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Efficacy of Nonhexavalent Chromium Posttreatment Rinses for Passivating Three DOD Legacy Coatings: Ion Vapor Deposition Aluminum, Type III Hardcoat Anodizing, and Electroplated Zinc

by Thomas Considine, John Kelley, and Thomas Braswell

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14. ABSTRACT All Department of Defense maintenance facilities are under increased pressure to reduce or eliminate the use of hexavalent chromium (CrVI). CrVI has been associated with negative long-term health effects and is listed as a known human carcinogen by the International Agency for Research on Cancer. This project was designed to address the Army Environmental User Requirements and Technology Assessments requirement PP-2-02-04, for Toxic Metal Reduction in Surface Finishing of Army Weapon Systems. The goal is to identify, validate, and demonstrate the efficacy of nonhexavalent chromium posttreatment sealers on three common legacy coatings: ion vapor deposition (IVD) aluminum, Type III hardcoat aluminum anodizing, and zinc electroplating. Although the CrVI-containing passivating rinse outperformed all of the alternatives, it did not meet specification requirements in all cases. The results show some alternative passivates performed well and perhaps can be viable alternative passivates for IVD aluminum and Type III hardcoat anodizing. No alternative sealer performed nearly as well as CrVI passivates on electroplated zinc coatings. More work is needed to develop an effective nonchromium passivating rinse for electroplated zinc coatings.					
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1. Introduction

All Department of Defense (DOD) maintenance facilities are under pressure to reduce or eliminate the use of hexavalent chromium (CrVI). CrVI has been associated with long-term health effects, including cancers of the respiratory system and is listed as a known human carcinogen by the International Agency for Research on Cancer (IARC)¹ and the American Conference of Governmental Industrial Hygienists (ACGIH).² Chromium and its inorganic compounds are included in the ACGIH Under Study list. Chromium is also subject to increasingly restrictive regulatory management. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for CrVI was lowered in 2006 from 52 to 5 $\mu\text{g}/\text{m}^3$.³ Any further reduction in the PEL could result in processes that employ or generate CrVI, making them unsustainable or impractical through costs associated with fugitive material mitigation and disposal. Litigation is currently in place to further lower the PEL and there is also probable risk of litigation from workforce due to CrVI exposure.

CrVI in all its forms has now been listed as a Substance of Very High Concern under the European Union's (EU) Registration, Evaluation, Authorization and Restriction of Chemicals and was given a sunset date of 21 September 2017.⁴ That meant that 18 months prior to the sunset date (i.e., 21 March 2016), the manufacture of these products ceased in the EU. Therefore, original equipment manufacturers working in the global market have been searching for alternatives to CrVI applications in order to remain competitive. As a result, lower-tiered supply chains may become obsolete if demand for CrVI-containing processes is reduced. The Environmental Protection Agency (EPA) is developing a new risk assessment under its Integrated Risk Information System (IRIS)⁵ that could place further restrictions on CrVI.

The urgency of this issue was underscored by a memorandum from the Under Secretary of Defense for Acquisition, Technology and Logistics, *Minimizing the Use of Hexavalent Chromium* (8 April 2009),⁶ referring to the need to minimize or eliminate the use of CrVI as an “extraordinary situation”, requiring DoD to “go beyond established hazardous materials management processes” and to “more aggressively mitigate the unique risks to DOD operations now posed by” CrVI. In addition, the memorandum directs the secretaries of the military departments to

- Invest in appropriate research and development on substitutes.
- Ensure testing and qualification procedures are funded and conducted to qualify technically and economically suitable substitute materials and processes ...

The DOD has established 48 Code of Federal Regulations (CFR) Part 223 in the Defense Federal Acquisition Regulation Supplement, Minimizing the Use of Materials Containing Hexavalent Chromium. The Clean Water Act sets effluent limits on pollutants 40 CFR 433 (Metal Finishing)⁷ and 40 CFR Part 413 (Electroplating).⁸ The Resource Conservation and Recovery Act⁹ also targets specific wastes.

Army Environmental Requirements and Technology Assessment (AERTA) requirement PP-2-02-04,¹⁰ Toxic Metal Reduction in Surface Finishing of Army Weapon Systems, has been established, and this project will address that requirement by eliminating CrVI in posttreatment plating and conversion coating sealers. The need to reduce or eliminate CrVI, along with other toxic metals, was detailed in the report *Reduction of Toxic Materials in Army Surface Finishing Processes: Environmental Requirement and Technology Assessment*,¹¹ completed by the US Army Aviation and Missile Command (AMCOM) G-4 in 2012.

The purpose of this project was to evaluate the performance of CrVI-free posttreatment sealers versus the baseline CrVI containing posttreatment rinse routinely used at Corpus Christi Army Depot (CCAD), Rock Island Arsenal, Red River Army Depot, and Anniston Army Depot (ANAD) for parts treated with ion vapor deposition (IVD) aluminum, Type III hard aluminum anodizing, and zinc electroplating. If the CrVI-free alternative posttreatment sealers perform successfully in a laboratory setting at the US Army Combat Capabilities Development Command Army Research Laboratory, full-scale demonstrations are planned at CCAD and ANAD.

2. Experimental Procedure

2.1 Application and Sealing of Legacy Coatings

2.1.1 Anodized Aluminum (Type III)

Aluminum alloy (AA) 2024-T3 was used for this experiment. Two panel sizes: 3 × 10 × 0.063 inches (corrosion and adhesion testing) and 4 × 4 × 0.063 inches (abrasion testing) were anodize coated in accordance with MIL-A-8625¹² Type III. The chromate seal was applied only to the baseline set of samples. The remaining coupons were sealed with the alternative sealers individually.

As per the standard anodize procedure, the coupons were affixed to aluminum contact racks for the conversion coating operation and processed by immersing the fixtures through the following process steps:

- 1) Clean: alkaline soak cleaner at 145 °F for 5–10 min.
- 2) Rinse: two-stage with ambient temperature counter current final rinse using city water.
- 3) Water break test: as racks are removed from final rinse, they are visually inspected to verify a water break-free surface on the coupons.
- 4) Alkaline etch: at 135 °F for 30–120 s.
- 5) Upon removal from the etch tank, visually inspect for a uniform smut deposit over the coupons.
- 6) Deoxidizing/desmut: an ambient nitric acid bath for 3–5 min to remove insoluble deposits from etching process.
- 7) Inspection: after removal, panels should be “white” aluminum with no indication of water break. This inspection step is very critical to achieve uniform anodize.
- 8) Anodize: sulfuric acid tank (at 5–15 g/L) is maintained at 32 °F. In a cathodically charged tank, the coupons act as anodes and the clean Al surface is converted to Al oxide. Target thickness is 1.8–2.0 mils nominal. The 2000-series Al requires a 10–12 min ramp up, then approximately 68 min to target thickness. The 2000-series Al, due to of copper content, needs a longer ramp up to stabilize the anodize deposition/conversion process.
- 9) Rinse: two-stage ambient rinse with deionized (DI) water.
- 10) Nitric acid dip: ambient 10–15% nitric acid concentration to rid coupons of any fugitive sulfuric acid carryover from anodize process.
- 11) Rinse: two-stage ambient DI water rinse.
- 12) Rinse: 140 °F DI rinse.
- 13) Dry: blow off with compressed air, inspect, and pack.

2.1.2 IVD Aluminum

IVD aluminum coating was applied to the samples listed in Table 1 at CCAD in accordance with MIL-DTL-83488D¹³ and using the CCAD Process Standard I.09,¹⁴ revision A: Class 1 - 0.0010 inch minimum thickness, Class 2 - 0.0005 inch minimum thickness, and Class 3 - 0.0003 inch minimum thickness.

Table 1 Substrate alloys and dimensions for test panels coated with IVD aluminum

Tests	Alloy	Dimensions (inches)
Corrosion and paint adhesion	AISI 4130 Steel	3 × 10 × 0.063
Paint adhesion	Ti-6Al-4V	3 × 10 × 0.032
Paint adhesion	AA 2024 T3	3 × 10 × 0.032

The actual thickness of the IVD aluminum coating was obtained over the number of application passes per sample. In this case, six passes provided a 0.0012-inch-thick, four passes provided 0.001-inch-thick, and two passes provided a 0.0004-inch-thick coating. Given that the thicknesses are minimums, the final IVD aluminum coating thicknesses of the samples tested were the following:

- Class 1: 0.0012 inch thick
- Class 2: 0.001 inch thick
- Class 3: 0.0004 inch thick

2.1.3 Electroplated Zinc

Panels of AISI 4130 steel size 4 × 6 × 0.032 inches were prepared for electroplating by first cleaning via soaking in an alkaline detergent bath for 10 min at 150 °F to remove surface contaminants. A secondary cleaning process was then performed with an electro-cleaner. Following the rinses, the substrate is pickled in acid in order to remove oxide and activate the surface. After additional rinses, the panels are then racked and immersed in the zinc electroplating solution, where a DC current is applied, depositing zinc onto the substrate surface.

The test coupons were coated in accordance with (IAW) ASTM B-633-11¹⁵ electrodeposited zinc coating to SC-4 (25 μm thick). The coupons were affixed to conductive contact racks for the plating operation and processed by immersing the fixtures through the following series of processing tanks:

- 1) Clean/vapor degrease: vapor degreaser charged with n-propyl bromide.
- 2) Visual inspection: check for dirt and grease stains.
- 3) Clean: immerse in hot tank at 140 °F sodium hydroxide solution (6 oz/gal of water) for 10 min.
- 4) Rinse: spray rinse with DI water.
- 5) Electro-clean: immerse in hot tank at 150 °F with anodic positive charge to parts/negative to tank for 2–3 min.
- 6) Acid activation: immerse in ambient soak tank at 35% hydrochloric acid.

- 7) Rinse: spray rinse with DI water.
- 8) Visual inspect: check for water break, smut, and rust debris.
- 9) Zinc plating: immerse in chloride zinc bath at 5–6 oz/gal concentration for 30 min at 12–15 amps per square foot.
- 10) Rinse: spray rinse using DI water.

The panels are once again rinsed and dried with compressed air. The alternative posttreatment sealers were applied according to manufacturer's instructions and the baseline panels were CrVI-sealed IAW ASTM B-633-11¹⁵ Type II colored chromate.

2.1.4 Application of Posttreatment Sealers

The chromate sealer was applied IAW ASTM B-633-11: Brite dip in 0.25% nitric acid, then chromate conversion bath, and rinse with DI water. All other sealers were applied as part of an immersion process at ambient laboratory conditions. A list of posttreatment sealers applied to each surface treatment is given in Table 2. Cleanliness was checked by ensuring a water-break-free surface prior to sealer application. Processes and dwell time for each sealer varied by manufacturer, and each process was followed to the letter by the application team. Sealers that called for a rinse were rinsed in DI water. All panels were forced-air dried using laboratory air to avoid puddling and/or flash rust where applicable. Dry panels were wrapped and sealed in volatile corrosion inhibitor-impregnated paper until needed for testing. Panels for adhesion testing were primed within 24 h of sealing on site at DEVCOM Army Research Laboratory with the appropriate primer. Both topcoats and primers were applied in accordance with MIL-DTL-53072.¹⁶

Table 2 Posttreatment sealers evaluated on each surface treatment

Sealer	MIL-A-8625 ¹²	MIL-DTL-83488 ¹³	ASTM B633-11 ¹⁵
Alodine 1200	x	x	x
Bonderite M-NT 7400	x	...	x
Chemeon TCP	x	x	x
Chemseal 100	x	x	x
Emerald Seal 308	x	x	x
SBond S-10	x	x	x
SurTec 555	x
SurTec 580	...	x	...
SurTec 650	x	x	...
Xbond 4000	x	x	x
Zircoseal 200	x	x	x

2.2 Test Methodologies

2.2.1 Accelerated Corrosion: Neutral Salt Fog (ASTM B117¹⁷)

The test coupons of anodized AA 2024-T3, IVD aluminum-coated 4130 steel, and zinc-electroplated 4130 steel were placed in neutral salt fog using an AutoTechnology Standard Salt Fog Chamber (Model 22) (Fig. 1), fixed in polypropylene trays, and mounted with hanger holes oriented toward the bottom to avoid corrosion products running down the face of the panel from the hole. The primary surface faces outward at an angle no more than 15° from the vertical. Neutral salt fog conditions are 95 °F with saturated humidity and an atomized fog of a certified 5% NaCl solution. Daily fog deposit volumes, pH, and other records are available upon request. Test panels were evaluated using criteria based upon the sealed substrate. For anodized AA 2024-T3, test coupons were made in sets of five, measured 3 × 10 inches in size, and were exposed for 336 h. More than 15 isolated pits across the set or 5 isolated pits on any individual test coupon indicated failure. A 0.062-inch border was afforded around the edges of the panels and contact points when determining pits. IVD aluminum-coated 4130 steel test coupons were similarly made in sets of five and measured 3 × 10 inches. Three IVD coating thicknesses were tested, Class 1, Class 2, and Class 3, for exposures of 672, 504, and 336 h, respectively. Any evidence of corrosion of the base metal was considered failure, though white corrosion products on the IVD aluminum surface were acceptable. Electroplated zinc coupons were made in sets of five and measured 3 × 6 inches in size. These samples were exposed for 12 h. The appearance of any corrosion products, emerging from the base metal or plating, was considered a failure. A summary of these conditions are presented in Table 3. Upon completion of testing, the panels were rinsed in DI water, air dried, and scanned on a flatbed scanner.



Fig. 1 Neutral salt-fog corrosion chambers used for testing

Table 3 ASTM B117 corrosion exposure times

Surface finish	Specification	Coating classification	Exposure time (h)
Anodized (AA 2024-T3)	MIL-A-8625 ¹²	Type III	336
IVD Al (4130 Steel)	MIL-DTL-83488D ¹³	Class 1	672
		Class 2	504
		Class 3	336
Electroplated Zn (4130 Steel)	ASTM B633-11 ¹⁵	Fe/Zn 25	12

2.2.2 Paint Adhesion: Wet Tape Adhesion Test (ASTM D3359¹⁸/FED-STD-141¹⁹)

Test coupons of anodized AA 2024-T3, IVD aluminum-coated 4130 steel, and zinc-electroplated 4130 steel panels in sets of three per posttreatment sealer were primed and painted with the chemical agent resistant coating (CARC) system in accordance with MIL-DTL-53072¹⁶ and allowed to fully cure before undergoing adhesion testing. The full CARC system is described in Table 4. Adhesion testing was done in accordance with FED-STD-141 Method 6301 and rated according to ASTM D3359 Procedure A. Test coupons were immersed in DI water for a period of 24 h, and then were removed and dried with a soft cloth. Two parallel lines, 1 inch apart, were scribed into the coating, through to the substrate. A 1-inch-wide piece of 3M 250 Flatback Masking Tape, roughly 7 inches long, was then affixed to the panel across the scribes and pressed into place using a roller. The tape was then removed at as close to a 180° angle as possible in a consistent and rapid motion. The coupons were then visually assessed for damage in accordance with ASTM D3359.

Table 4 Coatings system stack-up

Surface Finish	Primer	Topcoat
Anodized	MIL-PRF-23377N ²⁰	MIL-DTL-53039 TIV ²¹
IVD Al – Class 3 (AA 2024-T3)	MIL-PRF-23377N	MIL-DTL-53039 TIV
IVD Al – Class 3 (4130 steel)	MIL-DTL-53022 TIV ²²	MIL-DTL-53039 TIV
IVD Al – Class 3 (Ti-4AL-6V)	MIL-DTL-53022 TIV	MIL-DTL-53039 TIV
Electroplated Zn	MIL-DTL-53022 TIV	MIL-DTL-53039 TIV

2.2.3 Abrasion Resistance

Abrasion resistance was determined in accordance with International Standard ISO 10074.²³ To allow mounting of the test panel to the 5135 Taber Rotary Abrasion rotary table (Fig. 2), a 6.35-mm (0.25-inch)-diameter hole was drilled in the center of each test panel. The samples were then individually weighed with a precision balance prior to testing and their weight recorded. The Taber abrasion tester was set up with CS-17 abrasion wheels and the 1000-g counter weights to the pivot arm, and the rotary table was set to 60 RPM. Each sample was placed on the rotary table spindle and clamped down using the retaining ring and nut. The weighted arm for the Taber abrasion machine was placed so the CS-17 abrasion wheels rested on the surface of the anodized-coated test panel, and the laboratory temperature and humidity were recorded.

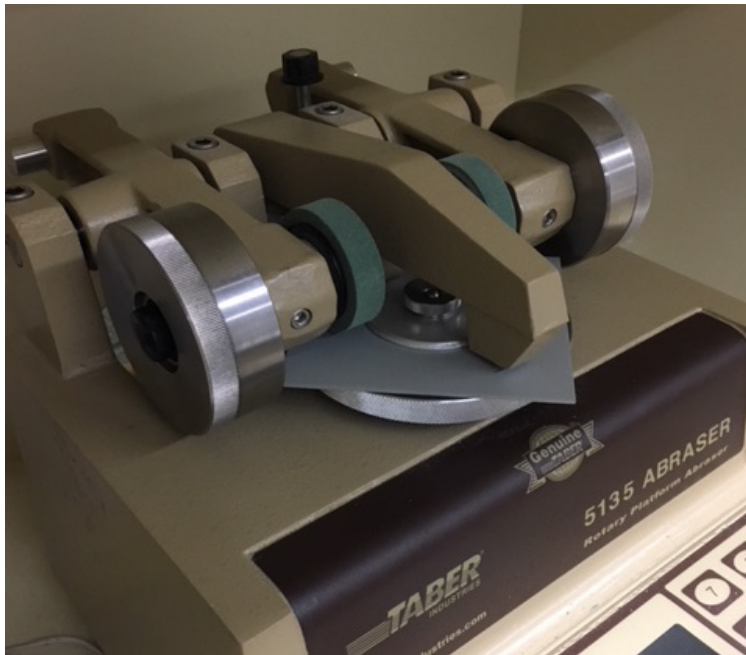


Fig. 2 Taber abrasion test setup

The vacuum nozzle of the Taber abrasion tester was adjusted to approximately 2–3 mm off the sample surface at 50% vacuum so debris from the abrasion process could be removed during operation. The CS-17 abrasion wheels were resurfaced using S-11 resurfacing paper following each test panel.

The Type III anodized test samples were run for 1,000 revolutions, weighed, and then placed back on the Taber abrasion machine to complete an additional 10,000 revolutions. After test completion, the samples were then removed from the abrasion tester and their final weights recorded.

Working with AMCOM G-4 and relevant specifications, performance objectives were established for the sealed legacy coatings. A full overview of the performance objectives are given in Table 5.

Table 5 Performance objectives

	Test methods	Data requirements	Performance objectives
MIL-A-8625 Anodize	Accelerated Corrosion	ASTM B117 ¹⁷ MIL-A-8625 ¹²	No more than 15 pits over 5 test panels, no more than 5 pits on any one panel, no signs of streaking, spotting, marks, or patchy gray areas
	Paint Adhesion	ASTM D3359 Procedure A ¹⁸ FED-STD-141 Method 6301 ¹⁹	No intercoat separation, adhesion rating $\geq 4A$
	Abrasion Resistance	MIL-A-8625, ISO 10074, Section 8.4 ²³	Max mass loss of 3 mg
MIL-DTL-83488 IVD Al	Accelerated Corrosion	ASTM B117 MIL-DTL-83488 Section 4.4.3 ¹³	No corrosion of base metal (white corrosion products acceptable)
	Paint Adhesion	ASTM D3359 Procedure A FED-STD-141 Method 6301	No intercoat separation, adhesion rating $\geq 4A$
ASTM B633 Zn Plating	Accelerated Corrosion	ASTM B117 ASTM B633	No corrosion products acceptable
	Paint Adhesion	ASTM D3359 Procedure A FED-STD-141 Method 6301	No intercoat separation, adhesion rating $\geq 4A$

3. Results

3.1 Anodized Aluminum, MIL-A-8625 Type III

3.1.1 Accelerated Corrosion

A set of five AA 2024-T3 panels for each sealer were exposed in ASTM B117 neutral salt fog for 336 h. Upon completion of the 336 h, the panels were removed and rinsed in DI water prior to inspections. Evaluations were made with respect to the number of pits on the panel. The performance objective is no more than 5

isolated pits on any individual panel, or no greater than 15 pits across the entire set of panels (150 square inches). No posttreatment sealer, chromic acid, or alternative was able to fully meet the performance objectives as written in the specification. Figure 3 shows the number of pits averaged across a set of five panels. The baseline chromic acid sealer was observed to have the least amount of pits across the set of panels, averaging approximately five pits per panel (Fig. 4). Three of the five baseline chromic acid-sealed panels tested had greater than 5 pits per panel, thus exceeding the 15 pits allowed over the entire set of panels and failing to meet the performance objective as required in MIL-A-8625. The alternative sealer with the least number of pits per panel was the Bonderite M-NT 7400, which showed an average of approximately 14 pits per panel (Fig. 5). Several posttreatment sealers performed poorly in salt fog testing in that they had in excess of 100 pits per panel. The final acceptance criteria given were a visual inspection, that no panel tested show signs of streaking, spotting, marks, or patchy gray areas. In this respect, all panels tested failed as well.

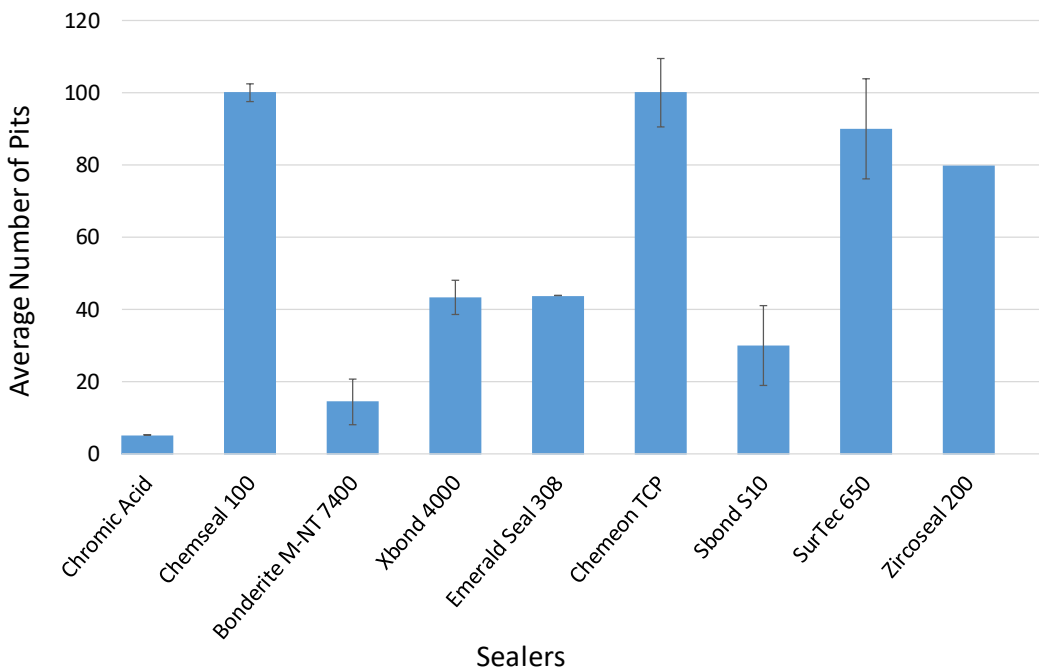


Fig. 3 Average number of pits per panel for sealed MIL-A-8625 Type III following 336 h of ASTM B117



Fig. 4 Chromic acid-sealed anodized panel

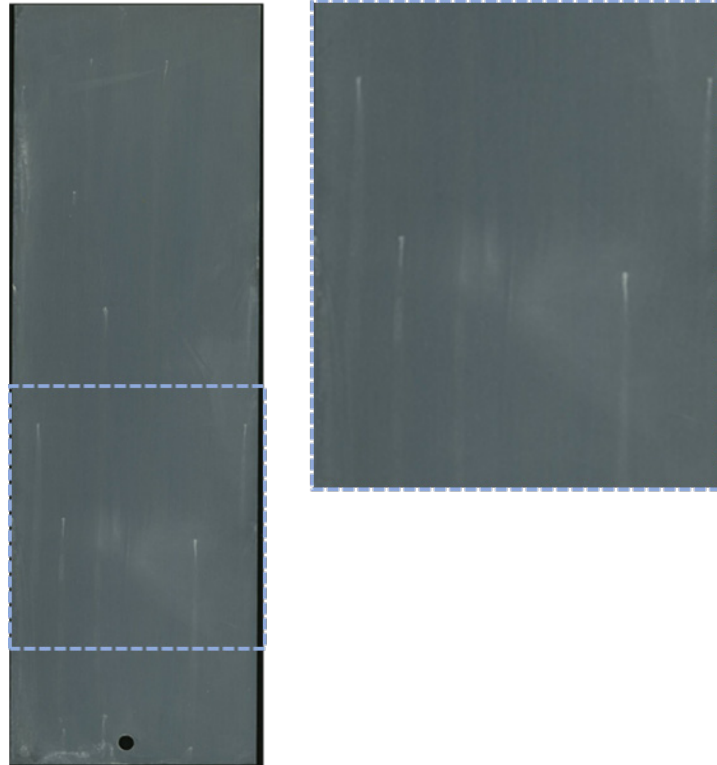


Fig. 5 Bonderite 7400-sealed anodized panel

3.1.2 Wet Adhesion

Three test coupons per sealer of anodized AA 2024-T3, primed with MIL-PRF-23377²⁰ and topcoated with MIL-DTL-53039,²¹ were tested in accordance with FED-STD-141¹⁹ Method 6301 and rated in accordance with ASTM D3359.¹⁸ Ratings were to be 4A or greater in order to be considered passing, and no intercoat separation was accepted. All panels tested were considered to pass. The results are given in Fig. 6. A sample of imaged coupons is given in Fig. 7.

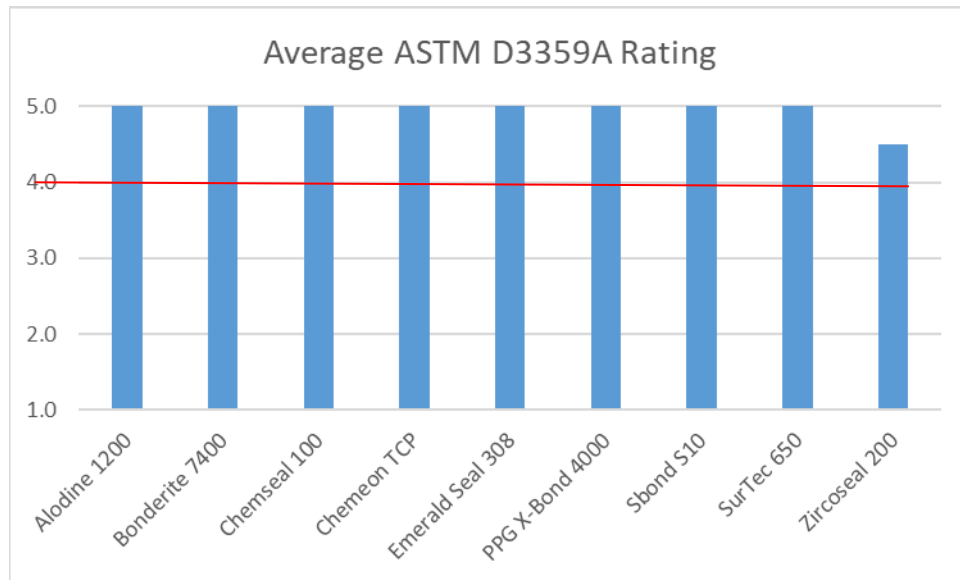


Fig. 6 Adhesion ratings on coated anodized panels

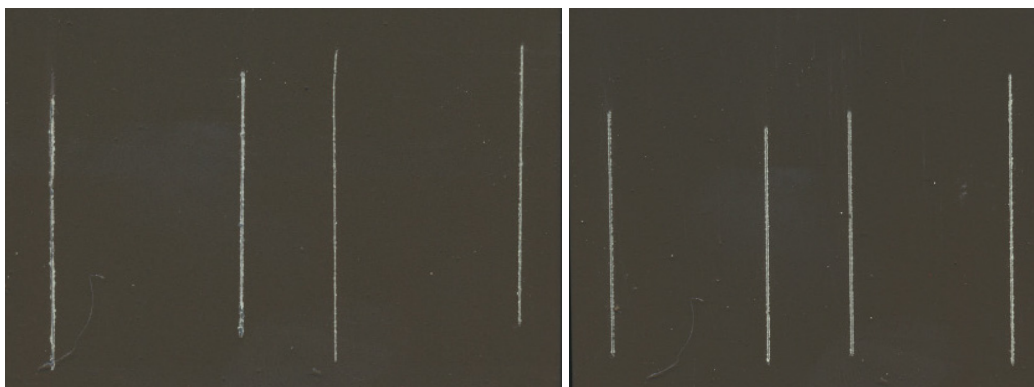


Fig. 7 Adhesion results on Alodine 1200 (L) and Bonderite M-NT 7400 (R)

3.1.3 Abrasion Resistance

Abrasion resistance of sealed Type III hardcoat anodizing on AA 2024-T3 showed little variation in terms of mass loss when examined at 1,000 cycles. After an additional 10,000 cycles (1,001–11,000 cycles), more divergence is shown in the wear resistance of the coatings having different posttreatment sealers. Chemseal

100-, Zircoseal 200-, and X-Bond-4000-sealed samples yielded more mass loss (28.44%, 42.55%, and 29.24% respectively) to abrasion than the unsealed control samples. The Bonderite M-NT 7400, SBond S10, and Chemeon TCP also incurred higher mass losses than the baseline chromic acid-sealed samples, but significantly less than the aforementioned alternative posttreatment sealers. The remaining sealers, SurTec 650 and Emerald Seal 308, all provided better abrasion resistance than the control samples, with the SurTec 650 sustaining 10% less and the Emerald Seal 308 with 28.5% less in mass loss. These two sealers tended to have more consistent results compared with the control samples as well, as seen in the error bars in Fig. 8. All of the posttreatment sealers tested exceeded the maximum allowable mass loss of 35 mg.

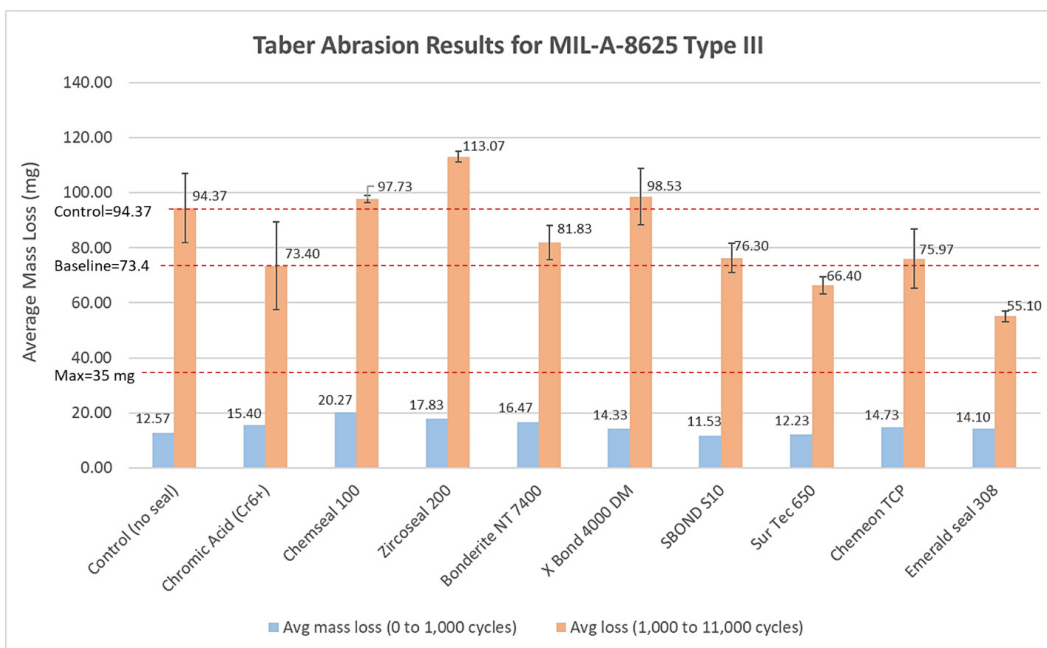


Fig. 8 Taber abrasion results of sealed anodized panels

3.2 IVD Aluminum

3.2.1 Accelerated Corrosion

Sets of five panels were exposed in ASTM B117¹⁷ in neutral salt fog for durations based upon the three thicknesses of panels tested (672 h for Class 1, 504 h for Class 2, and 336 h for Class 3). Inspections were made based on percent area corroded on each panel. Figure 9 shows the averaged percent corrosion across each set of panels and for each thickness tested. In general, the thinner the IVD aluminum coating, the higher the percent of substrate corrosion observed. For the thinnest coating (Class 3), the posttreatment sealers containing CrVI (Fig. 10) and the

trivalent chromium (CrIII)-containing Chemeon TCP (Fig. 11) performed similarly with respect to corrosion inhibition.

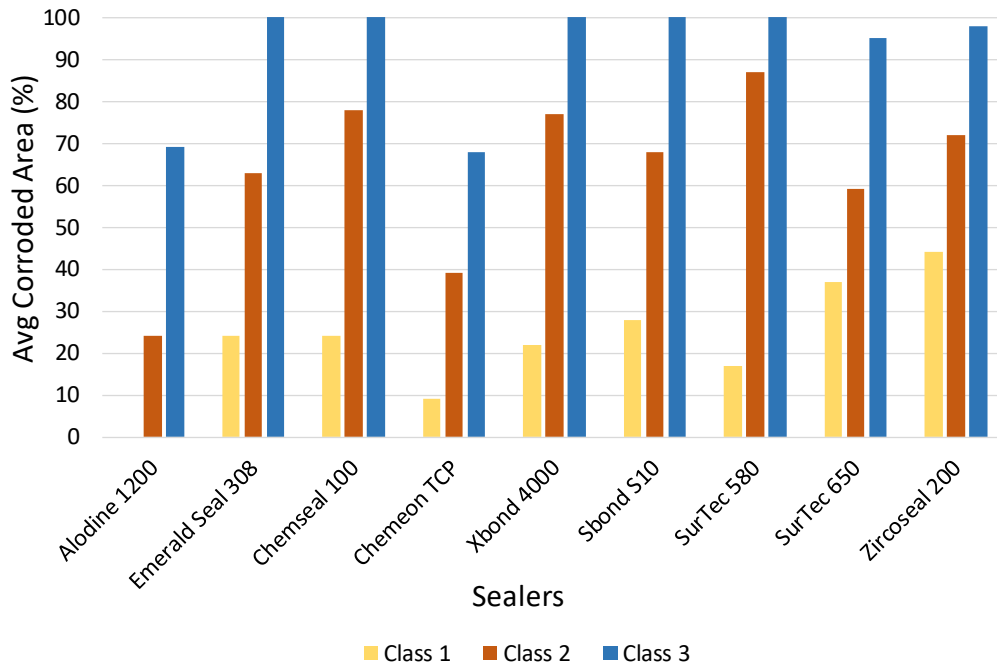


Fig. 9 Average area corroded of IVD aluminum-coated and sealed 4130 steel substrate

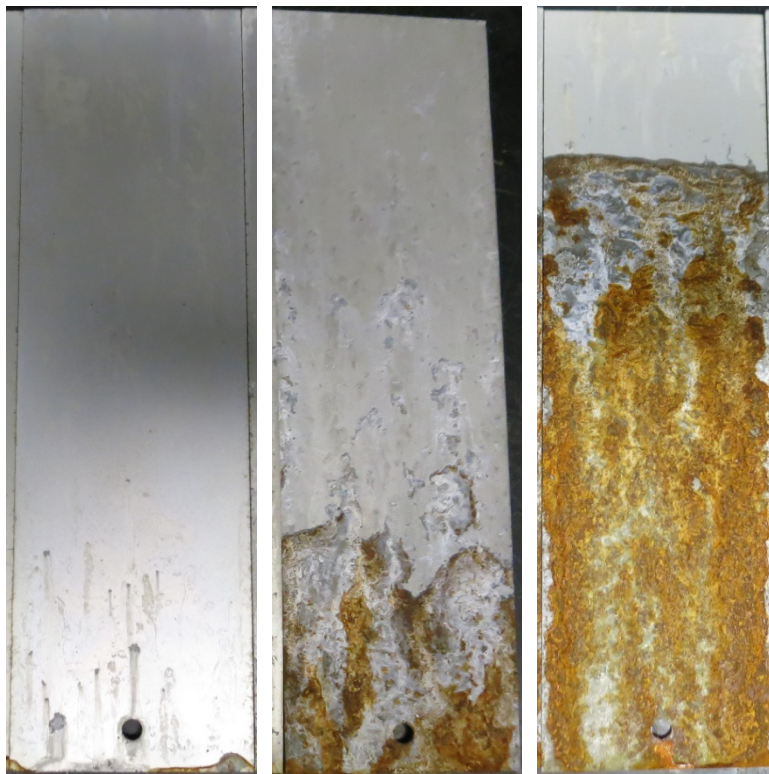


Fig. 10 CrVI-sealed IVD Al panels (left to right): Class 1, Class 2, and Class 3

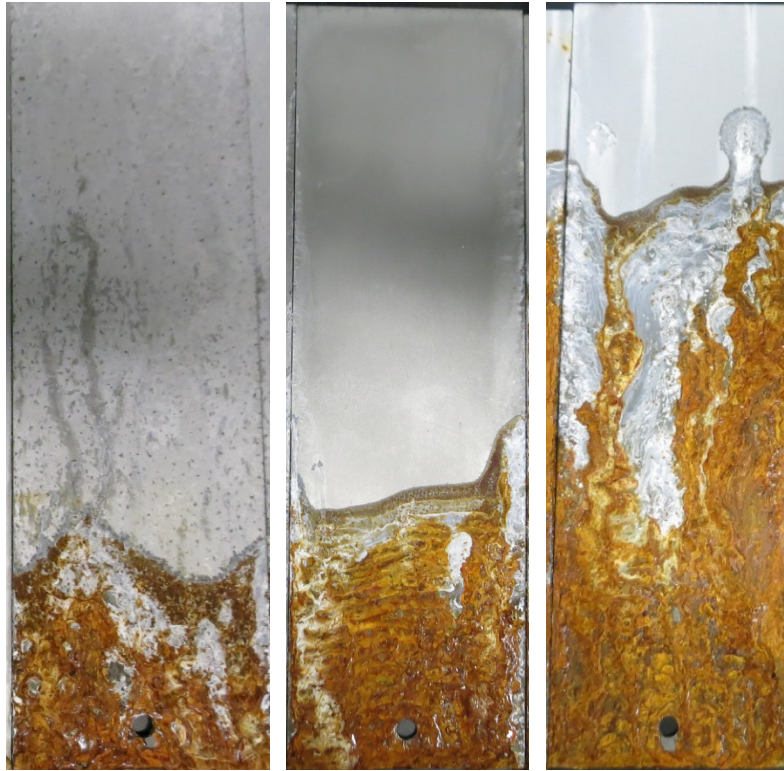


Fig. 11 Chemeon TCP-sealed IVD Al panels (left to right): Class 1, Class 2, and Class 3

Although the Class 2 coatings had more varied results, the CrVI containing Alodine 1200 baseline clearly outperformed all alternative posttreatment sealers. Of the alternatives containing CrIII, Chemeon TCP showed the least amount of corrosion. The Emerald Seal 308 could be a viable chromium-free alternative on thicker IVD aluminum coatings (Fig. 12).

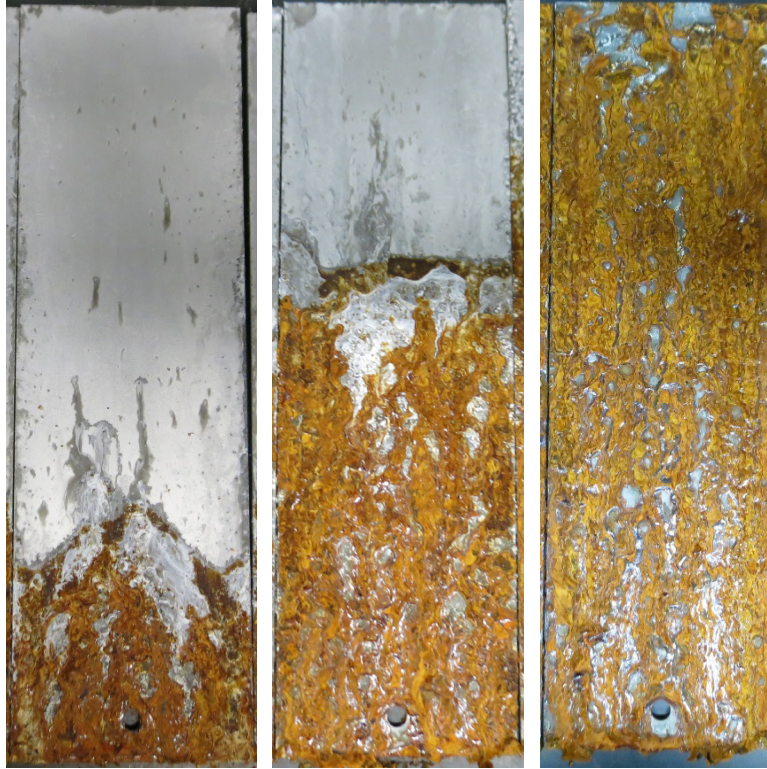


Fig. 12 Emerald Seal 308-sealed IVD Al panels (left to right): Class 1, Class 2, and Class 3

Posttreatment sealers on the thickest IVD aluminum (Class 3) performed well regardless of sealer. In this case, the CrVI-sealed panels had negligible corrosion, and the Chemeon TCP posttreated panels were under 20% corroded. Of the other alternative sealers on the thinnest (Class 1) coating, only the Zirco seal 200 allowed for greater than 40% corrosion while the Emerald Seal 308, Chemseal 100, and Xbond 4000 allowed just above 20%. The overall trend—the thicker the coating the better the resistance to corrosion—was expected, as fewer continuous pathways to the substrate through the porous coating exist.

3.2.2 Wet Adhesion

Three substrates were used for adhesion testing of IVD aluminum: 4130 steel, Ti-6AL-4V, and AA 2024-T3. After being IVD-coated and sealed, the AA 2024-T3 panels were primed with MIL-PRF-23377²⁰ and topcoated with MIL-DTL-53039,²¹ while the 4130 steel and Ti-6Al-4V panels were primed with MIL-DTL-53022²² and topcoated with MIL-DTL-53039. Panels were tested in accordance with FED-STD-146 Method 6301¹⁹ and rated in accordance with ASTM D3359.¹⁸ The performance requirement for wet adhesion is a rating of 4A or greater with no intercoat separation. Several posttreatment sealers were unable to meet this performance objective. Chemseal 100 failed adhesion on the IVD aluminum-coated AA 2024-T3; Chemeon TCP failed adhesion on both AA 2024-T3 and 4130 steel;

SurTec 650 failed adhesion on both AA 2024-T3 and Ti-6Al-4V; and Zircoseal 200 failed on Ti-6Al-4V as well.

Despite all substrates being coated with Class 3 IVD aluminum, sealer performance varied across substrates in some cases. This discrepancy in performance led to a review of the coating practices of the test panels. This review revealed that the primer thicknesses varied across the panels. Additionally, two different primers were used. The aluminum substrate panels were coated with MIL-PRF-23377,²⁰ while the steel and titanium substrate panels were primed with MIL-DTL-53022.²² Each substrate set was primed separately as a group. The varied performance observed could be explained in part by these coating inconsistencies, as the adhesion assessment is between the sealer over IVD aluminum, and performance should not be a function of the substrate under the IVD aluminum. These results are given in Tables 6 and 7 and illustrated in Figs. 13 and 14.

Table 6 Adhesion ratings for Class 3 IVD aluminum-coated 4130 steel, AA 2024-T3, and Ti-6Al-4V panels

Material	Alodine 1200	Emerald Seal 308	Chemseal 100	Chemeon TCP	Xbond 4000	Sbond S10	SurTec 580	SurTec 650	Zircoseal 200
Steel	4	4.3	5	3.7	4.7	5	5	5	5
Aluminum	5	5	3.3	3.3	4.7	5	4.7	2.7	4.3
Titanium	4.3	4.7	4	4	4	4.7	4.7	2.3	3.7

Note: Results with gray shading indicate failure to meet performance objective.

Table 7 Primer thicknesses (mils) for Class 3 IVD aluminum across each substrate

Material	Primer	Avg Top	Avg Mid	Avg Bottom	Total Avg
Steel	53022	3.44	3.37	3.31	3.37
Aluminum	23377	2.74	2.65	2.67	2.69
Titanium	53022	2.97	2.52	2.14	2.54

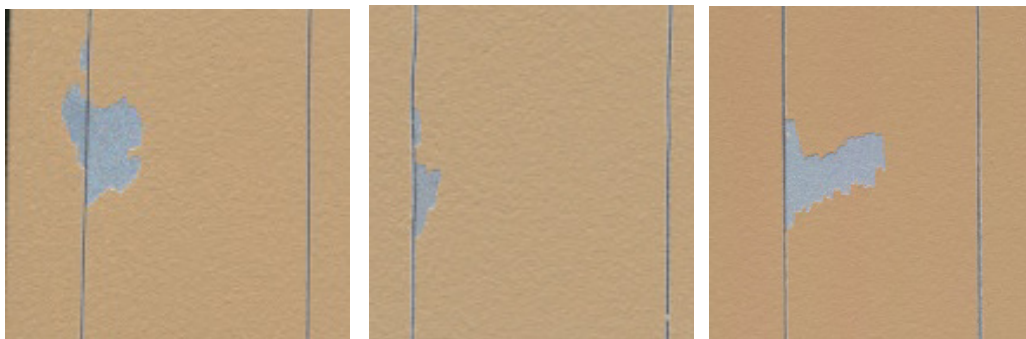


Fig. 13 Chemeon TCP-sealed IVD Al on AA 2024-T3 (L), Ti 4AL 6V (C), and 4130 steel (R)



Fig. 14 SurTec 650-sealed IVD Al on AA 2024-T3 (L), Ti 4AL 6V (C), and 4130 steel (R)

3.3 Electroplated Zinc

3.3.1 Accelerated Corrosion

Sets of five test coupons of each sealer were subjected to ASTM B117¹⁷ neutral salt fog for a 12-h duration. According to ASTM B633¹⁵ electroplated zinc with Type II colored CrVI-containing posttreatment such as sodium dichromate can pass 96 h of ASTM B117 salt spray testing, whereas the same substrate posttreated with colorless CrIII passivation shall withstand only 12 h. The testing of multiple posttreatment sealers on electroplated zinc against sodium dichromate revealed that none of the commercial off-the-shelf chromium-free or CrIII posttreatments tested were able to meet even the 12-h salt spray requirement. Per ASTM B633, any appearance of corrosion products constitutes failure. After exposure, only the Type II colored chromate-sealed panels met the performance objectives. The majority of the other sets tested experienced total corrosion across the surface of the panels tested, including those sealed with CrIII. Bonderite M-NT 7400 was an exception, in that there were still large areas across each panel without corrosion. These images can be seen in Figs. 15–17.

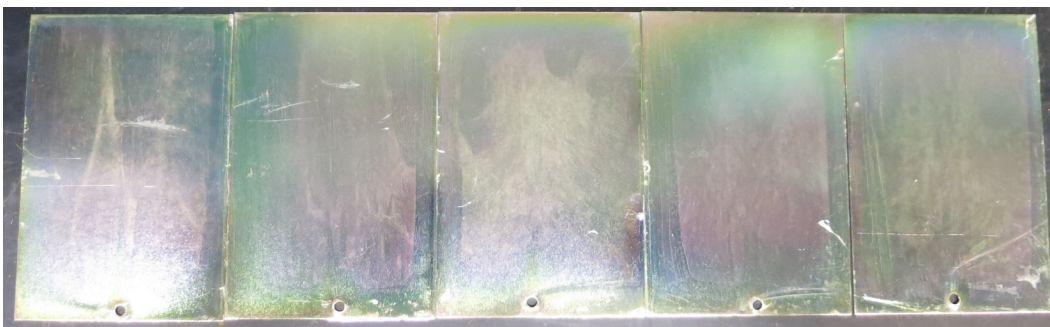


Fig. 15 ASTM B633 Type II colored chromate-sealed electroplated zinc



Fig. 16 Bonderite M-NT 7400-sealed electroplated zinc



Fig. 17 Chemeon TCP-sealed electroplated zinc

3.3.2 Wet Adhesion

Three test coupons per sealer of electroplated zinc over 4130 steel, primed with MIL-DTL-53022²² Type IV and topcoated with MIL-DTL-53039,²¹ were tested in accordance with FED-STD-141 Method 6301 and rated in accordance with ASTM D3359.¹⁸ Ratings must be 4A or greater in order to meet the performance objective, and no intercoat separation is acceptable. All sealed test panels tested surpassed the performance objectives with all achieving a rating of five. The examples given in Figs. 18 and 19 display that no lifting of the coating or intercoat separation occurred, and they are representative of the results seen on all samples tested.

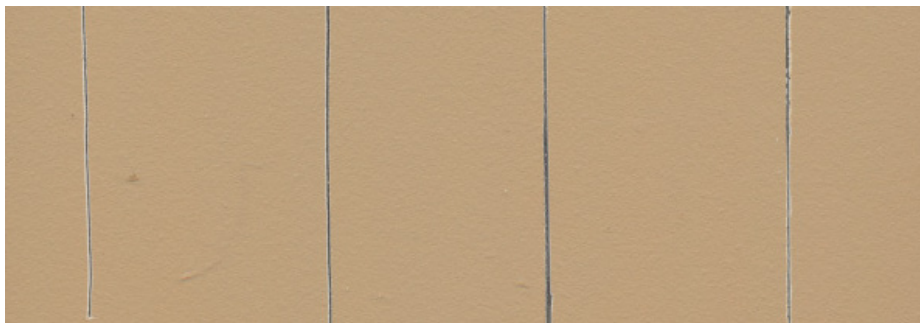


Fig. 18 Adhesion results on Alodine 1200



Fig. 19 Adhesion results on CHEMEON TCP

4. Summary and Conclusions

The only posttreatment for anodized AA 2024-T3 that was able to meet the accelerated corrosion pitting requirement IAW MIL-A-8625¹² was the chromic acid seal. The Bonderite M-NT 7400 provided good corrosion protection for the anodized aluminum; however, this came at a sacrifice to abrasion resistance. Emerald Seal 308 maintains the best abrasion resistance and provides good corrosion protection. This sealer would be preferred for MIL-A-8625 Type III coatings where abrasion resistance and corrosion protection is desired.

The CHEMEON TCP provided better corrosion protection on IVD aluminum surfaces than on Type III anodized aluminum. Although paint adhesion ratings of CARC over CHEMEON TCP-sealed IVD aluminum varied, it proved to be the best candidate for corrosion protection on IVD aluminum. However, if a nonchromium-containing posttreatment sealer is desired, Emerald Seal 308 or the SBond S10 should be considered as both provided better adhesion for organic coatings.

In general, the CrVI-containing posttreated coatings outperformed all of the alternatives in accelerated corrosion testing with few exceptions. This was especially true on electroplated zinc. Although the nonchromium-containing Bonderite N-MT 7400 provided better corrosion protection than the CrIII-containing CHEMEON TCP, none of the alternatives could come close to meeting the corrosion requirements for CrVI specified in ASTM B633.¹⁵

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List of Symbols, Abbreviations, and Acronyms

AA	aluminum alloy
ACGIH	American Conference of Governmental Industrial Hygienists
AERTA	Army Environmental Requirements Technology Assessment
AMCOM	US Army Aviation and Missile Command
ANAD	Anniston Army Depot
ARL	Army Research Laboratory
CARC	chemical agent resistant coating
CCAD	Corpus Christi Army Depot
CFR	Code of Federal Regulations
CrIII	trivalent chromium
CrVI	hexavalent chromium
DC	direct current
DEVCOM	US Army Combat Capabilities Development Command
DI	deionized
DOD	Department of Defense
EPA	Environmental Protection Agency
EU	European Union
IARC	International Agency for Research on Cancer
IAW	in accordance with
IRIS	Integrated Risk Information System
IVD	ion vapor deposition
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
RPM	revolutions per minute

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