on various substrates for corrosion prevention/inhibition of carbon steel, stainless steel, iron, titanium, copper, and aluminum alloys. Early work with respect to iron and stainless steel suggested that protection of scratches was provided through the observed polarization of the bare surface to a passive state. However, more recent results suggest that protection of iron and stainless steel in such imperfections can also stem from the inhibitor properties of the dopant and the ability of that inhibitor to migrate to the area suffering corrosion. The dopant migration mechanism is also believed to govern corrosion protection by some EAPs with respect to aluminum alloys via a "smart release" of inhibitor to the exposed metal.[17-19] Thus, this type of corrosion prevention/inhibition would deliver a similar mechanism to that of Cr(VI) without the environmental liabilities.

EXPERIMENTAL

Reagents: BAM-PPV was synthesized according to literature[15] and 4-chlorobenzotrifluoride (Oxsol-100) was used as received (Aldrich).

Methods: BAM-PPV solutions were prepared from Oxsol-100 solvent and applied via spray using high volume/low pressure (HVLP) spray equipment onto aluminum alloy (AA) 2024-T3.

Neutral salt fog spray exposure testing was performed to evaluate the ability of the coating systems to withstand a 5 wt% sodium chloride solution, pH-adjusted to a range of 6.5–7.2. This test was performed on full military coating systems using AA 2024-T3 substrates. UDRI/CTIO Laboratory Procedure CLG-LP-019, *Salt Fog Corrosion*, in accordance with ASTM B 117, *Standard Practice for Operating Salt Spray (Fog) Apparatus*, was used for guidance to run the test.[20] All samples subject to neutral salt spray exposure were photographed before and after the test to document the coating performance. There were three replicates per coating system. BAM-PPV was coated with Cr(VI) epoxy and non-Cr(VI) epoxy primers. CCC was used as the control pretreatment with Cr(VI) epoxy and topcoat. The primers chosen for this study are the Cr(VI) epoxy primer which is qualified to MIL-PRF-23377 Type 1 Class C and the Cr(VI)-free epoxy primer which is qualified to MIL-PRF-23377 Type 1 Class N. The topcoat was the MIL-PRF-85285, Type IV polyurethane topcoat. All coatings were full military coatings and exposed to neutral salt fog chamber for 2000 hr. Field testing of the non-Cr(VI) pretreatment was performed on non-critical military hardware using the Air Force C-5 cargo plane rear hatch door. A fully Cr(VI) coating system was used as control during the neutral salt fog exposure testing and during field testing.

RESULTS AND DISCUSSION

The samples were placed in a neutral salt fog chamber and examined for their corrosion resistance. The BAM-PPV using Oxsol-100 solvent was coated onto AA 2024-T3 substrates. The BAM-PPV-coated coupons were then compared to the performance of the standard CCC with the same primer and topcoat system. BAM-PPV was allowed a one-hour dwell prior to application of the material using HVLP spray gun. The BAM-PPV was set-to-touch after 30 min, but samples were not coated with primer until the following work day, giving these materials about 16 hr between pretreatment and primer application. Topcoat was applied four hours after primer application. Samples were left to cure at room temperature and ambient relative humidity (approximately 75°F and 50% RH) for 14 days prior to testing. Neutral salt fog spray testing demonstrated that the BAM-PPV coating systems performed adequately, meeting the 2000-hr neutral salt fog exposure requirement for alternatives to Cr(VI) military coatings (see *Table* 1). The BAM-PPV pretreatment systems demonstrated minor corrosion in the scribe, minor build-up after 2000 hr. The standard CCC showed typical corrosion build-up in the scribe with the MIL-PRF-85285

Table 1—ASTM B117 Neutral Salt Fog Spray Results (2000 hr)

Coating System	AA 2024-T3 Data	Appearance
Pretreatment + Primer + Topcoat	**Rating**	**Corrosion in Scribe**
CCC + chromated epoxy + polyurethane topcoat	Control (Pass)	Staining no control build-up
CCC + non-chromated epoxy + polyurethane topcoat	Pass	Minor corrosion build-up
BAM-PPV + chromated epoxy + polyurethane topcoat	Pass	Staining no corrosion build-up
BAM-PPV + non-chromated epoxy + polyurethane topcoat	Pass	Minor corrosion build-up

Figure 1—Air Force C-5 cargo plane.

Figure 2—C-5 cargo plane rear hatch door.

Type IV polyurethane topcoat, a phenomena that is well-documented in WPAFB lab testing of this system. In comparison, the BAM-PPV slightly underperformed as compared to the CCC but both demonstrated minor corrosion in the scribe. Adhesion testing of these systems was performed using the 1-mm grid for primer-only systems and the 2-mm grid on the topcoated systems. Data consistently showed that for all pretreatments, when primer was applied, the adhesion rating was 5 (no loss of adhesion), whereas when topcoat was applied, the adhesion rating was 4 (minor loss of adhesion). The data suggests that once primer is applied, the BAM-PPV does not demonstrate a debit on the adhesion to the substrate (AA 2024-T3).

After successful completion of the laboratory testing by WPAFB, a preliminary field test was demonstrated on non-critical military hardware (*Figures* 1 and 2) using the BAM-PPV as a pretreatment coating. The rear hatch door on a C-5 cargo plane was selected due to the convenience of the C-5 maintenance team at WPAFB and the non-critical status of the door coating. The large door allowed a good fit with testing the BAM-PPV exposure to various environments and its robustness in the

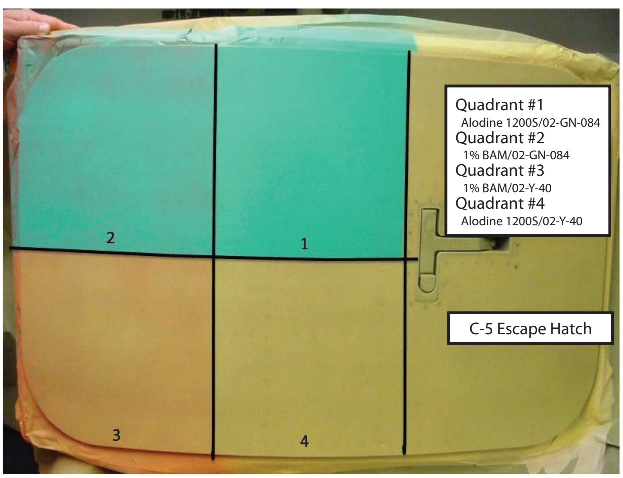

Figure 3—Air Force C-5 rear hatch door coated with BAM-PV and controls.

Table 2—BAM-PPV and Cr(VI) Control Coatings on C-5 Cargo Plane Rear Hatch Door

Test Coating System	Pretreatment	Primer	Topcoat
Quadrant 1	Chromate conversion coating	Non-Cr(VI) epoxy primer (MIL-PRF-23377 Type 1 Class N)	Polyurethane topcoat (MIL-PRF-85285) Type IV
Quadrant 2	BAM-PPV	Non-Cr(VI) epoxy primer (MIL-PRF-23377 Type 1 Class N)	Polyurethane topcoat (MIL-PRF-85285) Type IV
Quadrant 3	BAM-PPV	Cr(VI) epoxy primer (MIL-PRF-23377) Type 1 Class C2	Polyurethane topcoat (MIL-PRF-85285) Type IV
Quadrant 4	Chromate conversion coating	Cr(VI) epoxy primer (MIL-PRF-23377) Type 1 Class C2	Polyurethane topcoat (MIL-PRF-85285) Type IV

Table 3—Dry Film Thickness after 296.7 Flight Hours

Panel ID	Coating System	Dry Film Thickness (mils) Initial	Dry Film Thickness (mils) 41.4 flight hr	Dry Film Thickness (mils) 296.7 flight hr
Quadrant 1	Chromate conversion coating + MIL-PRF-23377 Type 1 Class N + MIL-PRF-85285 Type IV	5.46	5.54	5.67
Quadrant 2	BAM-PPV + MIL-PRF-23377 Type 1 Class N + MIL-PRF-85285 Type IV	5.14	5.22	5.05
Quadrant 3	BAM-PPV + Chromate conversion coating + MIL-PRF-23377 Type 1 Class C2 + MIL-PRF-85285 Type IV	5.12	5.73	4.98
Quadrant 4	Chromate conversion coating + MIL-PRF-23377 Type 1 Class C2 + MIL-PRF-85285 Type IV	4.92	5.85	5.75

field. The BAM-PPV pretreatment coating was applied onto the C-5 cargo plane's rear hatch door with a non-Cr(VI) primer and topcoat (*Table* 2). A Cr(VI) full military coating [CCC + MIL-PRF-23377,C + MIL-PRF-85285] was used as the control for this field demonstration. The rear hatch door was divided into four quadrants and coated with the controls and BAM-PPV (*Figure* 3). A 1 wt% solution of BAM-PPV dissolved in Oxsol-100 was used to coat the C-5 aircraft door. HVLP was used as the delivery system to apply the BAM-PPV solution onto the C-5 cargo door using multiple passes to get an approximate thickness of 2 µm. This coating thickness was selected due to the good corrosion performance seen in the neutral salt fog studies of BAM-PPV. The coated door was flown for 12 months and examined periodically (visual inspection) every three months. The aircraft was flown under ambient conditions in the Midwest and Northeast regions of the United States with one overseas flight to Europe, giving a total of 296.7 flight hours. The conditions included down-time at military depots for routine maintenance and inspection. The C-5 cargo plane was exposed to normal weather conditions found in these regions of the United States which included rain, sleet, snow, northern coastal moisture, and sun. The door with the BAM-PPV pretreatments and controls survived the field demonstration intact without loss of adhesion or corrosion. *Tables* 3 and 4 provide the details from this WPAFB field demonstration. In *Table* 3, no significant change in dry film thickness was observed from 41.4 to 296.7 flight hours. The small changes that were observed were due to dirt build-up on the coatings. The overall assessment of this BAM-PPV coating via visual inspection (see *Table* 4) over a 12-month period showed no corrosion damage to the coating or delamination.

Table 4—Assessment of BAM-PPV Field Test on C-5 Cargo Plane Rear Hatch Door

Visual Inspection Test	Performance at 12 Months
Degree of Chalking of Exterior Paints	No Damage
Degree of Cracking of Exterior Paints	No Damage
Degree of Erosion of Exterior Paints	No Damage
Degree of Blistering of Paints	No Damage
Degree of Flaking of Exterior Paints	No Damage
Evaluation of Painted Specimens Subjected to Corrosive Environments	No Damage

CONCLUSIONS

The neutral salt fog and adhesion testing on BAM-PPV as an alternative pretreatment coating to CCC showed acceptable performance to warrant field testing studies by the Air Force. After the best performing military coating (non-Cr(VI)) with BAM-PPV was evaluated for its performance, field tests on non-critical components were initiated. These field test studies continued for one year with visual inspection every three months. After 296.7 hours' flight time, both domestic and international, the BAM-PPV coatings performed as well as the Cr(VI) controls. BAM-PPV, therefore, can be further developed for commercial scale up as an alternative to CCC pretreatments on AA 2024-T3 alloy.

ACKNOWLEDGMENT

Financial support by the Environmental Security Technology Certification Program, Program Directors Dr. Jeffrey Marqusee and Mr. Bruce Sartwell is gratefully acknowledged.

References

1. Anderson, N. and Zarras, P., "Electroactive Polymers as Green Alternatives to Hexavalent Chrome," *Currents*, p 60, Spring 2005.
2. Korinek, K.A., "Chromate Conversion Coatings," In *ASM Handbook Volume 13: Corrosion,* Korb, L.J. and Olson, D.L. (Eds.), ASM International, USA, p 389, 1998.
3. Xia, L.; Akiyama, E., Frankel, G., and McCreery, R., *J. Electrochem. Soc*., 147 (7), 2556 (2000).
4. Illevbare, G.O., Scully, J.R., Yuan, J., Kelly, R.G., *Corrosion*, 56 (3), 227 (2000).
5. Kendig, M., Jeanjaquet, S., Addison, R., and Waldrop, J., *Surface and Coatings Technol*., 140, 58 (2001).
6. Kendig, M.W., Davenport, A.J., and Isaacs, H.S., *Corrosion Science*, 33 (1), 41 (1993).
7. Blasiak, J. and Kowalik, *J. Mutat. Res*., 469, 135 (2000).
8. National Emissions Standards for Chromium Emissions from Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks, Environmental Protection Agency. *Federal Register*, RIN 2060-AC14, January 25, 1995.
9. Zarras, P. and Stenger-Smith, J.D. "An Introduction to Corrosion Protection Using Electroactive Polymers," In *Electroactive Polymers for Corrosion Control*, Zarras, P., Stenger-Smith, J.D., and Wei, Y. (Eds.), ACS Symposium Series 843, American Chemical Society, Washington DC, Chapter 1, pp 2-17, 2003.
10. Wessling, B. and Posdorfer, J., *J. Electrochemica. Acta.,* 44, 2139 (1999).
11. Thompson, K.G., Bryan, C.J., Benicewicz, B.C., and Wrobleski, D., *Los Alamos National Laboratory Report,* LA-UR-92-360, 1991.
12. Wrobleski, D.A., Benicewicz, B.C., Thompson, K.G., and Bryan, B.J., *ACS Polym. Prepr*., 35 (1), 265, 1994.
13. McAndrew, T.P.; *TRIP*, 5(1), 7 (1997).
14. Kuş, E., Grunlan, M., Weber, W.P., Anderson, N., Zarras, P., and Mansfeld, F., "Evaluation of the Protective Properties of Novel Chromate-free Polymer Coatings Using Electrochemical Impedance Spectroscopy (EIS)," In *New Developments in Coatings Technology*, Zarras, P., Wood, T., Richey, B., and Benicewicz, B.C. (Eds.), ACS Symposium Book Series 962, American Chemical Society, Washington, DC, Chapter 19, pp 297-311, 2007.
15. Zarras, P., He, J., Tallman, D.E., Anderson, N., Guenthner, A.J., Prokopuk, N., Webber, C., Stenger-Smith, J.D., Pentony, J.M., Hawkins, S., and Baldwin, L., "Electroactive Polymer Coatings as Replacements for Chromate Conversion Coatings," In *Smart Coatings,* Provder, T. and Baghadachi, J. (Eds.), ACS Symposium Book Series 957, American Chemical Society, Washington, DC, Chapter 10, pp 135-151, 2007.
16. Zarras, P., Stenger-Smith, J.D., Anderson, N., Webber, C., and Prokopuk, N., "Investigation of Electroactive Polymers (EAPs) and Other Pretreatments as Replacements for Chromate Conversion Coatings: A Neutral Salt Fog and Electrochemical Impedance Spectroscopy (EIS) Study," In *New Developments for Coatings Technology*, Zarras, P., Wood, T., Richey, B., and Benicewicz, B.C. (Eds.), ACS Symposium Book Series 962, American Chemical Society, Washington, DC, Chapter 4, pp 40-53, 2007.
17. Cook, A., Gabriel, A., and Laylock, N., *J. Electrochem. Soc*., 151, B529, (2004).
18. Kinlen, P.J., Graham, C.R., and Ding, Y., *ACS Polymer Preprints*, 45, 146 (2004).
19. Kendig, M. and Hon, M., *Corrosion*, 60, 1024 (2004).
20. ASTM B117 Standard Practice for Operating Salt Spray (Fog) Apparatus, *Annual Book of ASTM Standards,* ASTM International, West Conshohocken, PA, Vol. 03.02, p 1, 2007.

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