

ENVIRONMENTALLY SAFE NON-CHROMIUM CORROSION COATINGS FOR AEROSPACE APPLICATIONS

Patrick J. Kinlen, George Koustis and Mike Kiely
Crosslink, 950 Bolger Court, Fenton, Missouri 63026
636-349-0050

Abstract

Currently, the most effective corrosion inhibitor systems used for coating aluminum alloys used in the aerospace industry are primers and pretreatments containing hexavalent chromium compounds. These primers, while being extremely effective, are under significant pressure to be eliminated because they contain hexavalent chromium, a known carcinogen. Federal, state and local agencies have issued regulations that limit or prohibit the use of chromate materials. Developing effective alternatives to chromate in these coatings would benefit worker's safety, lower regulatory compliance codes and reduce the environmental impact of maintaining aircraft by eliminating toxic Cr (VI) from the waste stream. Our goal is to provide a commercially viable, environmentally and worker-friendly coating, replacing paint primers presently containing hexavalent chromium for protection of aluminum alloys in aerospace applications. We have developed novel materials based on electroactive organic polymers (EAPs) that release corrosion inhibitors (molecules or ions) in response to local galvanic corrosion processes. Released inhibitor molecules then diffuse to the corroding site and inhibit the anodic and/or cathodic reaction. In this sense, these coatings are "smart", in that they release the inhibitor only when corrosion occurs.

Introduction

Among all the non-toxic inhibitors studied, 2,5-dimercapto-1,3,4-thiadiazole (DMcT; Figure 1) has been shown by Crosslink to be an excellent candidate for the replacement of Cr (VI) system because of its ability to stop cathodic activity (oxygen reduction) on the surface of aluminum.

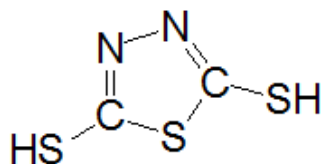


Figure 1. Structure of DMcT.

DMcT and its derivatives have been effectively and safely utilized as antioxidants and anticorrosion additives in lubricating oils and fluids as well as additives for metal passivation.¹ DMcT, either in monomeric or polymeric form, alone or in combination with other electroactive polymers, provides the basis for a new, non-Cr (VI) primer. Coating systems that include EAPs alone or in combination with specific corrosion inhibitor compounds show promise as the basis for effective coatings which eliminate the need for Cr (VI). The ultimate primer will be a product that enables protection of all aluminum alloys used in aerospace applications.

Coating systems developed from EAPs are potentially effective alternatives to hexavalent chromium for corrosion-inhibiting and protective coating primer systems that meet the requirements of environmental friendliness and human health compatibility. A comprehensive review chapter has recently been published describing use of EAPs for corrosion protection.² 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. But, more recent results suggest that protection of iron and stainless steel in such imperfections can also stem from the inhibitor properties of the dopant (a term interchangeable with inhibitor in this document) and the ability of that inhibitor to migrate to the area suffering corrosion.^{3,4} Debate surrounds which view is correct. The dopant migration mechanism is believed to govern corrosion protection by EAPs with respect to aluminum alloys.⁵ Our past results have demonstrated the galvanically stimulated release of corrosion inhibitors.^{6,7} We have shown that the switching of the EAP redox state is triggered by local electrochemical reactions occurring on the surface of a metal during the corrosion process. The dopant ion is released upon reduction of the EAP. Such reduction can occur during galvanic ion exchange between the oxidizing metal surface and the adjacent EAP material. Our initial focus is on protection of aluminum alloys such as 2024-T3 and 7075-T6 which are of primary interest in the aerospace industry.

Experimental

Synthesis: Polyaniline Doped with DMcT

PANI-DMcT was synthesized by oxidative polymerization using ammonium persulfate as described previously.⁵

Formulations and Testing

Solventbased 2K epoxy formulations have been the focus of most of this work. Chromate controls have included commercial as well as in-house formulations which used the same basic mill base as the experimental, non-chromate controls. Primer coatings have been tested on 2024-T3 and 7075-T6 alloys that have been conversion coated. 3" x 6" panels were coated by spray application with HVLP guns. Coatings were allowed to cure for two weeks prior to testing. For ASTM B117 salt spray testing, scribes were cut using a mechanical engraver, and the backs and edges of the panels were taped with polyester electroplater's tape.

Results

Salt Fog Testing

Figure 2 shows the exposed areas of salt spray tested panels (taped areas were cropped from the picture). These panels are representative of the results obtained when testing PANiDMcT inhibitors in solvent-borne epoxy formulations. Up to 2000 hours, a PANiDMcT epoxy primer is capable of performing on par with the strontium chromate control. The results suggest that the DMcT/PANI combination is a promising substitute for chromate as a primer additive.

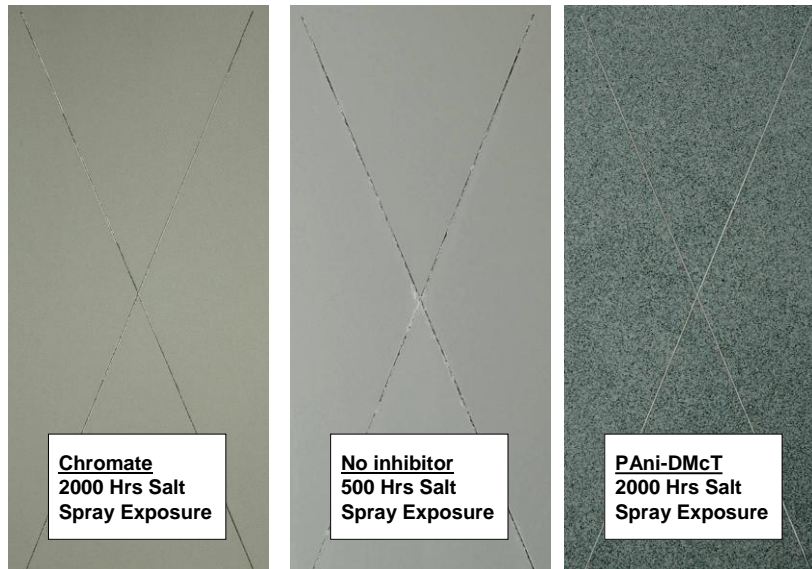


Figure 2. Comparison of Representative 2K PANI-DMcT Epoxy Formulations after ASTM B117 Saltspray Exposure.

Mechanism of Protection

The mechanism shown in Figure 3 depicts a pinhole through a coating on an aluminum alloy (2024) where DMcT is the dopant (D) and the EAP is polyaniline. Oxygen reduction on the cathodic corrosion site initiates corrosion in the adjacent matrix. As Al and Mg leave the surface, copper sponge remains behind. At the same time, DMcT released from the reduced EAP adsorbs onto the copper-rich intermetallic inclusions shutting down the oxygen reduction reaction and the subsequent corrosion.

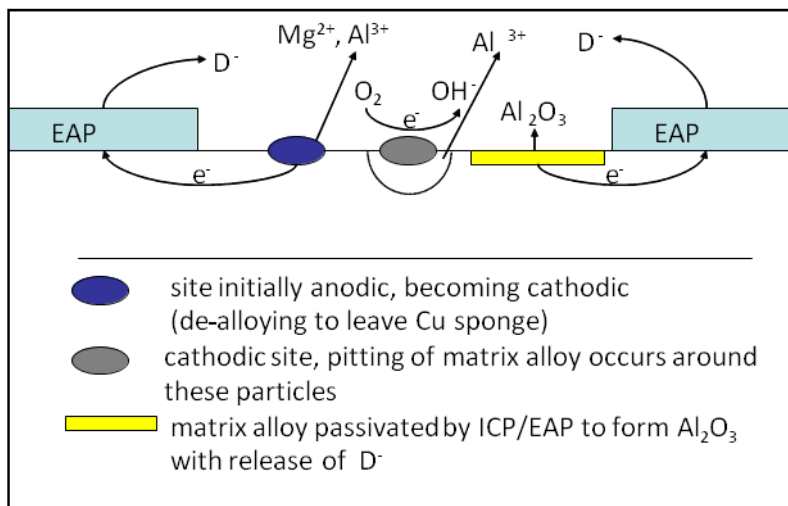


Figure 3. DMcT Reductively Released by Corrosion Processes on AA 2024.

The above description clearly shows that EAPs doped with an appropriate corrosion inhibitor system can be developed to effectively stop corrosion of aluminum alloys. The results

support the concept that these coatings have the ability to provide pinhole and scratch protection. They avoid the environmental and toxicity issues and costs associated with chromates.

Human Health and Environmental Benefits

Due to the susceptibility of aluminum alloys to corrosion, aerospace manufacturing processes incorporate Cr (VI) into the aluminum surface through a conversion coating process (CCP). In addition, Cr (VI) salts are added as inhibitors to subsequently applied paint systems. Worldwide, inhibitors alone amount to 11,000 tons of Cr (VI) pigment/year. Both the CCP and painting processes may expose workers to unacceptable levels of Cr (VI) unless OSHA compliance guidelines are strictly followed.⁸ In addition, toxic wastes are generated which require treatments and disposal at hazardous waste sites. Replacing Cr (VI) with the “smart” EAP inhibitor system would eliminate these risks, as well as exposure and environmental hazards associated with production of Cr (VI) pigments and salts from chromate ore, paint production using Cr (VI) pigments, maintenance and re-work of coated parts, and ultimate disposal at the end of the product life-cycle.

Conclusions

Coating systems based on EAPs have the potential to be an effective alternative to hexavalent chromium for corrosion-inhibiting and protective coating systems that meet the requirements of environmental friendliness and human health compatibility. These EAPs have been demonstrated in the laboratory to “intelligently” detect initiation of corrosion and then provide a mechanism to shut down such corrosion quickly before significant metal degradation has occurred. The intelligence arises from designing the EAPs to contain cathodic or anodic inhibitors that can respond quickly to corrosion initiation. These chemical characteristics indicate that incorporation of this EAP system into paint systems such as epoxy and polyurethane could eliminate the need for chromium-based primer coatings and their associated environmental and safety risks. Such a development can significantly reduce the direct and indirect human and environmental health costs of corrosion protection of aluminum alloys within both the military and commercial sectors.

Acknowledgments

Crosslink is grateful for financial and technical support from Boeing/Rockwell Scientific, NAVAIR (Patuxent River, Maryland) contract number N00421-05-C-0042 and SERDP/ESTCP contract number N68936-09-C-0013.

References

1. Wei D, Cao L, and Wang L, “An investigation into the antiwear, antioxidation, and anticorrosion behaviour of some derivatives of 2,5-dimercapto -1,3,4-thiadiazole”, *Lubrication Science* **1995**, 7(4), 365-77 as well as United States Patents 4,382,869, 4,661,273, 4,678, 592, 4,584,114, and 4,704,426.
2. Kinlen P J and Kendig M, "Smart" Corrosion Protective Coatings, In: *Smart Materials*, Schwartz M, Ed, CRC Press, Boca Raton, FL **2009**, pp 23/1-23/16.
3. Cook, A, Gabriel, A, Laycock, N, "On the Mechanism of Corrosion Protection of Mild Steel with Polyaniline." *J. Electrochem. Soc.* **2004**, 151 B529-B535.
4. Kinlen, P J, Ding, Y, Silverman, D, "Corrosion Protection of Mild Steel Using Sulfonic and Phosphonic Acid Doped Polyaniline" *Corrosion* **2002**, 58 490-497.
5. Kinlen P J, Graham C R, and Ding Y, “Corrosion protection of aluminum alloys by controlled release of inhibitors from inherently conductive polymer coatings”, *Polymer Preprints* **2004**, 45, 146.

6. Kendig M, and Hon M, "Environmentally triggered release of oxygen- reduction inhibitors from inherently conducting polymers" *Corrosion* **2004**, 60, 1024.
7. Kendig M and Kinlen P, "Demonstration of Galvanically Stimulated Release of a Corrosion Inhibitor", *Journal of the Electrochemical Society* **2007**, 154(4), C195-C201.
8. Small Entity Compliance Guide for the Hexavalent Chromium Standards, OSHA 3320-10N 2006.