Current Progress in the Development of a Complete Cr-Free System

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Abstract

There are currently no chromium-free replacements for traditional hexavalent chromium pretreatments that perform as well as chrome unpainted and that are commercially available for the corrosion protection of 2000 series aluminum alloys used in aerospace. Two approaches have been used to provide the military with a chrome (VI) alternative. One approach is the use of a chromium (III) based pretreatment, however, the process still contains chromium, and toxic forms of cobalt are sometimes used and present in waste streams. The other option is a system approach where the corrosion resistance of the conversion coatings are evaluated not as stand alone coatings, but rather as a complete paint coating system. One of several issues arising from this approach is that most of the commercially viable pretreatments are not conversion coatings, but rather adhesion promoters that do not provide inherent corrosion protection if the outer paint coatings are breached. Based on the corrosion protection mechanisms learned from rare earth-based primers, a pretreatment chemistry is being developed that is designed to provide inherent corrosion protection for Al 2024-T3 and have improved interaction with the chrome-free primers to provide a higher state of the art chrome-free pretreatment and system. No chromium is present in the proposed pretreatment or primers used in the coating system. Salt spray performance data of the conversion coating by itself and in conjunction with a chrome-free primer will be illustrated. The proposed mechanism of the new conversion coatings is reviewed using SEM characterization of the conversion coating's surface morphology and interpretation of salt spray corrosion resistance. An update of the current chrome-free primer technology and continued implementation is also provided.

A. Introduction

A completely chromium-free primer has been qualified to several specifications including the U.S. Navy's 23377 and 85582 Class N specifications, as well as Lockheed's LMA-MR003 and Boeing's HMS 15-1100. Further, the solvent-borne and water-reducible versions of the chromium-free primer have been implemented on several weapon platforms including the F-15, F-22, JSF, Apache', and Boeing's new KC-767 fuel tankers for the Italian Air Force. Despite the primer's ability to perform as well as chromated primers, the mechanism by which it protects is not full known. There is elemental evidence that does proof the ability of the chrome-free inhibitor to migrate to the scribed/defected areas in a paint scheme, which suggests that the inhibitor is an active film former.

During the qualification and implementation of the chrome-free primer, the identification of a short-term electrochemical test that would predict the performance of the primer coatings in neutral salt spray was of interest.
The following experiment was performed. The goal of the experiment was to identify a short-term electrochemical test, such as EIS or DC polarization that would correlate to the longer ASTM B-117 neutral salt spray exposure evaluation. The idea would be that a short-term test that correlated well to the longer exposure of salt spray would save time and resources. For reasons indicated below, the predictive tests failed to predict the superior performance of these chrome-free primers.

B. Experimental Design

I. Neutral Salt Spray Evaluation

Several chrome-free primers were evaluated in neutral salt spray. A water-reducible primer and a high-solids primer were used as chromated controls. Panels were run in neutral salt spray for 3,000 hours.

II. Examples of the two most common electrochemical techniques are as follows:

II.A Electrochemical Impedance Spectroscopy (EIS):

Step 1: Immerse painted panel in D.I. water for 24 hours.
Step 2: Remove painted panel from D.I. water.
Step 3: To remaining solution (that should contain the corrosion inhibitor that leached out of the primed panel and into the water phase) add 3.5 wt% NaCl
Step 4: Measure the impedance of a deoxidized 2024-T3 Al panel in the "inhibitor-containing" solution.

II.B DC-Polarization

Step 1: Dissolve 3g corrosion inhibitor in 240 cc's beaker.
Step 2: Once dissolved, run DC polarization using a deoxidized Al 2024-T3 panel as the working electrode.
Step 3: Obtain the open circuit potential and determine the pitting potential.

The problem encountered with each electrochemical test is that they are at one point dependent upon the inhibitor having appreciable water solubility, just like chromates do. For EIS the problem is that no appreciable inhibitor dissolves or goes into solution during the 24 hour water soak (Step 1). With DC polarization, the problem is the inhibitors are inert and do not appreciably dissolve (Step 1).

C. Results

I. Neutral Salt Spray Evaluation

After 3000 hours of neutral salt spray exposure, chrome-free primer Candidates 2 and 8 performed the same as the chromated control primers 12 and 13 over CrCC Al 2024-T3 bare. The remaining candidates exhibited no blistering after 3,000 hours of exposure, however they exhibited varying degrees of salt formation in the scribed areas. The performance of the Candidate 2 as compared to the chrome control over different pretreatments and Al alloys is shown in Figure 1.

II.A. Electrochemical Evaluation - EIS

After performing EIS per the procedure stated above, it was predicted that none of the chrome-free primers would perform as well as the chrome controls. A summary of these results is illustrated in Figure 2. According to EIS, the ranking for the Cr-free primers would be Candidates 5, 3, 4 with all other candidates performing equally, yet none of the candidates would have performed as well as the chrome controls. Candidates 5, 3, and 4 were all based on the same experimental resin technology.

II.B. Electrochemical Evaluation - DC-Polarization

Since the inhibitor did not appreciably dissolve in Step 1 of the DC-polarization test, the pitting potential was the open-circuit potential. Therefore no inhibitor was present in solution and the DC test was discounted immediately from further evaluations.

D. Electrochemical Testing Conclusion

The prediction obtained using EIS had no correlation to the results obtained using neutral salt spray. Not only was there no correlation between the top three candidates predicted by EIS (5, 3, and 4) and neutral salt spray, but EIS was unable to identify Candidates 2 and 8 as being promising, which performed the same as the chromated controls did. It did predict that the water-borne had more corrosion protection than the high-solids, which may make sense in terms of the porosity of the films for the chromate to dissolve. But again, it was not successful in predicting the excellent performance of these candidates. Since the chrome-free primers have demonstrated performance levels to that of chromated controls in both accelerated testing such as neutral salt spray, filiform, SO2, as well as environmental exposure at Daytona Florida and the flight deck of an active duty aircraft carrier, then the issue is not the performance of the primer, but rather the ability of a short-term test to predict it's performance. Currently, there is no short-term electrochemical test that can successfully predict the performance of these chrome-free primers. This is attributed to the necessity of the short-term tests that are currently being used for evaluating coatings to rely on the inhibitor's inherent solubility constants.

E. Implementation of Chrome-Free Primer

Based on the performance and qualifications of the chrome-free primer, it has been implemented on several weapon platforms. The solvent-borne version of the chrome-free primer has been approved for use on all F-15's on both the OEM level at Boeing-St. Louis as well as the depot and maintenance levels at Robins AFB, where over 200 F-15 have been primed. Nellis AFB has applied the solvent-borne version on an A-10 and F-16. The water-reducible primer is being used extensively, as well. It is the only chrome-free primer that is approved for use on and being applied to interior and exterior OEM parts, such as the Joint Strike Fighter. The primer is being used on the F-22 program as well as the Apache' helicopter program.

The most recent platform to use the chrome-free primer is the KC-767 Fuel Tanker program. Three fuel tankers have had the solvent-borne version of the chrome-free primer applied, followed by the APC topcoat. The aircraft are OEM and have been delivered to the Italian Air Force.

F. Chrome-Free Conversion Coating

A chrome-free conversion coating has also been developed and is beginning to be implemented that is based on rare-earth compounds. The conversion coating has achieved seven days neutral salt spray performance over Al 2024, Al 7075-T6, Clad Al 2024, Al 5052-H32, and Al 6061. Though different from chromates, this chrome-free conversion coating does offer similar advantages. One important advantage that this conversion coating provides over other chrome-free pretreatments is that it provides unpainted corrosion protection over various aluminum substrates using the same conversion coating solution and same application procedures and times. Further, it provides a self-healing characteristic similar to that of chrome, where if conversion coating is scribed and then exposed to neutral salt spray, the conversion coating heals itself and protects the exposed metal area.

G. Implementation of Chrome-free Conversion Coating

There are two conversion coating chemistries that have been developed and are planned to be implemented in 2009. One conversion coating is an immersion process designed to work with CRS, HRS, HDG, EZG, and Al 6061 and Al 5052-H32. This conversion coating is capable of plating a protective layer on the various substrates using the same immersion times. It is operated at room temperature. Over ferrous substrates, a self-healing characteristic has been observed. The testing and qualification of this coating was performed by the automotive manufacturer, the developing company, and a third independent party. This multi-metal conversion coating process is going to be implemented at a major automotive factory in the U.S. The process line will require 4,000 gallons of conversion coating material. The titration and monitoring methods for this new technology have also been established, so that the plating tanks can be maintained for continuous use. There was no known titration or monitoring method in the art. The titration and monitoring method for this new technology is a scientific feet in and of itself. The patent for this technology is pending.

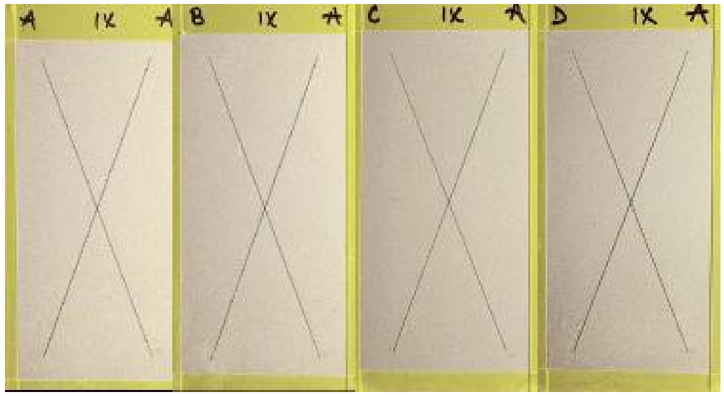
The other conversion coating is a spray-applied process. It has been designed to protect Al 2024, 7075, 6061, clad 2024, and 5052. This spray-applied conversion coating provides inherent corrosion protection unpainted. It will be used on an F-15 at Robins AFB. The primer that will be used in conjunction with this conversion coating will be a chrome-free, high-solids primer. It will be the first completely chrome-free conversion coating and chrome-free primer system that will be used on an entire military aircraft where the conversion coating has achieved seven days unpainted salt spray protection. Further, it will be the first application where the deoxidizer, conversion coating, primer, and topcoat will be provided to the customer from the same vendor. This spray-applied conversion coating is patented technology based on rare-earth compounds.

H. Conclusions

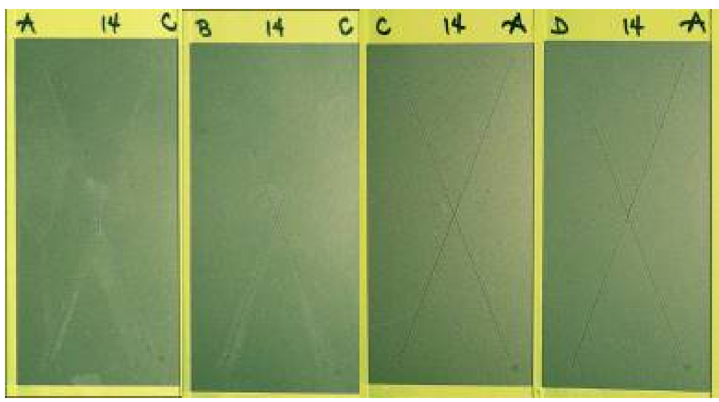
This is the most implemented chrome-free primer that also provides the same corrosion protection as chromates. It is environmentally compliant. It's ability to release an inherently insoluble corrosion inhibitor that migrates to and protects an exposed scribed area has been demonstrated. EIS and other electrochemical techniques validate that the inhibitor release is not detected as a function of water exposure, however, long-term testing such as salt spray, filiform, and SO2 exposure prove the chrome-free primer's ability to protect the underlying metal substrates. The primer's use on several major military platforms has demonstrated its successful implementation.

The chrome-free conversion coating has demonstrated its ability to provide inherent corrosion protection to a metal substrate. Since it provides inherent corrosion protection unpainted, it is more than just an adhesion promoter. Its ability to provide corrosion protection in conjunction with a chrome-free primer illustrates its ability to provide an advanced chrome-free system to military and commercial platforms. The implementation of this conversion coating and primer will issue a new era of corrosion science and technologies.

Candidate 2 (Chrome-Free)



Candidate 12 (MIL-PRF-85582 C2)



CrCC 7075 CrCC 2024 SAA 7075 SAA 2024

Figure 1. Performance of New Generation Non-Chrome Primer Applied Over Various Pretreatments and Alloys Compared to a Chromate Control After 3000 Hours Salt Spray Exposure.

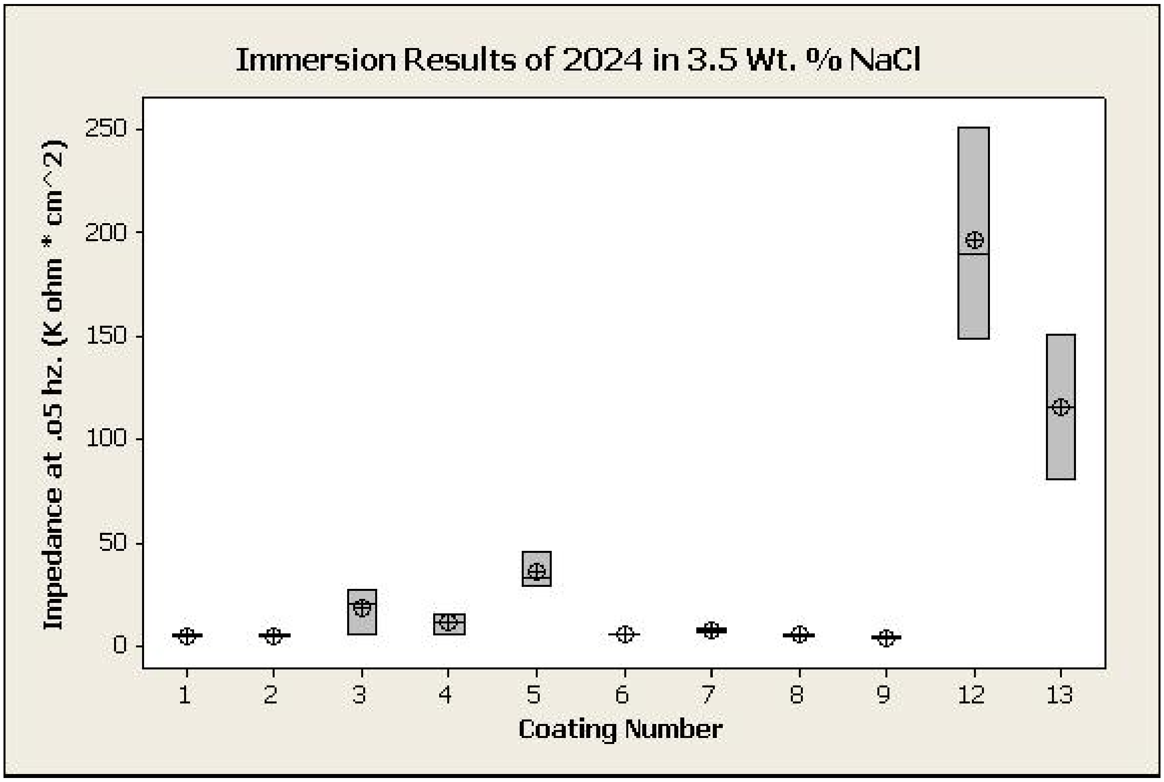


Figure 2. Electrochemical comparison of Several Versions of New Generation Non-Chrome Primers (Coatings 1-9) to Chromate Controls (Coatings 12-13) Using EIS, indicating low inhibitor solubility.