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NON-CHROMATED COATING SYSTEMS FOR CORROSION PROTECTION OF AIRCRAFT ALUMINUM ALLOYS (PREPRINT)

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Non-Chromated Coating Systems For Corrosion Protection Of Aircraft Aluminum Alloys

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ABSTRACT

The Air Force requires the development of an environmentally compliant chromate-free aircraft coating system that meets or exceeds current corrosion protection capabilities. A number of non-chromated pretreatments and primers have been independently developed over the past years. This report compares the corrosion resistance performance of selected fully non-chromate systems to the standard chromate containing coating system. The data identified two non-chromated systems that performed comparably to the standard chromated aircraft coating system.

Key Words: aluminum alloys, corrosion, non-chromate systems

INTRODUCTION

Corrosion protection of aluminum-skinned aircraft and development of improved environmentally benign coating systems for aluminum aerospace alloys are high priority topics. To date, the corrosion inhibition of aluminum alloys has relied extensively on hexavalent-chromium compounds included in both surface pre-treatment and organic primers. However, the toxicity and carcinogenic properties of chromium (VI) has caused federal agencies such as OSHA and EPA to impose severe restrictions on its use. [1] Changing federal regulations dictate the use of fundamentally new coating systems that are capable of meeting the new standards.

A number of non-chromated pretreatments and primers have been developed and tested over the past several years in response to these growing environmental toxicity concerns.

Previous testing of non-chromate systems has focused on either replacement of the chromate conversion coating (CCC) with a non-chrome surface preparation or replacement of the MIL-PRF-23377H chromated epoxy primer with a non-chromated primer. Limited work has been performed on evaluation of non-chrome combinations of both.

The present work compares the performance of select fully non-chromated systems with the current chromated aircraft coating system and establishes a relative ranking of performance between the systems. Several non-chromated surface treatments and primers were studied in combination with an Advanced Performance Coating (APC) grade of MIL-PRF-85285D polyurethane topcoat.

EXPERIMENTAL

A total of 12 fully non-chromated systems, consisting of both experimental and commercially available products, were tested on 3" x 6" AA2024-T3 panels and compared to the performance of the standard chromate system in the following tests: ASTM B 117 Salt Spray [2], ASTM D 2803 Filiform Corrosion Test [3], ASTM D 4541 Pull-Off Strength (PATTI) Test [4], and Electrochemical Impedance Spectroscopy (EIS) testing.

The non-chromate pre-treatments evaluated included: 1. a commercially available surface cleaning and pretreatment (CSP), 2. an experimental Self-assembled Nanophase Particle sol-gel pre-treatment (SNAP), and 3. a commercially available mixed silane/zirconate sol-gel (MSZ). Two non-chrome epoxy primers were evaluated: 1. an experimental epoxy primer (EEP) and 2. a commercial water-borne non-chromated epoxy primer (WEP).. Combinations of five non-chromate systems were tested and compared to the standard chromate system, which includes a chromate conversion coating (CCC) pre-treatment, MIL-PRF-23377H primer, and APC grade MIL-PRF-85285D topcoat. Details on these specific coating systems are provided in Table 1.

The SNAP solution was made from 3-glycidoxypropyl-trimethoxysilane (GPTMS) and tetramethoxysilane (TMOS) in 3:1 ratio. The experimental details and panel cleaning procedures used are described in detail previous work [5]. The SNAP was applied to cleaned aluminum alloy panels by dip-coating at a speed of 0.2 cm s^{-1} to form a film with a thickness of ~ 1 µm.

The surfaces of the panels for application of MSZ, CSP and CCC coating were treated with the surface treatment method used at Warner-Robins ALC [7]. The CCC pre-treatment was applied using the MIL-C-5541E process specification [9] by immersion for a period of 3 to 5 min to generate a coating weight between 40 and 60 mg/ft^2.

MSZ, a water-based sol-gel system, was applied by the manufacturer’s suggested spray method. The material was mixed according to the manufacturer’s instructions [10] and left for a 30-min dwell time. The application was spray-applied to upright coupons for several passes to ensure that the coupon was drenched for not less than 30 sec but not more than 2-min. The thickness of the films, measured by SEM, ranged from 0.6 µm to 0.9 µm.

CSP, a water-based cleaning/pre-treatment material, was applied by the manufacturer’s instructions [11]. The material was applied by the “flood” approach, where it was applied in excess to the de-oxidized surface of aluminum coupons and allowed to dry. A second application was performed by “flooding” the coupon surface but also by “buffing” the surface, while still moist, with a lint-free cloth. A third application was performed, but in this step the material was applied directly to a lint-free cloth and applied to the surface of the coupon.

Panels coated with each of the four types of pre-treatments were air-dried overnight before primers were applied. EEP and WEP primers were applied to all systems using an HVLP spray gun in an environmentally controlled paint booth at 75°F and 50% RH. Primers were mixed according to manufacturer's recommendations [12]. Coated panels were air-dried overnight before the topcoat was applied. The APC grade of MIL-PRF-85285D polyurethane topcoat was mixed and applied using HVLP according to the manufacturer's instructions [13]. All panels were cured for 14 days prior to any testing. The average coating thicknesses for the primers was 30 µm, and 40 µm for the topcoat.

RESULTS AND DISCUSSION

Coated specimens were evaluated for filiform corrosion using the guidelines in MIL-PRF-23377H. A template was used to evaluate the extent of filiform corrosion growth [3]. Figure 1 represents the data for filiform corrosion growth, using the Filiform Rating Scale, in which ratings between 0 and 60 reflect acceptable filiform growth. Samples marked "control" are standards to evaluate the accepting of the test conditions. Several observations were made from comparison of the non-chromated systems to the CCC/MIL-PRF-23377H/APC chromate containing coating system, which had a reading of 40 on the Filiform Rating Scale. The non-chrome systems with similar readings consisted of CSP/WEP/APC, CSP/EEP/APC, and MSZ/EEP/APC. The systems MSZ/WEP/APC, SNAP/WEP/APC, and SNAP/EEP/APC had slightly higher ratings of filiform growth at 45, 51 and 55, respectively. Nevertheless, these values are still considered acceptable according to MIL-PRF-23377H.

Coated samples were scribed and exposed to ASTM B 117 Salt Spray (5% NaCl) for 2,000 hours. The MIL-PRF-23377H specification calls for chromate containing primers to exhibit no corrosion in the scribe after 2,000 hours, and for all systems (chromate and non-chromate) to exhibit no blistering, lifting, or substrate pitting after 2,000 hours of exposure. Most of the primer-only non-chromate systems demonstrated undercutting and blistering. Many of the topcoated chromate free systems also showed undercutting and blistering at the end of the test, but were generally less severe. The non-chromate primers with the MSZ pretreatment and APC topcoat performed best overall (Figure 2), showing similar performance to the chromate control system after 2,000 hrs. It should be noted that the MIL-PRF-23377H requirement for no corrosion in the scribe applies to chromate systems (Class C) only and does not apply to the non-chromate systems (Class N). The non-chromate systems with SNAP or CSP surface treatment did not demonstrate acceptable corrosion protection, showing moderate corrosion in the scribe, some undercutting, and blistering. In general, the presence of topcoat over the primers decreased blistering with the exception of CSP/EEP/APC, which had a few small blisters.

EIS data were used to compare coating systems behavior after 2,000 hours of B 117 Salt Spray. Both scribed and unscribed samples of each system were tested in triplicate. Impedance values of above 1×10^9 Ω cm^2 were indicative of coating systems affording excellent barrier protection. Coatings with modulus values below 1×10^6 Ω cm^2 were considered poor, and modulus values between 1×10^6 and 1×10^9 Ω cm^2 indicated moderate to good barrier properties. EIS results for all unscribed topcoated panels after 2,000 hours of Salt Spray demonstrated high values of impedance modulus |Z| at low frequencies, indicating good to excellent corrosion properties for all tested systems, with values on the order of $10^8 – 10^9$ Ω cm^2 (Figure 3). |Z| values for all scribed non-chromate systems were on the order of $1\text{x}10^5$ Ω cm^2 and are indicative of poor corrosion protections.

The PATTI test results are presented in Table 2. The coating systems with the CSP pretreatment appeared to have the overall lowest pull-off strength values, both with and without the APC topcoat. The failure mode can be described as a combination of cohesive failure within the primer layer and adhesive failure between the primer and the substrate. The data for the remaining paint systems were comparable.

CONCLUSIONS

Analysis of the experimental data presented in Table 3 shows the ability of some of the tested fully non-chromate coating systems to provide corrosion protection comparable to that of the chromate control system (CCC/MIL-PRF-23377H/APC), but only when the criterion of a clean scribe is overlooked as stated in MIL-PRF-23377H for Class N primers. After 2,000 hours of exposure in Salt Spray test, non-chromate systems with the MSZ surface treatment and either WEP or EEP primer demonstrated comparable corrosion protection. The low-frequency impedance modulus values for unscribed panels with complete non-chromate coating systems after 2,000 hours of Salt Spray were in the same range as those for the chromated coating system. This indicates that barrier properties are not sacrificed with use of the selected non-chrome pre-treatments and primers. Impedance of coating systems without topcoat or scribed panels did not meet the evaluation criteria outlined earlier. For filiform corrosion, all tested non-chromate topcoated systems demonstrated comparable performance to the standard chromate system. Due to the fact that the ASTM D 4541 PATTI test does not have a military specification requirement, the coatings adhesion properties were assessed using the standard chromated system as the baseline. Overall, the systems with the CSP conversion coating demonstrated the lowest values in the tensile pull-off test.

Based on these comparisons, two fully non-chromated systems, MSZ/WEP/APC and MSZ/EEP/APC, demonstrated promising performance in all tested areas.

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TABLE 1. Combinations of Coatings Systems Tested

Surface Treatments	Primers	Top Coat
1. **CSP**: Pantheon Chemical product PreKote® 2. **SNAP**: Self-assembled NAnophase Particle sol-gel prepared in laboratory 3. **MSZ**: AC Technologies product AC-131 (Boegel EP-II) 4. **CCC**: Henkel Corp. product Alodine® 1200S; qualified to MIL-C-5541	1. **EEP**: Experimental Deft, Inc. product 02-GN-083 epoxy primer. 2. **WEP**: PRC-DeSoto product Eco-prime™ CF EWAE048A/B; qualified to MIL-PRF-85582; Type I Class N 3. **MIL-PRF-23377H**: Deft, Inc. product 02-Y-40A; Type I Class C	1. **APC**: Deft, Inc. product 99-GY-001; Color 36173; qualified to MIL-PRF-85285D

TABLE 2. Patti Results: Pull-Off Strength for Coating Systems

Pretreatment	Primer	Topcoat	Pull-Off Strength (psi)	*St dev*
CCC	MIL-PRF-23377H	APC	2158	292
SNAP	WEP	APC	2294	235
SNAP	EEP	APC	2335	185
MSZ	WEP	APC	2471	157
MSZ	EEP	APC	2239	273
CSP	WEP	APC	1981	355
CSP	EEP	APC	2149	255
CCC	MIL-PRF-23377H	none	1954	259
SNAP	WEP	none	2239	208
SNAP	EEP	none	2239	213
MSZ	WEP	none	2117	353
MSZ	EEP	none	2280	190
CSP	WEP	none	1763	414
CSP	EEP	none	1586	511

TABLE 3. Performance Comparison of Tested Coating Systems

Coating System	Filiform Test	Salt Spray Test	EIS Test	PATTI Test
CCC/23377H/APC	40	No blisters or undercutting	10^8 Ω cm^2 or greater	2100 psi or better
SNAP/WEP/APC	comparable	lower	comparable	comparable
SNAP/EEP/APC	comparable	lower	comparable	comparable
MSZ/WEP/APC	comparable	comparable	comparable	comparable
MSZ/EEP/APC	comparable	comparable	comparable	comparable
CSP/WEP/APC	comparable	lower	comparable	comparable
CSP/EEP/APC	comparable	lower	comparable	comparable
CCC/23377H	n/a	No blisters or undercutting	10^6 Ω cm^2 or greater	1950 psi or better
SNAP/WEP	n/a	lower	lower	comparable
SNAP/EEP	n/a	lower	lower	comparable
MSZ/WEP	n/a	lower	lower	comparable
MSZ/EEP	n/a	lower	lower	comparable
CSP/WEP	n/a	lower	lower	lower
CSP/EEP	n/a	lower	lower	lower

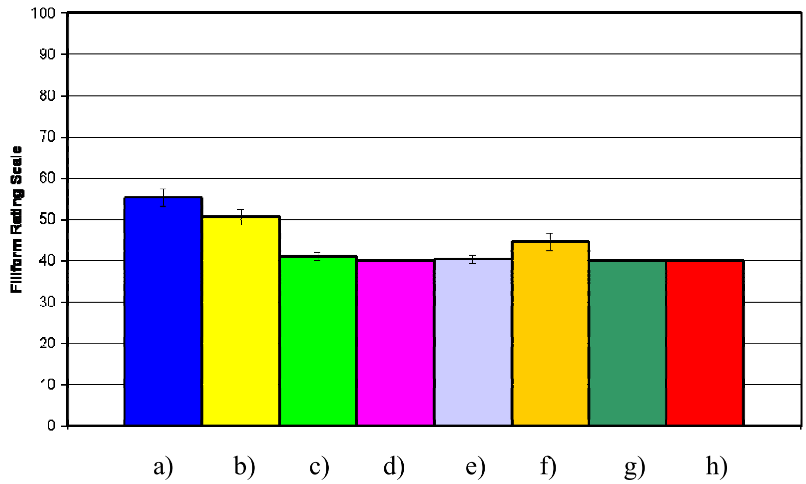

FIGURE 1. Filiform Rating: a) SNAP/EEP/APC; b) SNAP/WEP/APC; c) CSP/WEP/APC; d) CSP/EEP/APC; e) MSZ/EEP/APC; f) MSZ/WEP/APC; g) CCC/MIL-PRF-23377H/APC; h) control

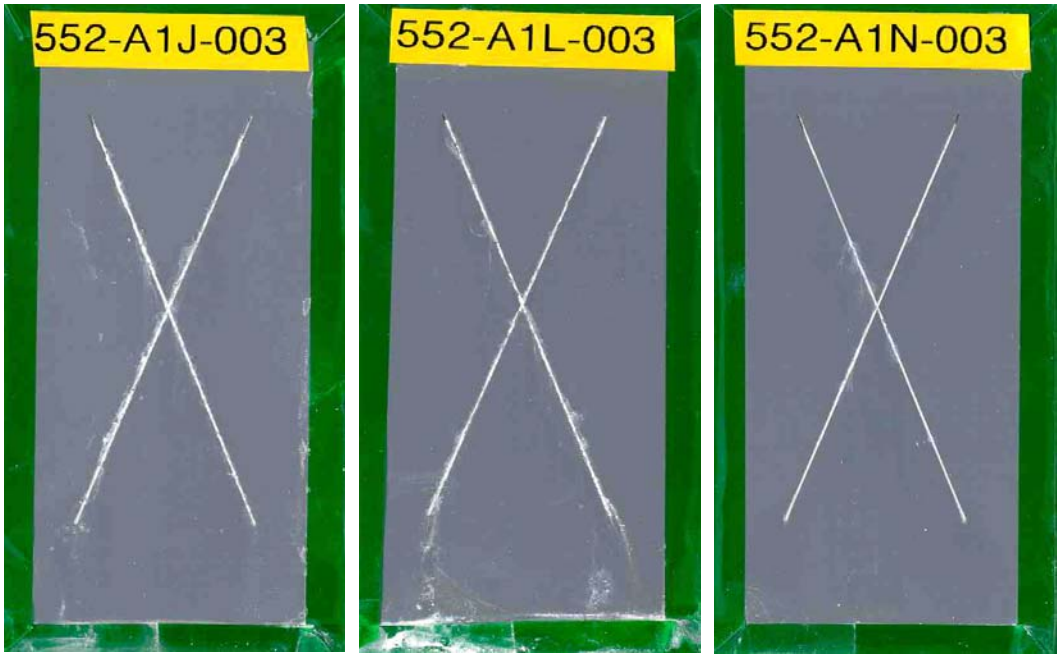

FIGURE 2. Complete coating systems after 2,000 hours of Salt Spray:
a) MSZ/EEP/APC; b) MSZ/WEP/APC; c) CCC/MIL-PRF-23377H/APC

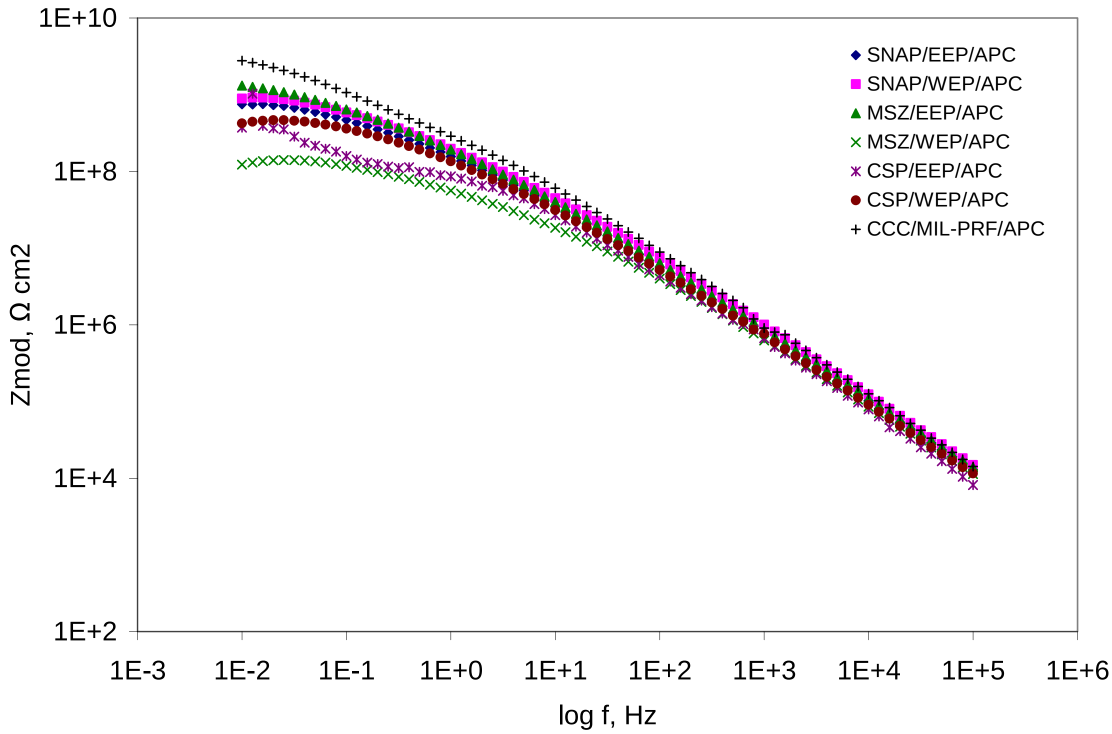

FIGURE 3. EIS for topcoated unscribed panels after 2,000 hours of Salt Spray exposure