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Efficacy of MIL-DTL-5541 Compliant Non-Chromate Conversion Coating Repair Materials

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ABSTRACT

Non-chromate conversion coatings compliant with MIL-DTL-5541 have been demonstrated to provide protection comparable to their chromate counterparts. Repair materials are available to address defects in bath-applied conversion coatings from most manufacturers for these products that have been approved under MIL-DTL-81706, though with significant variations in their application methodology and efficacy. In this work, repair material chemistries from three different vendors were evaluated, working towards a single application method that can be used independent of the selected chemistry. Each coating was then benchmarked against an industry standard chromate conversion coating repair material in terms of both the corrosion performance as well as the capability of each coating to maintain the ability to make low resistance electrical contact to the surface.

Key words: Aluminum, Chromate, Non-chromate, Conversion Coating, Repair

INTRODUCTION

Chromate conversion coatings are relied upon to ensure the long-term corrosion performance and surface electrical properties of aluminum alloys, as well as to improve the bond strength and adhesive properties of organic coatings and adhesives. Chromate based chemistries have been all but eliminated in Europe, and it is believed the EPA will stage their elimination in the USA within the next 5 to 10 years. The development of chemistries to replace chromate has been a hot area of research for over 30 years, and now a series of commercial alternatives have become available. These new coatings differ in their chemistry and performance characteristics, as well as their functional limitations, from chromate. Repair materials available from a variety of manufacturers, used to address defects in the conversion coating, have been found to vary in terms of their application methodology and efficacy as will be discussed below. The purpose of this work is to evaluate a variety of application methods and chemistries in an effort to ultimately develop a single procedure that can be used to apply each effectively.

The coating repair materials evaluated in this work all formally comply with MIL-DTL-81706 as Class 3 coatings and are listed in the associated qualified product list (QPL), QPL-81706 (Class 3 coatings have requirements both for corrosion performance as well as their ability to preserve the ability to make low electrical contact resistance measurements to the surface). Each is a repair material to be used for materials applied in compliance with MIL-DTL-5541. The three specific non-chromate chemistries (and the bath-applied coatings they are designed to repair) are all trivalent chromium process (TCP) coatings based upon a series of NAVAIR patents – namely US patent numbers 6375726, 6511532, 6521029, and 6527841. The particular chemistries evaluated here include Alodine (Bonderite) 1132[*] as a chromate-based control, and three non-chromate materials - Alodine (Bonderite) 871[*], Aluminescence TX[†], and TCP-HF[‡]. Each product was in the form of a ready to use solution held within a repair pen. The design of the repair pen was nominally identical from each vendor, and used a non-woven pad to deposit the conversion coating chemistry onto the sample surface, much like a magic marker.

As described in the patents that form the basis for the non-chromate conversion coating chemistries evaluated here, each is an acidic aqueous solution containing a trivalent chromium compound (e.g., chromium (III) sulfate), an alkali metal hexafluorozirconate (e.g., potassium hexafluorozirconate), and one or more alkali metal fluoro compounds (e.g., potassium tetrafluoroborate) as well as water soluble thickeners and/or surfactants. While the specific chemistry of the deposition materials for each of the three TCP coatings evaluated here varies, mechanistically they yield very similar coatings. Details on the deposition/formation mechanism for these chemistries are described extensively in the literature (Dong, 2010; Qi, 2015; Li, 2011).

There has been significant reluctance in adoption of non-chromate conversion coatings in high consequence military systems. While the chemistries themselves have been demonstrated to be very effective, the methodologies to repair them, and the efficacy of the coatings prepared through such methods is not well documented/studied. This is further complicated in applications where the electrical properties of the coating, and the ability to maintain those properties following environmental exposure, is needed. Through this work, common procedures/protocols have been developed that facilitate the implementation of a variety of coating chemistries in a production environment and help mistake proof the coating repair process. In the work presented here, the repair materials were used to coat large panels of a surface. While this is atypical for a repair operation (where less than 5% of the total surface area is addressed, as noted in MIL-DTL-5541), it provides a means to more effectively assess the performance of the coatings in terms of macroscopic corrosion damage and evaluation of electrical properties. All of the repair materials are currently qualified as being in conformance with MIL-DTL-81706 as Type 2 (non-chromate), Class 3 coatings (and listed in the QPL), and thus should be able to yield performance in line with MIL-DTL-5541 when applied properly, even to large areas.

EXPERIMENTAL PROCEDURE

Sample Geometry and Surface Preparation

All samples used in this study were in the form of 3” x 10” (7.6 x 25.4 cm) sheet as required to demonstrate compliance with MIL-DTL-5541. Four alloys were evaluated – AA2024 (UNS A92024) in the T3 temper, AA5083 (UNS A95083) in the H32 temper, AA6061 (UNS A96061) in the T6 temper, and AA7075 (UNS A97075) in the T6 temper. For each alloy, all the samples evaluated in this study were from the same heat of material, ensuring variations in performance were due to the coatings and not variations in the substrate material.

The surface preparation method was based upon a combination of the procedures recommended by each coating manufacturer, replicating what would be done to a damaged conversion coated component that was to be repaired. The alkaline etching followed by desmutting used for bath-based

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application of the conversion coatings was thus not appropriate here. Each panel was prepared by first mechanically abrading the surface with a series of abrasive pads that had been wet with deionized water. Abrading began with Scotchbrite[§] 7440, followed by Scotchbrite[§] 6448, and finally Scotchbrite[§] 7448. Each abrasive pad was used for approximately 5 minutes, scrubbing the panel lengthwise, then turning the panel 90 degrees and repeating the process. Samples were scrubbed in each direction for approximately 1 minute before changing orientation. Once the abrasion process was complete, the panels were cleaned using a heavy-duty wipe (Wypall[**] L30) wet with ACS reagent grade isopropyl alcohol until all traces of the abrasive pads had been removed. Panels were then rinsed in flowing deionized water for 2 minutes, then blown dry with filtered, dry nitrogen.

Coating Application Methodology

Chromate Conversion Coating Repair Material

The touch-up pen was actuated such that the non-woven applicator tip was saturated with coating solution (this action was repeated throughout the coating process to ensure the tip remained saturated with coating solution). The pen was then used to apply the coating by performing multiple passes in one direction (e.g., along the length of the panel surface) on the test panel, with each pass overlapping the previous pass by 50%. This operation was completed by hand, and as such there is some operator-dependent variability in the extent of overlap. Once the entire panel was coated, the solution was allowed to dry. The coating was then applied a second time, with the application direction 90 degrees from that used in the first coating. The applicator was used to make sufficient passes to coat the entire surface of the panel, with each pass overlapping the previous pass by 50%. The solution was again allowed to dry on the panel surface, at which point the coating process was complete.

Non-Chromate Conversion Coating Repair Material 1

The touch-up pen was actuated such that the non-woven applicator tip was saturated with coating solution (this action was repeated throughout the coating process to ensure the tip remained saturated with coating solution). The pen was then used to apply the coating by performing multiple passes in one direction (e.g., along the length of the panel surface) on the test panel, with each pass overlapping the previous pass by 50%. Once the entire panel was coated, the solution was allowed to dry. The coating was then applied a second time, with the application direction 90 degrees from that used in the first coating. The applicator was used to make sufficient passes to coat the entire surface of the panel, with each pass overlapping the previous pass by 50%. The solution was again allowed to dry on the panel surface, at which point the coating process was complete.

Non-Chromate Conversion Coating Repair Material 2

The touch-up pen was actuated such that the non-woven applicator tip was saturated with coating solution (this action was repeated throughout the coating process to ensure the tip remained saturated with coating solution). The pen was then used to apply the coating by performing multiple passes in one direction (e.g., along the length of the panel surface) on the test panel until the entire surface was visibly wet with the solution, after which the solution was allowed to dry. The sample surface was then rinsed with flowing deionized water and blown dry with filtered, dry nitrogen.

Non-Chromate Conversion Coating Repair Material 3

The surface to be coated was cleaned/activated using a mildly acidic liquid cleaner by loading a heavy duty wipe with a 7.5 vol% solution of the cleaner for 5 minutes by repeatedly wetting the surface with the cleaner once every 30 seconds. The surface was then rinsed for 2 minutes in flowing deionized water, then blown dry using filtered, dry nitrogen. The touch-up pen was actuated such that the non-woven applicator tip was saturated with coating solution (this action was repeated throughout the coating process to ensure the tip remained saturated with coating solution). The pen was then used to apply the coating by performing multiple passes in one direction (e.g., along the length of the panel

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surface) on the test panel until the entire surface was visibly wet with the solution, with the coating gently reapplied (every 30-60 seconds) as needed for a period of 6 minutes, taking care to ensure the surface was wet with coating solution for the entire time interval. Next, the sample was rinsed for 2 minutes in flowing deionized water, then blown dry with filtered, dry nitrogen.

Coating Evaluation

Coatings were evaluated in the as-coated condition in accordance with MIL-DTL-5541 for a Class 3 coating. The electrical contact resistance of each coating was measured by pressing a 1 in^2 (6.5 cm^2) flat copper platen onto the surface of the coupon using a force of 200 psi (1.38 MPa) and passing a current of 100 mA while measuring the contact resistance using a nano-voltmeter. All measurements were made in a 4-wire arrangement. For each coupon, a total of 10 contact resistance measurements were made. Measurements were made in the same locations for each sample (two linear arrays of 5 measurements). Contact resistance measurement was considered destructive due to the risk of copper deposition onto the aluminum surface, so samples evaluated for contact resistance were not used in subsequent salt fog testing.

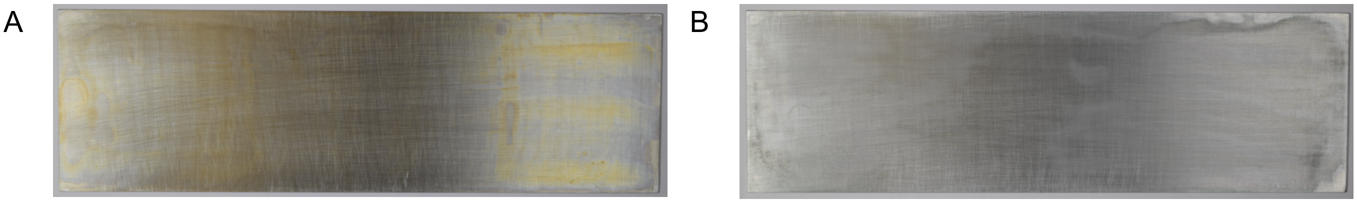
Coatings were next evaluated after exposure for 1 week to an ASTM B117 salt fog chamber using 5 wt% NaCl solution. Once complete, the samples were evaluated visually for the number of pits on each sample (ignoring any sites 0.25 in (6 mm) from the coupon edges). Finally, the electrical contact resistance of the salt-fog exposed samples was measured, using the same parameters as used to assess the initial contact resistance.

To account for statistical variability in coating performance, 3 replicates of each coating/substrate alloy were evaluated for the initial contact resistance, and 8 replicates were used to evaluate the salt fog performance and resulting contact resistance of aged coupons.

RESULTS

Coating Appearance

The visual appearance of representative coated samples is illustrated in Figure 1. The samples shown in the figure are on AA6061, and the coatings appeared similar on other alloys, though the non-uniformities were somewhat greater on the high strength alloys (AA2024 and AA7075). Coating procedures that allowed the coating chemistry to dry on the surface left more significant stains than the chemistry that was not allowed to dry. Subsequent rinsing of the coatings that were allowed to dry with deionized water was only marginally effective at reducing the visual intensity of the stains. The coating chemistry that remained wet the entire time of the coating process exhibited very little staining. Following salt fog exposure, damage (when present) in the form of pitting was found in most cases to coincide with visual heterogeneities in the as-applied coating.



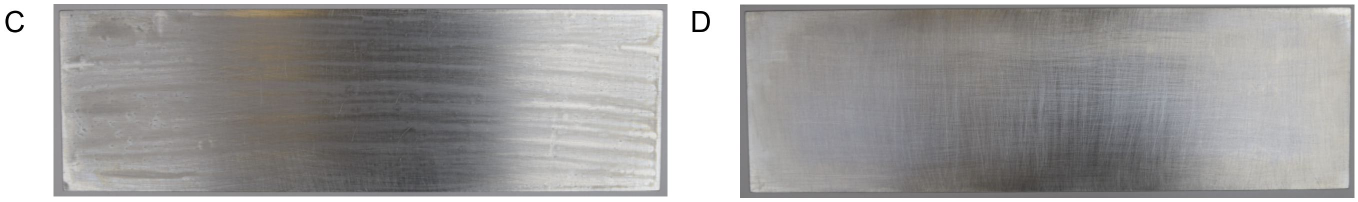


Figure 1: Illustration of the visually non-uniform nature of each of the conversion coating repair materials evaluated in this study. Each coupon pictured is 3” x 10” in size (7.6 x 25.4 cm). Shown are the (a) chromate-based material, (b) non-chromate coating 1, (c) non-chromate coating 2, and (d) non-chromate coating 3

Corrosion Performance – Pit Density Following Salt Fog

After completion of a 1 week salt fog exposure, the coated samples were rinsed with water to remove any deposited salts, then dried and the number of localized corrosion sites on each coupon assessed. The results of these tests are presented in Figure 2. MIL-DTL-5541 requires that there be no more than 5 localized corrosion sites/pits on each coupon (i.e., 5 localized corrosion sites per 30 in^2 (193 cm^2) of exposed surface), and that none of those sites that are present be larger than 0.031 in. (0.8mm) in diameter. In the case of AA2024, the chromate and non-chromate repair materials where the coating chemistry was allowed to dry on the surface exhibited a large number of localized corrosion sites, particularly for the non-chromate chemistry where greater than 15 sites per sample were observed. For AA5083, with the exception of non-chromate chemistry 1 (where the coating solution was dried and not rinsed from the surface), all of the materials performed well, with pit counts well below the specification limit. For AA6061, all of the chemistries performed well, though non-chromate chemistry 1 was again the poorest performing material of the group. In the case of the difficult to protect AA7075, both the chromate and non-chromate chemistry where the material was allowed to dry and not rinsed performed very poorly, with greater than 15 corrosion sites per coupon. However, both of the other non-chromate coating chemistries performed well, with the average number of corrosion sites below the specification limit.

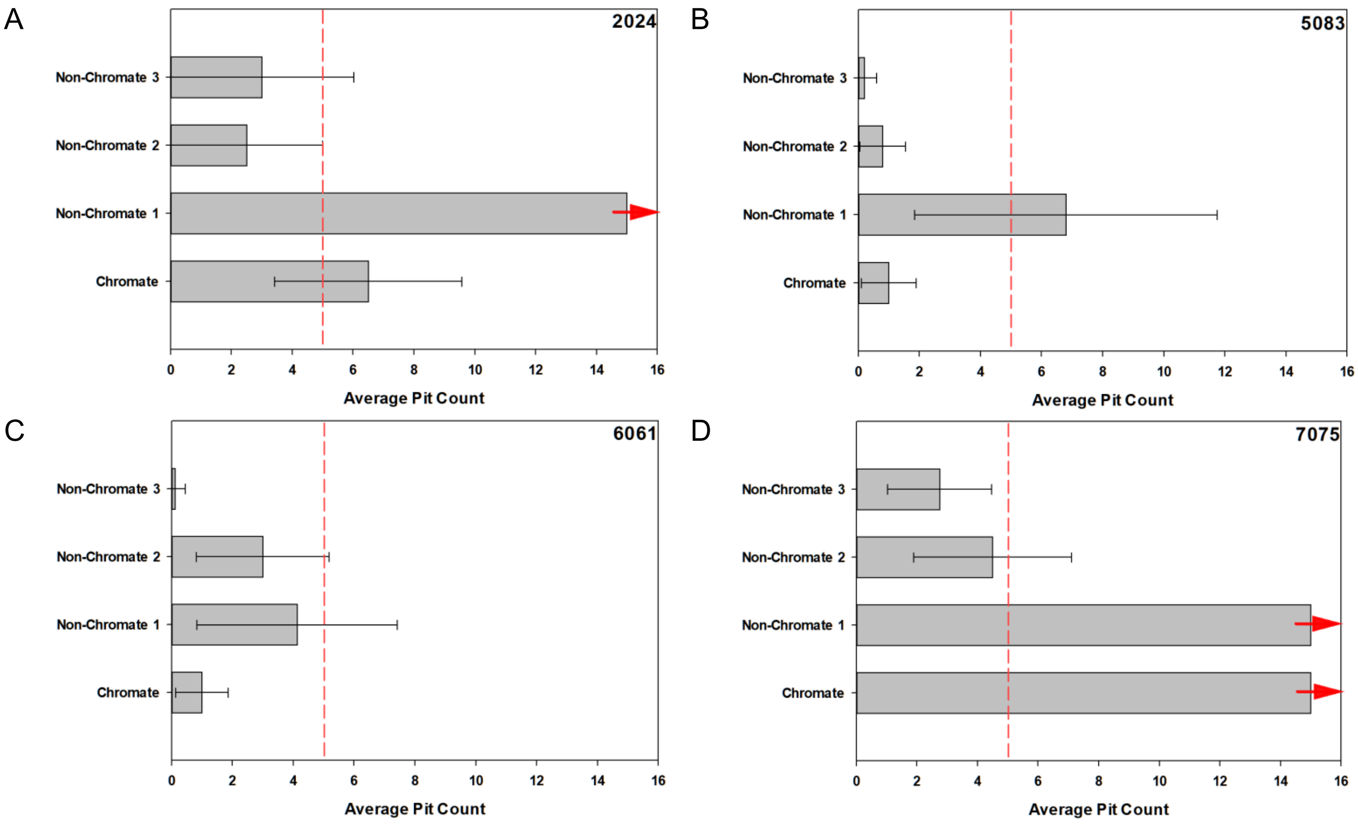


Figure 2: Average number of localized corrosion sites found on each test coupon as a function of material. Shown are (a) AA2024, (b) AA5083, (c) AA6061, and (d) AA7075.

Coating Electrical Performance

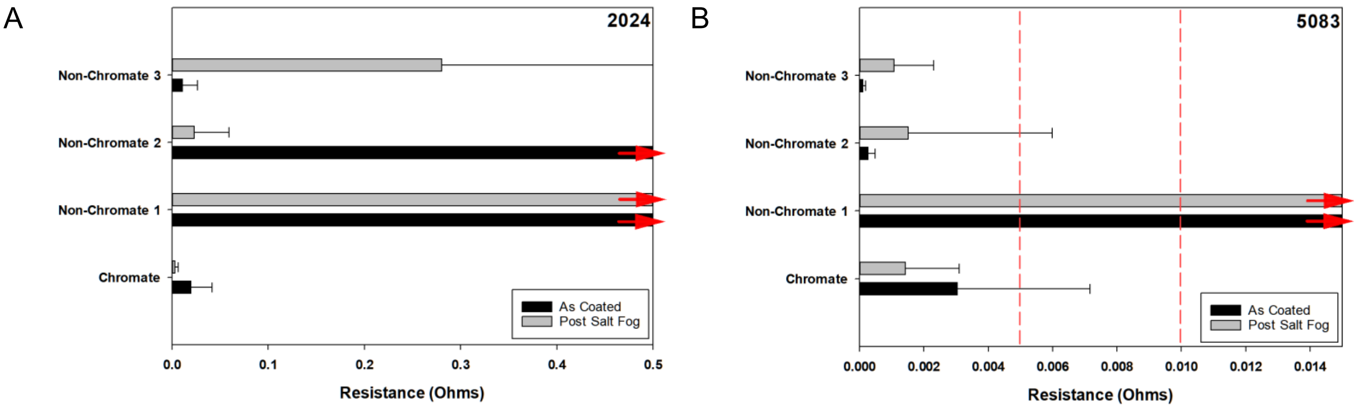
Class 3 coatings per MIL-DTL-5541 are required to have an electrical contact resistance of less than 5 milliohms/in^2 (0.78 milliohms/cm^2) in the as-coated condition, and less than 10 milliohms/in^2 (1.6 milliohms/cm^2) following 1 week of ASTM B117 salt fog exposure. This is readily achieved by MIL-DTL-

81706 approved chemistries applied via immersion in a coating bath for all of the aluminum alloys evaluated in this study. The non-uniform nature of the repair materials, however, resulted in significantly higher contact resistances in some cases. In order to separate regions where a heavy deposit of coating material salts or corrosion product from a pit was present (and thus the contact resistance would be very large) from regions where the coating was intact, sites where such a deposit was present were not included in the determination of the contact resistance. In Table 1, the number of such locations is tabulated for each coating chemistry/substrate alloy combination for samples evaluated prior to and following salt fog exposure. In the case of as-coated samples, the total number of measurements made for each coating chemistry/substrate alloy combination was 30 (3 replicate samples, 10 measurements per sample) and for post salt-fog, the total was 80 (8 replicate samples, 10 measurements per sample)

Table 1: High Resistance Areas for Each Coating Material/Substrate Combination

	Chromate		**Non-Chromate 1**		**Non-Chromate 2**		**Non-Chromate 3**	
Alloy	**As Coated**	**Salt Fog**	**As Coated**	**Salt Fog**	**As Coated**	**Salt Fog**	**As Coated**	**Salt Fog**
2024	1	5	3	14	7	0	0	5
5083	0	0	0	0	0	0	0	0
6061	0	0	0	0	0	0	0	0
7075	0	0	0	15	0	0	0	2

The contact resistance for each of the coating material/substrate combinations both before and after salt fog testing is presented in Figure 3. Each bar represents the average of all of the good measurements, and the error bars represent 1 standard deviation from the mean. For AA2024, none of the non-chromate coating materials were able to meet MIL-DTL-5541 Class 3 requirements - only the chromate conversion coating material was successful. Several of the materials exhibited average contact resistances of greater than 1 ohm/in^2 (155 milliohms/cm^2). In the case of non-chromate coating 2, the post salt-fog test was dramatically lower in resistivity than the as-coated material. One possible explanation would be that the salt fog was able to wash residual salts from the coating process from the sample surface (though this was not proven here). For both AA5083 and AA6061, with the exception of non-chromate coating 1, all of the materials were able to meet the MIL-DTL-5541 Class 3 specification limits. For the notoriously difficult to protect AA7075 samples, none of the coating materials were able to meet the specification limits for contact resistance, though performance was better than observed for AA2024.



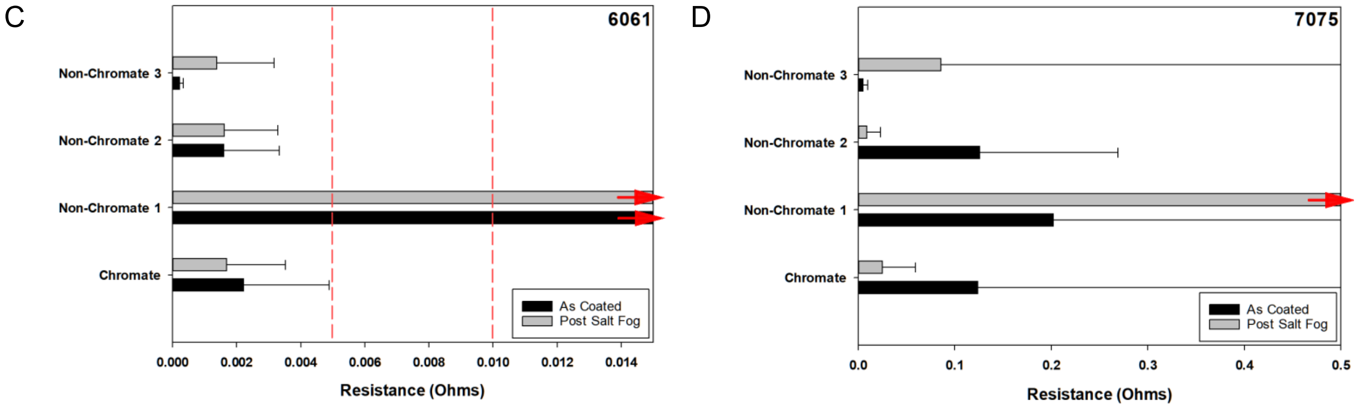


Figure 3: Contact resistance acquired in accordance with MIL-DTL-5541 for each coating material on (a) AA2024, (b) AA5083, (c) AA6061, and (d) AA7075. For (b) and (c) lines have been added to show the specification limit for as-coated (5 milliohms/in^2) and salt fog exposed (10 milliohms/in^2) samples. Each value represents the average of all measurements made for that coating material/substrate combination after removing regions where resistance measurement was not possible.

Considering the contact resistance data as a whole, materials where the procedure allowed the coating material to dry on the metal surface performed more poorly than those where the surface was kept wet through the entire coating procedure, then rinsed. The data suggests that the residual coating solution adversely impacts the electrochemical performance of the coating as well as increasing the contact resistance of the coating.

In MIL-DTL-5541, touch up/repair is limited to regions where the initial coating (typically applied via immersion in a coating bath) has been removed due to mechanical damage or processing, and furthermore, that the total area shall not be greater than 5% of the total area of the component. Thus, it the most common use for the repair materials evaluated in this study would be to address small regions on a component, and not to serve as the primary coating on a functional interface. However, all of the chemistries evaluated in this study are formally approved under MIL-DTL-81706 and listed under the associated QPL as Class 3 compliant chemistries – thus they should be capable of meeting Class 3 performance requirements as a primary interface when evaluated on AA6061. None of the coating materials were able to meet the contact resistance requirements for Class 3 coatings per MIL-DTL-5541 on all of the alloys evaluated here, though all but one of them were able to meet requirements on AA6061. As such, these materials may not be appropriate as a primary coating for materials other than AA5083 and AA6061, depending on the contact resistance required by the application for which they are being used.

SUMMARY/CONCLUSIONS

A series of conversion coating repair materials were evaluated for their ability to meet the MIL-DTL-5541 specification for Class 3 coatings. All of the coatings are commercially available products, and have formal approval under MIL-DTL-81706 and are listed in the associated QPL. A number of observations/conclusions can be made based upon the data acquired through this study.

- All of the coatings where the manufacturers procedure allowed or required that the coating material dry on the aluminum surface were non-uniform in appearance.
- The visual heterogeneities observed on the sample surfaces often corresponded to regions where the corrosion performance of the coating was substantially compromised.
- All but one of the non-chromate coating chemistries were able to rigidly meet MIL-DTL-5541 Class 3 requirements.
- None of the non-chromate coating materials were able to meet the contact resistance requirements on AA2024 or AA7075

- The observed performance of the materials evaluated here indicate that caution must be used when employing these chemistries as a primary coating (i.e., not as a repair material), particularly on high strength alloys such as AA2024 or AA7075, as while all are MIL-DTL-81706 qualified, none were able to achieve the low contact resistances stipulated on for a Class 3 coating

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