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Testing of Zirconium-based Pretreatments at NASA Kennedy Space Center's Beachside Atmospheric Corrosion Test Site

by Daniel Pope, Fred Lafferman, Mark Kolody,
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14. ABSTRACT The objective of this work was to optimize zirconium-based pretreatment applications in a lab setting and test samples using a galvanic panel with stainless steel fasteners. The zirconium-based pretreatments were applied at the same time using the same cleaning and deoxidizing methods as currently approved hexavalent and trivalent chromium conversion coatings. The panels were then primed with chrome-free aviation primer and chemical-agent-resistant topcoat. The galvanic panels were exposed for 1 year at Kennedy Space Center’s Beachside Atmospheric Corrosion Test Site in Florida and monitored for corrosion on a monthly basis. This effort identifies performance of possible hexavalent chromium conversion coating alternatives in an aggressive outdoor environment.					
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1. Introduction

The Chemical Agent Resistant Coating (CARC) System application and inspection specification, MIL-DTL-53072,¹ requires that metal surfaces on tactical assets be treated to improve adhesion and corrosion resistance prior to coating with an epoxy primer and a camouflage topcoat. However, there are a multitude of problems associated with currently fielded legacy pretreatment technologies, including the use of hexavalent chromium (Cr^{6+}). Problems inherent with the chromate conversion coatings begin with the potential exposure to hazardous materials of paint, pretreatment, and blast media applicators during the application and removal processes and the associated Occupational Safety and Health Administration (OSHA) impacts. Additionally, continually increasing costs associated with disposal of wastes contaminated with Cr^{6+} and the Resource Conservation and Recovery Act impacts add to the issues experienced when fielding legacy pretreatments. A major issue is the potential for near-term obsolescence as these materials are facing increasing regulatory scrutiny with several recently revised specifications already eliminating their use. Verification of suitable alternatives will continue to be crucial as the Cr^{6+} -containing products are prohibited. Numerous international Cr^{6+} regulations affect the usage of coatings containing these compounds and thus already impact maintenance and repair in overseas posts. To be ready when additional regulations outright ban these products, the US Army needs to take action proactively. The primary objective of this testing is to demonstrate and validate novel Cr^{6+} -free pretreatment technologies in relevant Department of Defense (DOD) environments. There is a need to implement innovative and cost-effective replacement technologies to address the multiple health, safety, and compliance issues associated with the legacy systems while maintaining military readiness for national defense. In addition, the new technology must have the following attributes: 1) compatibility with original equipment manufacturer/depot infrastructure, 2) corrosion performance equivalent to (or better than) current Cr^{6+} - and phosphate-based pretreatments, 3) broad compatibility with the current suite of military coatings and, 4) compatibility with all substrates used by the DOD.

The following are the regulatory drivers that serve as justification for testing, validation, and demonstration of non Cr^{6+} pretreatment coatings:

- 1) OSHA regulation 1910.1026²: Regulatory requirements and allowable exposures to Cr^{6+}
- 2) DOD policies³ minimizing the use of hexavalent chromium (Cr^{6+})

- 3) Directive-Type Memorandum (DTM), DTM 12-003, *Control and management of surface accumulations from lead, hexavalent chromium, and cadmium operations memorandum for minimizing the use of hexavalent chromium (Cr+6)*⁴
- 4) Code of Federal Regulations (CFR) 48 § 223.73, *Minimizing the use of materials containing hexavalent chromium*. Defense Federal Acquisition Regulation Supplement and Procedures, Guidance, and Information⁵
 - a. Prohibition (223.7303): As provided in CFR policy 223.7301, no DOD contract may include a specification or standard that results in a deliverable containing hexavalent chromium or the use of hexavalent chromium during sustainment phases of any aviation system. This prohibition is in addition to any imposed by the Clean Air Act and applies to all DOD contracts awarded after 8 Apr 2009, regardless of the place of performance.
 - b. Exceptions (223.7304): The prohibition in 223.7303 does not apply if the use of hexavalent chromium in a specification or standard is specifically authorized at a level no lower than a general or flag officer or a member of the Senior Executive Service from the Program Executive Office or equivalent level, in coordination with the component Corrosion Control and Prevention Executive. The prohibition in 223.7303 does not apply to legacy systems and their related parts, subsystems, and components that already contain hexavalent chromium. However, alternatives to hexavalent chromium should be considered during aviation system modifications, new procurements of legacy systems, or maintenance procedure updates.
- 5) The European Union's (EU's) Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)⁶ regulation will potentially impact maintenance and repair in the near future as many of the chemicals used (precursor and final products) reach their "sunset" dates. These "sunset" dates will eliminate any future production as well as severely limit or totally restrict the US Army's ability to transport, store, use, and dispose of these chemicals in the EU without specific authorization/exemption.
- 6) Memorandum from John Young, Under Secretary of Defense, Acquisition, Technology and Logistics, to Secretaries of Military Departments, *Minimizing the use of hexavalent chromium*⁷

- 7) *Reduction of toxic materials in Army surface finishing processes: environmental requirement and technology assessment* report completed by the US Army Aviation and Missile Command⁸
- 8) US Army Environmental Requirements and Technology Assessment (AERTA) requirement, AERTA PP-2-02-04, *Toxic metal reduction in surface finishing of Army weapon systems*, specifically the requirement for an alternative to Cr⁶⁺ conversion coating⁹

This testing supporting US Army Toxic Metal Reduction Program for Cr⁶⁺-free conversion coatings will eliminate the usage of both hexavalent and trivalent chromium in the pretreatment of aluminum substrates prior to application of the CARC coating system. This includes limiting the waste stream generated from the application and removal of existing legacy pretreatments from operating depot and corrosion repair locations. The alternative chrome-free pretreatments will be validated for corrosion resistance against the baseline chromate-containing pretreatments while exposed at NASA Kennedy Space Center's (KSC's) Beachside Atmospheric Corrosion Test Site in Florida.

The purpose of this effort is to test chrome-free surface treatments, as part of the coating stack-ups commonly seen on Army aviation assets, on galvanic panels that include aluminum and stainless steel. The chrome-free treatments will be compared to currently fielded legacy materials that are approved to MIL-DTL-81706,¹⁰ including hexavalent and trivalent chromium products. The panels will all be cleaned and prepared in a fashion similar to what is currently used to qualify products to the MIL-DTL-81706 specification at the Naval Air Systems Command (NAVAIR) at Patuxent River Naval Air Station (Patuxent River, Maryland).

2. Technical Approach

Zirconium pretreatments will be tested and evaluated through laboratory application and static outdoor testing. The products tested are mature technologies presently manufactured and supplied to either industrial or military users, but not yet approved for Army application. Zirconium pretreatments provide a high-quality, continuous zirconium-based pretreatment on multiple types of ferrous, zinc, and aluminum substrates by immersing the metal into a dilute solution of fluorozirconic acid (FZA) at ambient temperature for 30–120 s. It is important that products tested can be applied via immersion and spray with minor formulation adjustments. The dilute, aqueous FZA pretreatment bath has a pH of 4.5 and does not contain any volatile organic compounds. During the treatment process, the substrate is etched slightly, which results in a pH increase at the substrate/solution interface. This change in pH results in the precipitation and subsequent bonding of

zirconium oxide and additives to the surface of the substrate. The chemistry does not contain any regulated heavy metals such as chromium or nickel. Other environmental and performance benefits include 1) significant reduction (>90%) in the amount of sludge byproducts produced, 2) reduced energy consumption since the process can operate at ambient temperatures and requires less stages, 3) reduced material usage since the coating thicknesses are only 20–50 nm, and 4) multi-substrate application. Presently this technology is used within the automobile industry as a replacement for both zinc phosphate and Cr⁶⁺ by immersion technology.

Zirconium pretreatments will be applied via immersion to bare test coupons per manufacturer's recommendations. This does not include using the manufacturer's recommendations for cleaning the panel prior to applying the surface treatment. Instead, cleaning and deoxidation will follow the methods used by NAVAIR as part of their qualification process. This will ensure a pristine surface consistent with what will be used, or the controls. Once applied, the treated coupons will be allowed to dry and/or cure in accordance with the manufacturer's recommendations and prior to receiving a primer in accordance with MIL-PRF-23377¹¹ or MIL-PRF-85582.¹²

3. Experimental Procedure

3.1 Products

Table 1 lists the products selected for testing. The products include zirconium pretreatments from Henkel Corporation (Düsseldorf, Germany) and PPG Industries, Inc. (Pittsburgh, Pennsylvania). The controls selected are approved products on the DOD's Qualified Products Database for MIL-DTL-81706. The Type I material was Henkel's Bonderite (formerly Alodine) 1200 and is a Cr⁶⁺ conversion coating. The Type II material used was the SurTec 650 trivalent chromium conversion coating (SurTec, Inc., Brunswick, Ohio).

Table 1 Surface treatments tested

Manufacturer	Material	Chemistry	pH	Bath temp	Duration
Henkel	Bonderite 1200	Cr ⁶⁺ conversion coating (MIL-DTL-81706 Type I)	1.8–2.1	70–100 °F	2 min
SurTec	650	Trivalent chromium conversion coating (MIL-DTL-81706 Type II)	2.5–3.9	68–95 °F	3 min
Henkel	5200	Zirconium pretreatment	3–3.6	70–120 °F	2 min
PPG	X-Bond 4000	Zirconium pretreatment	4.4–5.2	60–115 °F	2 min

3.2 Coatings

The surface treatments in the test are meant to be part of a coating stack-up. To simulate what would be seen on an Army aviation asset, a Cr⁶⁺-free epoxy primer and a CARC urethane topcoat were used. Table 2 lists the coatings used in this testing.

Table 2 Primers and topcoats used in testing

Specification	Details	Product
MIL-PRF-23377 Class N	Primer: hexavalent chrome-free, high solids, solvent-based epoxy	Hentzen 16708TEP/136708CEH
MIL-DTL-53039 ¹³ Type IX	Topcoat: solvent-based urethane	Sherwin F93H00118

3.3 Test Coupons

The test panel selected was a variation of a panel presented by NAVAIR at ASETS Defense 2012.¹⁴ The setup incorporated titanium and stainless steel fasteners. Because the stainless steel fastener creates more galvanic potential with the 2024 aluminum substrate, only stainless steel fasteners were used in this test. The failures from this better match the failures seen in the field that originate from fasteners, rivets, or faying surfaces. Legacy pretreatments are not presently tested for this type of galvanic stress within the MIL-DTL-81706 specification.

All of the products were tested over 2024-T3 aluminum panels. For adhesion testing, a 4- × 6- × 0.063-inch panel was used. The surface had a mill finish. There was no chemical treatment on the panel prior to application of the test products. These panels were purchased from Q-Lab Corporation (Westlake, Ohio). For the galvanic test, large sheets of 1/4-inch-thick 2024-T3 aluminum were cut into

3- × 6-inch coupons. The panels were drilled four times using a no. 11 drill bit. Figure 1 shows the location of the holes in the panel. After the holes were drilled, all holes and edges of the panel were deburred. Once the panels were fully coated, the holes 1.5 inches from the top received an “X” scribe through the coatings, with the center of the X as the center of the bore hole. The length of each scribe was approximately 1 inch. The 316 stainless steel fasteners were dry-installed into the panel in positions noted in Fig. 1. A washer of the same material as the bolt was used on the front of the panel to ensure consistent contact with the panel. The fasteners were torqued to 100 ± 5 oz-inches. All of the fasteners were torqued from the back of the panel to prevent any unnecessary damage to the coating.

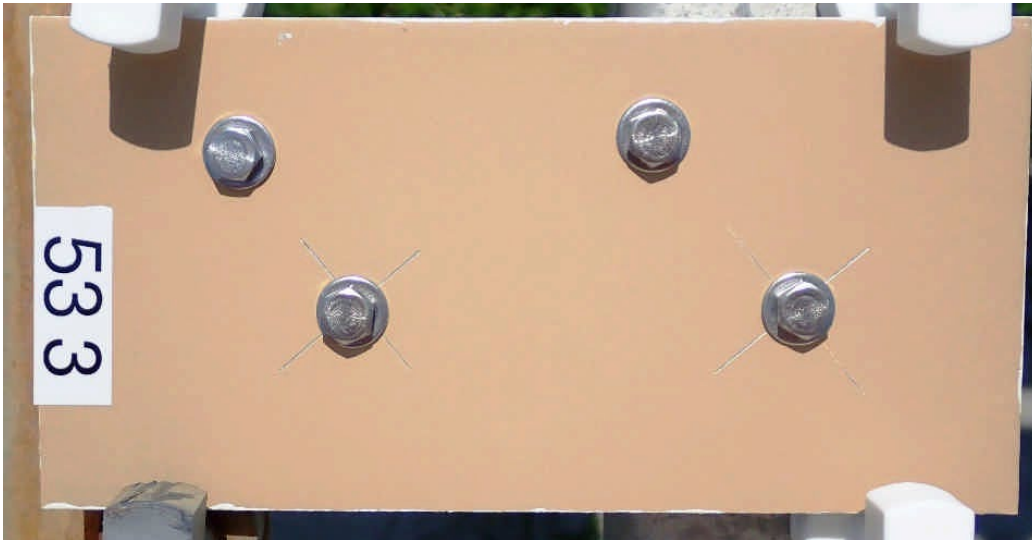


Fig. 1 Example of test panel with stainless steel fasteners. Top row of fasteners are not scribed. Bottom row of fasteners are installed over an “X” scribe in the panel.

3.4 Beachside Atmospheric Corrosion Test

The NASA KSC’s Beachside Atmospheric Corrosion Test Site is located approximately 1.5 miles south of Launch Complex 39A directly on the Atlantic Ocean at latitude $28^{\circ}59'40.6''$ N, longitude $80^{\circ}58'28.3''$ W, and approximately 150 ft from the mean high-tide line (Fig. 2). This site provides an aggressive and very corrosive high-salt, high-humidity Florida seacoast environmental exposure for the test articles. The corrosion rates measured at the site vary from 0.127 to 0.51 mm/y (5.0 to 20.0 mpy), with a weighted average of 0.28 mm/y (11.0 mpy).¹⁵ The samples placed at the atmospheric test site on 13 June 2018 were exposed for 1 year. The panels were rated every month.



Fig. 2 NASA beachside corrosion test site

Corrosion was monitored and recorded at each fastener. To determine the degree of corrosion emanating from the washer surface, series of pictorial examples (from ASTM D610¹⁶) will be used as a reference. The extent of corrosion is reported on a scale from 0–10 (worst–best.) In some cases, corrosion from the edges and scribe can make a proper evaluation impossible. For this situation, “NR” (not rated) will be listed as the rating.

4. Results

4.1 Application

For the test matrix, the manufacturer’s recommended procedures were used for the pretreatments. The cleaning and deoxidation of the panels followed NAVAIR’s process for qualification. The products used, along with immersion duration, are in Table 3. First, the panels were immersed in an aqueous alkaline degreaser for 10 min. They were rinsed afterward and tested for water break. If a water-break-free surface was not achieved, the alkaline degreaser step would be repeated. Once a water-break-free surface was achieved, the panels were immersed into the chemical milling bath for 5–10 min. Next they were immersed in the deoxidizer for 5 min. After the deoxidizer, the panels were rinsed and checked for a water-break-free surface one final time before being immersed in the pretreatment. Duration of the pretreatment immersion can be found in Table 1.

Table 3 Materials used for cleaning and surface preparation

Process	Product	Immersion duration
Alkaline degreaser	Turco 6849	10 min
Chemical milling	10% NaOH (by wt.)	5–10 min
Deoxidation	Turco Smut-Go NC	2 min

Note: NaOH = sodium hydroxide

Dates and times for application of pretreatments, primers, and topcoats are in Table 4. All of the pretreatments were given ample time to dry prior to being primed. The primer was applied approximately 2 mil wet for a dry-film build of 0.6–0.9 mil. The topcoat was applied 3–3.5 mil wet for a dry-film build of 1.5–2 mil. Panels were allowed to dry in the spray booth where the temperature was recorded between 68 and 69 °F with a relative humidity of 45%. Panels were allowed to cure for 2 weeks. After this period, all panels were edged with a brush application of MIL-DTL-53022¹⁷ Type IV primer to limit edge effects on the samples prior to start of atmospheric exposure.

Table 4 Application times

Set	Pretreated		Prime		Topcoat	
Bonderite 1200	4/10/2018	11:15	4/11/2018	7:00	4/11/2018	14:00
SurTec 650	4/10/2018	9:45	4/11/2018	7:00	4/11/2018	14:00
Bonderite 5200	4/10/2018	8:45	4/11/2018	7:00	4/11/2018	14:00
X-Bond 4000	4/10/2018	10:30	4/11/2018	7:00	4/11/2018	14:00

An immersion application was selected for testing. All four products in this test, or similarly formulated products with a different manufacturer’s code, can be used for spray application. It is important that hexavalent and trivalent chromium-free alternatives can be sprayed or immersed to meet the needs of Army aviation and ground equipment in repair settings.

4.2 Beachside Atmospheric Corrosion Results

Galvanic test panels were sent to KSC for exposure at the beachside atmospheric corrosion test site. The panels were installed on the racks 13 June 2018. The panels were installed onto test racks used for previous corrosion studies and designed according to ASTM G50.¹⁸ The racks were placed at a 30° angle facing the Atlantic Ocean in an open configuration. Inspections occurred monthly on the dates listed in Table 5.

Table 5 Inspection dates

Month	Date
Start	6/13/2018
1	7/13/2018
2	8/13/2018
3	9/13/2018
4	10/15/2018
5	11/13/2018
6	12/13/2018
7	1/16/2019
8	2/15/2019
9	3/13/2019
10	4/16/2019
11	5/13/2019
12	6/14/2019

The results of the inspections can be found in Tables 6–9. Images of each panel at the 3-, 6-, 9-, and 12-month inspections can be found in Figs. 3–14. Each pretreatment had three panels exposed. Each panel received a rating for each fastener for a total of four ratings per panel. Ratings of 7 or higher are highlighted in green and are considered passing. Ratings of 5 and 6 are highlighted in yellow and considered borderline. Ratings of 4 or lower are highlighted in red and considered failing. Areas that were not able to be accurately rated due to the spread of corrosion are marked “NR” These areas were considered failing and highlighted in red.

Results for the panels pretreated with the Cr⁶⁺-containing Bonderite 1200 are in Table 6. In general, no corrosion of concern was witnessed on the three panels until Month 5. The first failure was witnessed at Month 6 on Panel 3. Overall, areas where the fastener was dry-installed over the scribe showed more damage than fasteners dry-installed over the unscribed surface. After 12 months there are areas of significant corrosion on two of the three panels. Images for these panels at 3, 6, 9, and 12 months can be seen in Figs. 3–5. Besides the corrosion captured in Table 6, there is no other visible damage on these panels.

Table 6 Bonderite 1200 results

Pretreatment	Panel	Position	Month												
			1	2	3	4	5	6	7	8	9	10	11	12	
Bonderite 1200	A3	Top left, not scribed	10	10	10	10	10	10	10	10	10	10	10	10	10
		Top right, not scribed	10	10	10	10	10	10	10	10	10	10	10	10	10
		1 Bottom left, scribed	10	8	7	7	6	5	5	5	5	5	4	3	3
		Bottom right, scribed	10	8	7	7	6	5	5	5	5	5	5	5	4
	A3	Top left, not scribed	10	9	8	7	7	7	6	6	6	6	6	6	6
		Top right, not scribed	10	9	8	7	7	7	7	7	7	7	7	7	6
		2 Bottom left, scribed	10	9	8	8	8	7	7	7	7	7	7	7	7
		Bottom right, scribed	10	10	8	8	7	7	6	6	6	6	6	6	6
	A3	Top left, not scribed	10	10	10	10	10	10	10	10	10	10	8	8	7
		Top right, not scribed	10	10	10	10	10	10	10	10	10	10	10	10	8
		3 Bottom left, scribed	10	9	7	7	6	5	5	5	5	5	5	5	4
		Bottom right, scribed	10	7	7	7	7	4	4	4	4	4	3	3	3



Fig. 3 Panel A3-1 top-bottom: 3-, 6-, 9-, and 12-month inspection images

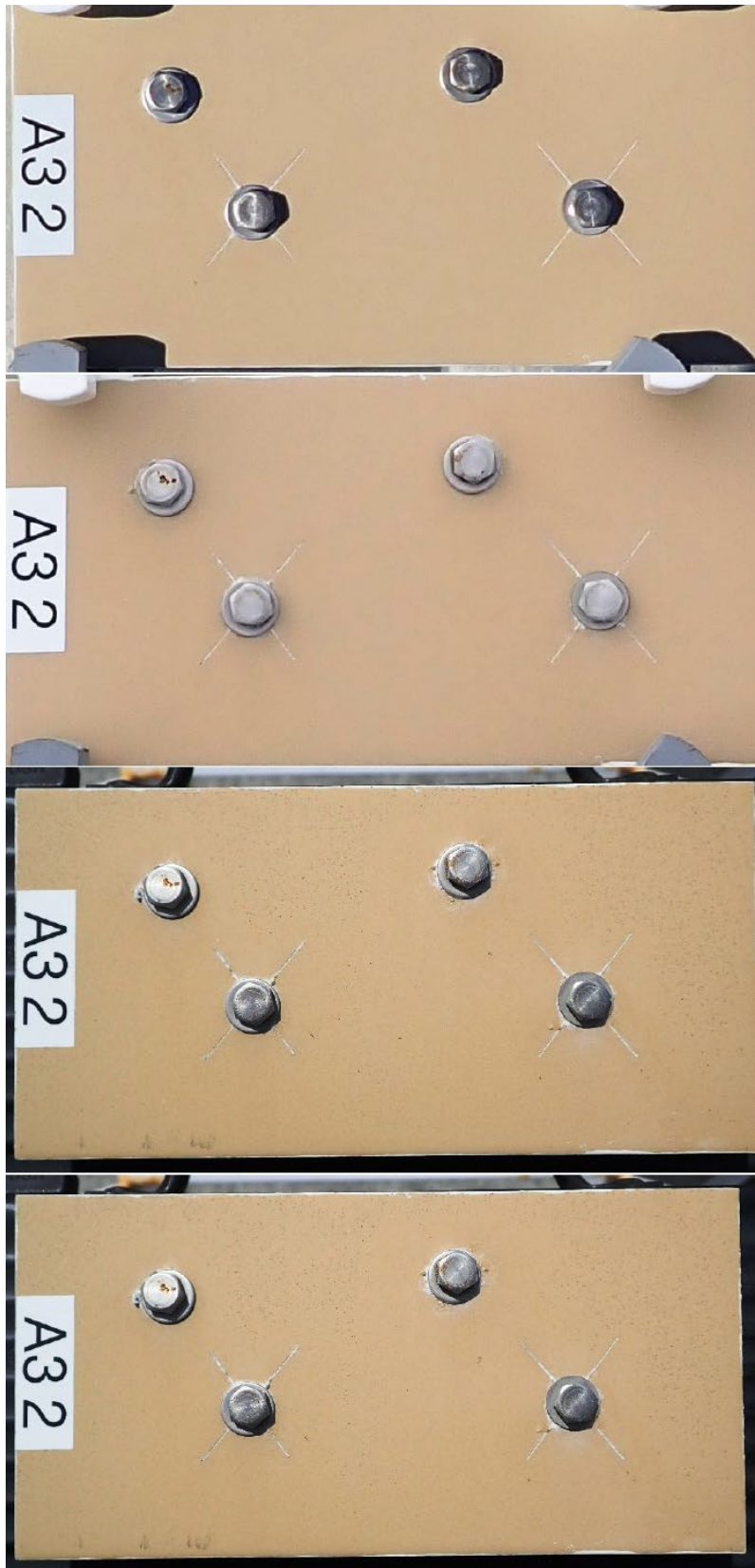


Fig. 4 Panel A3-2 top-bottom: 3-, 6-, 9-, and 12-month inspection images

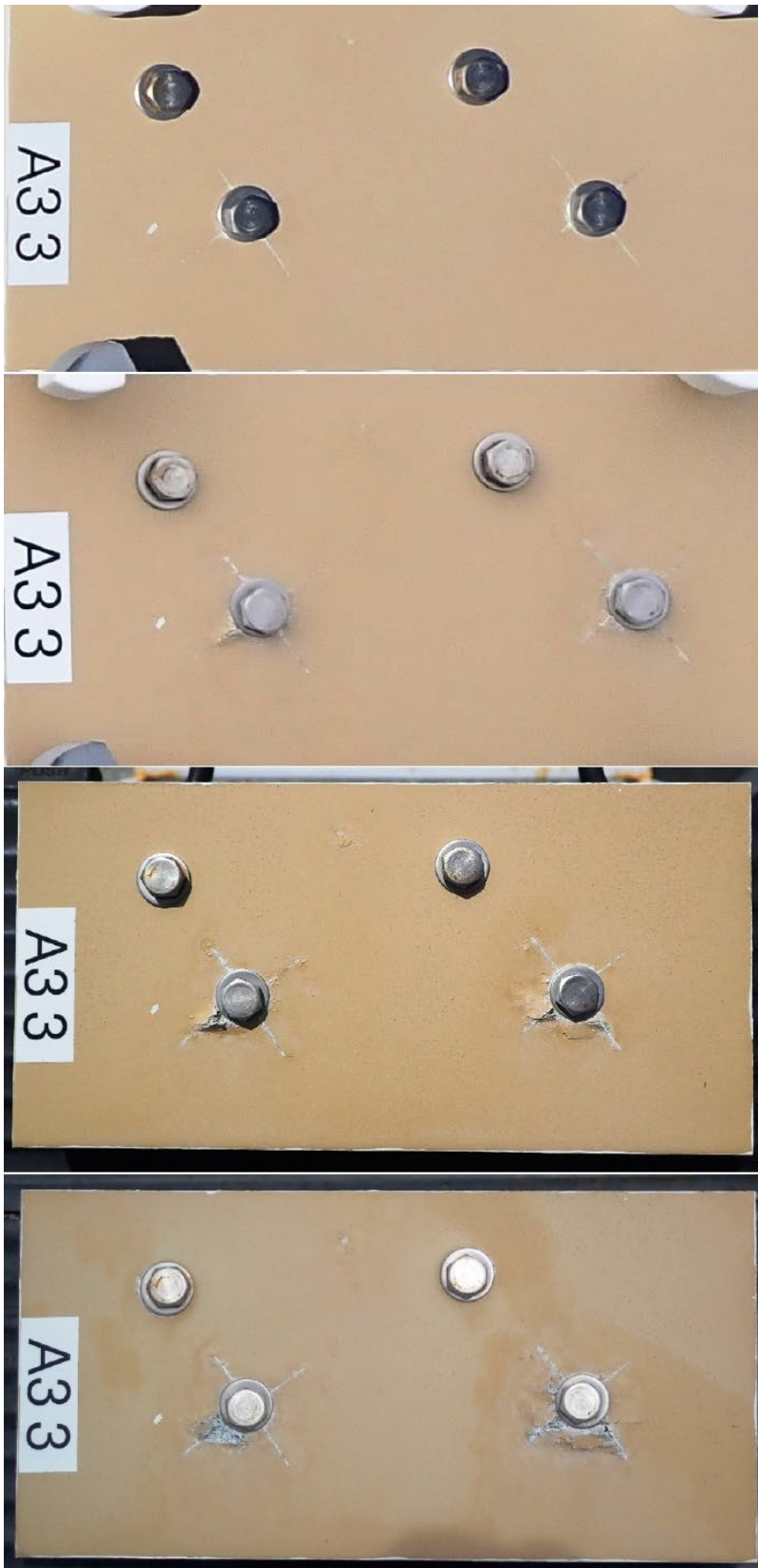


Fig. 5 Panel A3-3 top-bottom: 3-, 6-, 9-, and 12-month inspection images

Results for the panels pretreated with the trivalent chromium-containing SurTec 650 are in Table 7. By Month 3 there was a significant amount of corrosion around the fasteners installed over the scribes. By Month 9 the areas of corrosion originating from fasteners installed over scribes had spread to the fasteners without the scribes, which made many of the unscribed fasteners impossible to properly rate. After 12 months, ratings at 11 of the fasteners were labeled as failures with the 12th being a borderline result. Also, ratings were more consistent between areas where the fasteners were installed over a scribe as compared to areas with fasteners installed over unscribed areas. Images for these panels at 3, 6, 9, and 12 months can be seen in Figs. 6–8. These images show corrosion that originated from the top edge of each panel at the 9-month mark. Panel S3-3 in Fig. 8 shows at 12 months the corrosion from the top edge had reached the top left fastener, making it impossible to accurately rate the corrosion from that fastener.

Table 7 SurTec 650 results

Pretreatment Panel	Position	Month												
		1	2	3	4	5	6	7	8	9	10	11	12	
SurTec 650	S3 1	Top left, not scribed	10	10	10	10	10	8	7	7	7	NR	NR	NR
		Top right, not scribed	10	9	9	8	7	7	7	6	NR	NR	NR	NR
		Bottom left, scribed	10	6	4	3	2	1	1	0	0	0	0	0
		Bottom right, scribed	10	6	4	3	3	2	1	0	0	0	0	0
	S3 2	Top left, not scribed	10	10	10	10	10	10	10	10	NR	NR	NR	NR
		Top right, not scribed	10	10	10	10	10	10	10	10	10	6	5	
		Bottom left, scribed	10	5	4	3	3	2	2	0	0	0	0	0
		Bottom right, scribed	10	5	4	3	2	2	1	0	0	0	0	0
	S3 3	Top left, not scribed	10	10	10	10	10	8	8	NR	NR	NR	NR	NR
		Top right, not scribed	10	10	10	10	10	7	5	4	3	3	2	2
		Bottom left, scribed	10	5	4	3	2	0	0	0	0	0	0	0
		Bottom right, scribed	10	5	4	3	3	3	2	1	1	0	0	0

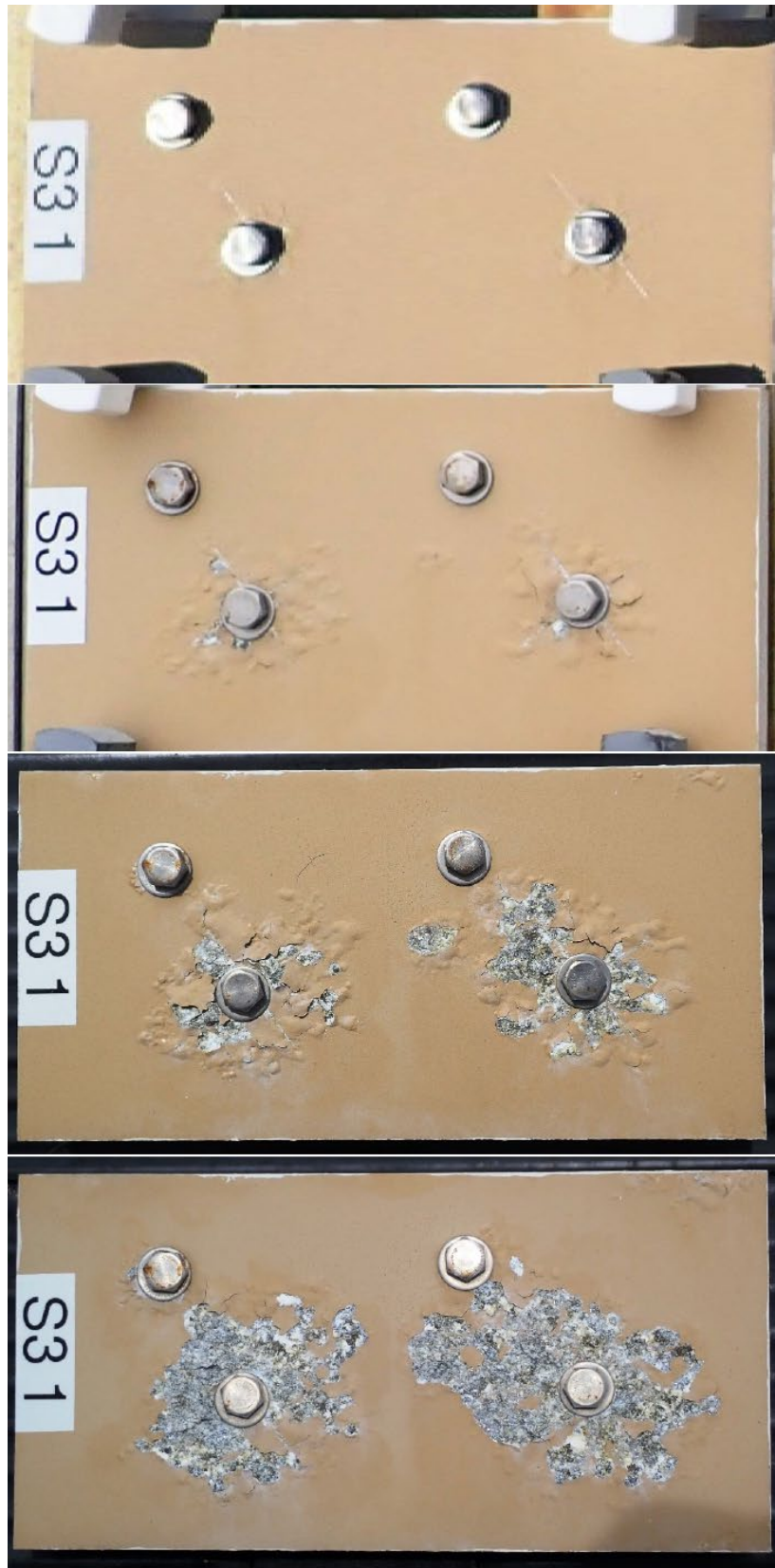


Fig. 6 Panel S3-1 top-bottom: 3-, 6-, 9-, and 12-month inspection images

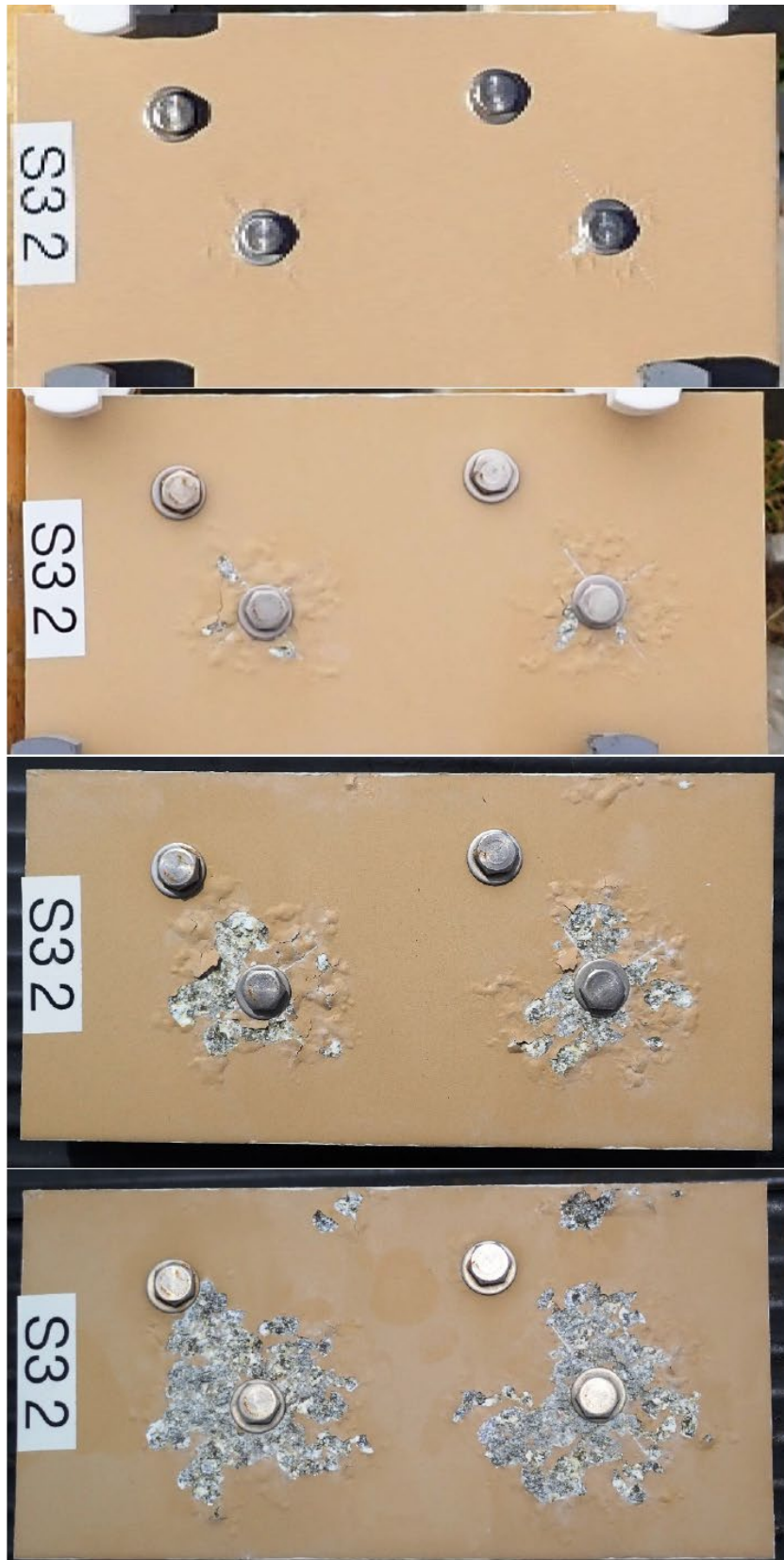


Fig. 7 Panel S3-2 top-bottom: 3-, 6-, 9-, and 12-month inspection images

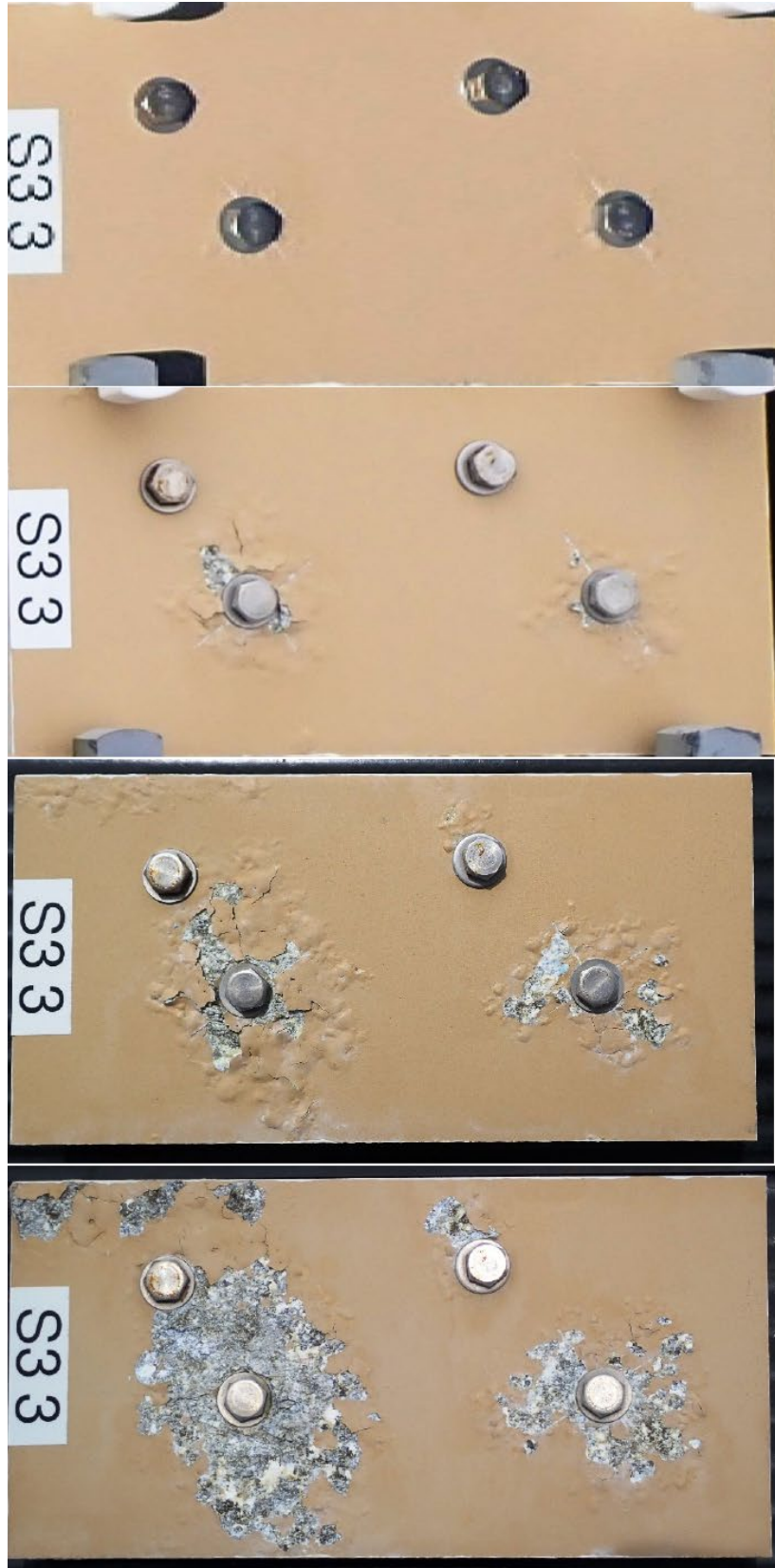


Fig. 8 Panel S3-3 top-bottom: 3-, 6-, 9-, and 12-month inspection images

Results for the panels pretreated with zirconium-based Bonderite 5200 are in Table 8. By Month 3 there was one borderline result by a fastener that was not scribed. The first area rated as a failure was at Month 6. By Month 12 there were significant failures, but no failures as great as what was captured with the trivalent chromium samples. Images for these panels at 3, 6, 9, and 12 months can be seen in Figs. 9–11. Besides corrosion captured in Table 8, there is no other visible damage on these panels. The corrosion on these panels was more similar to what was witnessed on the Cr⁶⁺ conversion coating samples in Figs. 3–5 than the trivalent chromium conversion coating samples in Figs. 6–8.

Table 8 Bonderite 5200 results

Pretreatment	Panel	Position	Month											
			1	2	3	4	5	6	7	8	9	10	11	12
Bonderite 5200	53 1	Top left, not scribed	10	10	10	10	10	10	10	10	10	10	10	10
		Top right, not scribed	10	10	10	10	10	9	6	5	5	3	3	3
		Bottom left, scribed	10	9	8	7	7	7	7	6	5	5	5	5
		Bottom right, scribed	10	8	8	5	5	5	5	4	3	3	3	3
	53 2	Top left, not scribed	10	8	7	6	5	4	4	4	3	3	3	3
		Top right, not scribed	10	7	6	6	6	5	5	5	5	5	5	5
		Bottom left, scribed	10	9	7	6	6	6	6	4	4	4	4	4
		Bottom right, scribed	10	8	8	7	7	7	7	5	4	4	4	4
	53 3	Top left, not scribed	10	10	7	7	6	6	6	5	4	4	4	4
		Top right, not scribed	10	10	9	7	7	5	5	4	4	4	4	4
		Bottom left, scribed	10	9	7	6	6	5	5	4	4	4	4	4
		Bottom right, scribed	10	9	7	6	6	6	6	6	5	5	5	5



Fig. 9 Panel 53-1 top-bottom: 3-, 6-, 9-, and 12-month inspection images

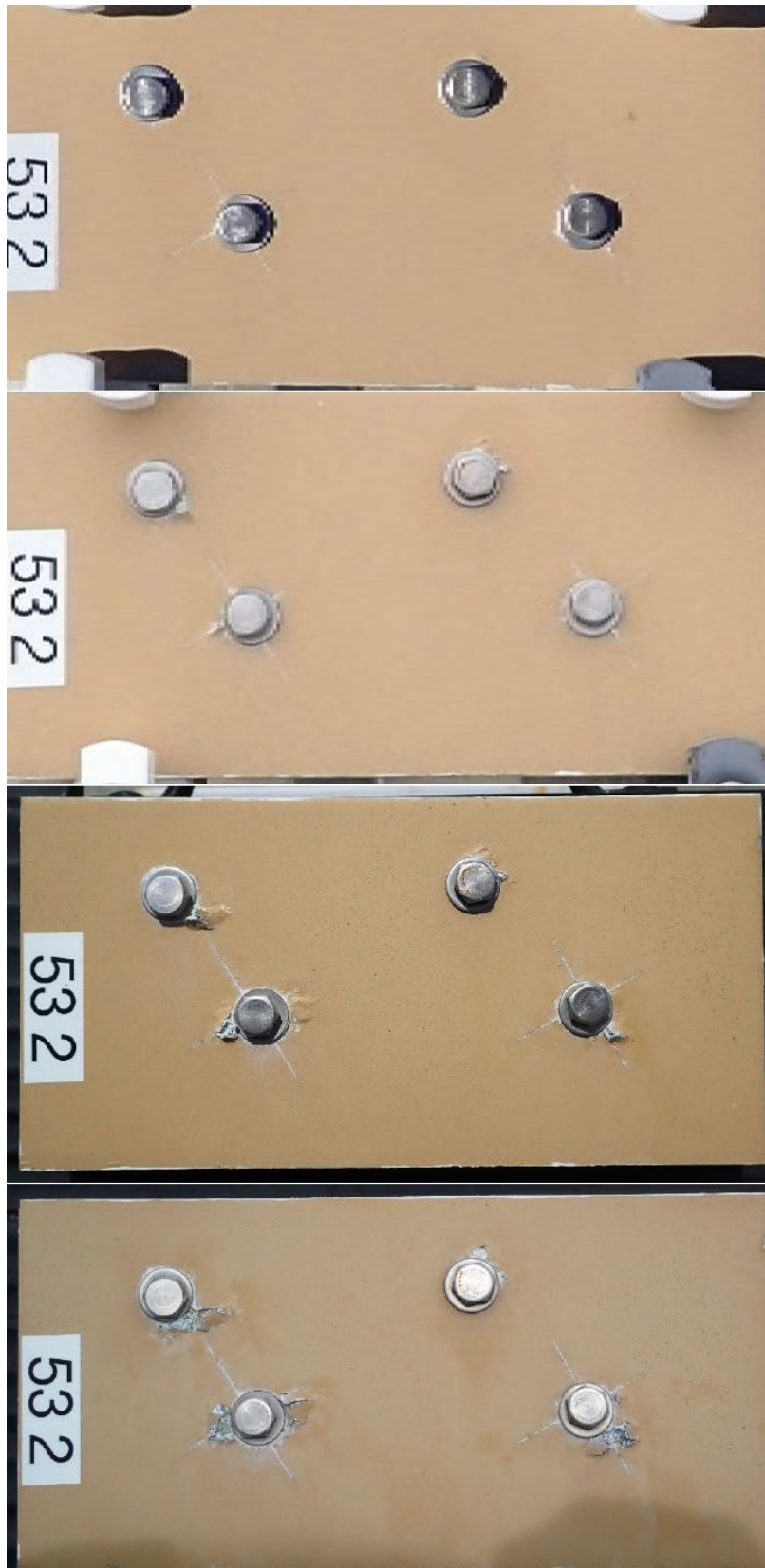


Fig. 10 Panel 53-2 top-bottom: 3-, 6-, 9-, and 12-month inspection images

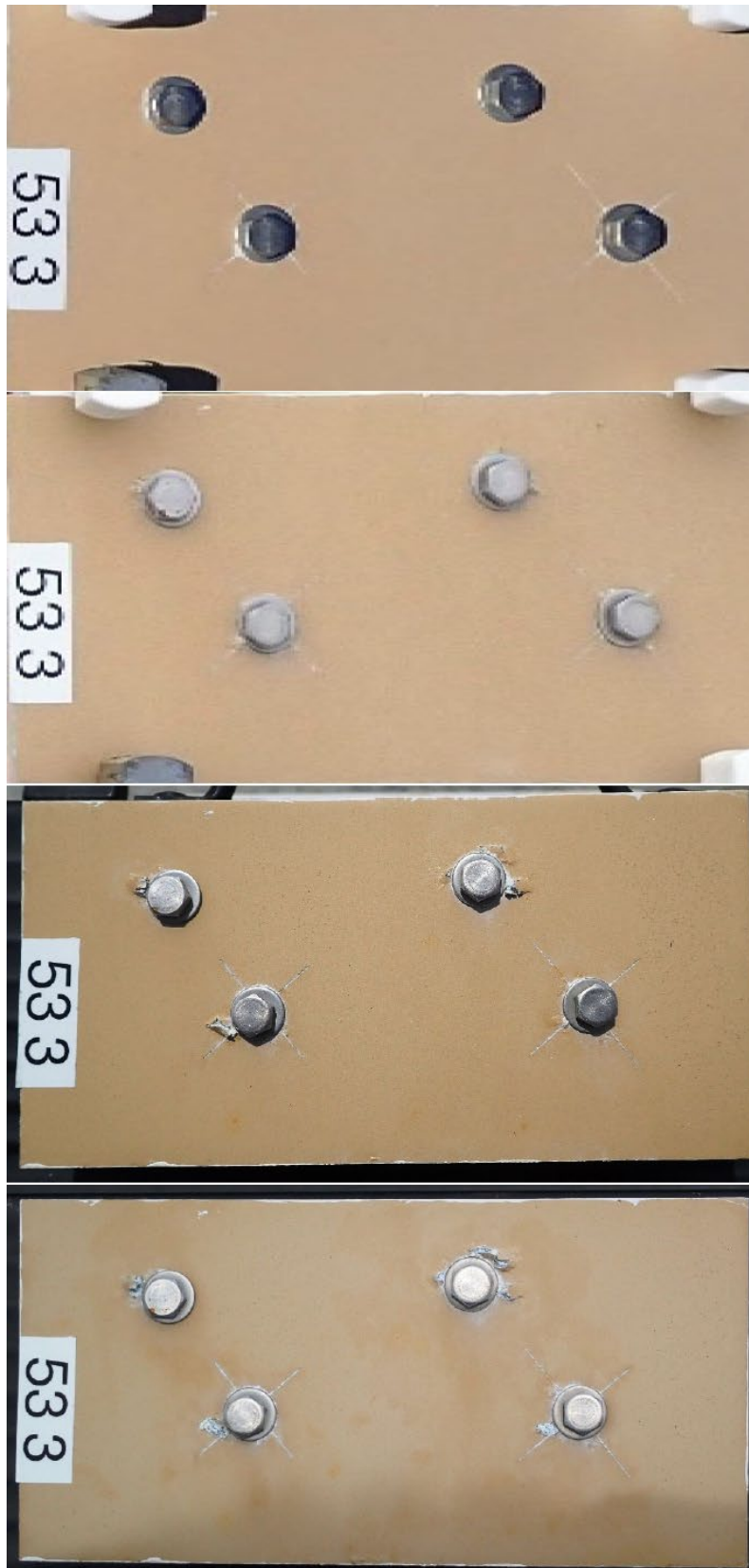


Fig. 11 Panel 53-3 top-bottom: 3-, 6-, 9-, and 12-month inspection images

Results for the panels pretreated with the zirconium-based X-Bond 4000 can be found in Table 9. By Month 3 there was a significant amount of corrosion around the fasteners installed over the scribes. By Month 9 the areas of corrosion originating from fasteners installed over scribes had spread to the fasteners without the scribes, which made many of the unscribed fasteners impossible to properly rate. After 12 months, ratings at 11 of the fasteners were labeled as failures with the 12th being a borderline result. Also, ratings were more consistent between areas where the fasteners were installed over a scribe as compared to areas with fasteners installed over unscribed areas. Images for these panels at 3, 6, 9, and 12 months can be seen in Figs. 12–14. Besides corrosion captured in Table 9, there is no other visible damage on these panels. The corrosion on these panels was more similar to what was witnessed on the Cr⁶⁺ conversion coating samples in Figures 3–5 than the trivalent chromium conversion coating samples in Figs. 6–8.

Table 9 X-Bond 4000 results

Pretreatment	Panel	Position	Month											
			1	2	3	4	5	6	7	8	9	10	11	12
X-Bond 4000	X3 1	Top left, not scribed	10	10	8	8	8	7	7	7	6	6	6	6
		Top right, not scribed	10	10	7	7	6	6	6	5	5	5	5	5
		Bottom left, scribed	10	8	7	7	6	6	6	5	5	5	5	5
		Bottom right, scribed	10	8	7	6	6	6	6	5	5	5	5	5
	X3 2	Top left, not scribed	10	6	6	6	5	5	5	5	5	4	4	4
		Top right, not scribed	10	10	10	10	7	5	5	4	4	3	3	3
		Bottom left, scribed	10	7	7	7	6	5	5	5	4	3	3	3
		Bottom right, scribed	10	7	6	5	5	4	4	4	4	4	4	4
	X3 3	Top left, not scribed	10	7	6	6	6	5	5	5	4	4	4	4
		Top right, not scribed	10	10	10	10	10	10	10	8	7	6	6	6
		Bottom left, scribed	10	8	6	6	6	6	6	6	6	6	6	5
		Bottom right, scribed	10	7	6	6	6	5	5	5	5	4	3	3

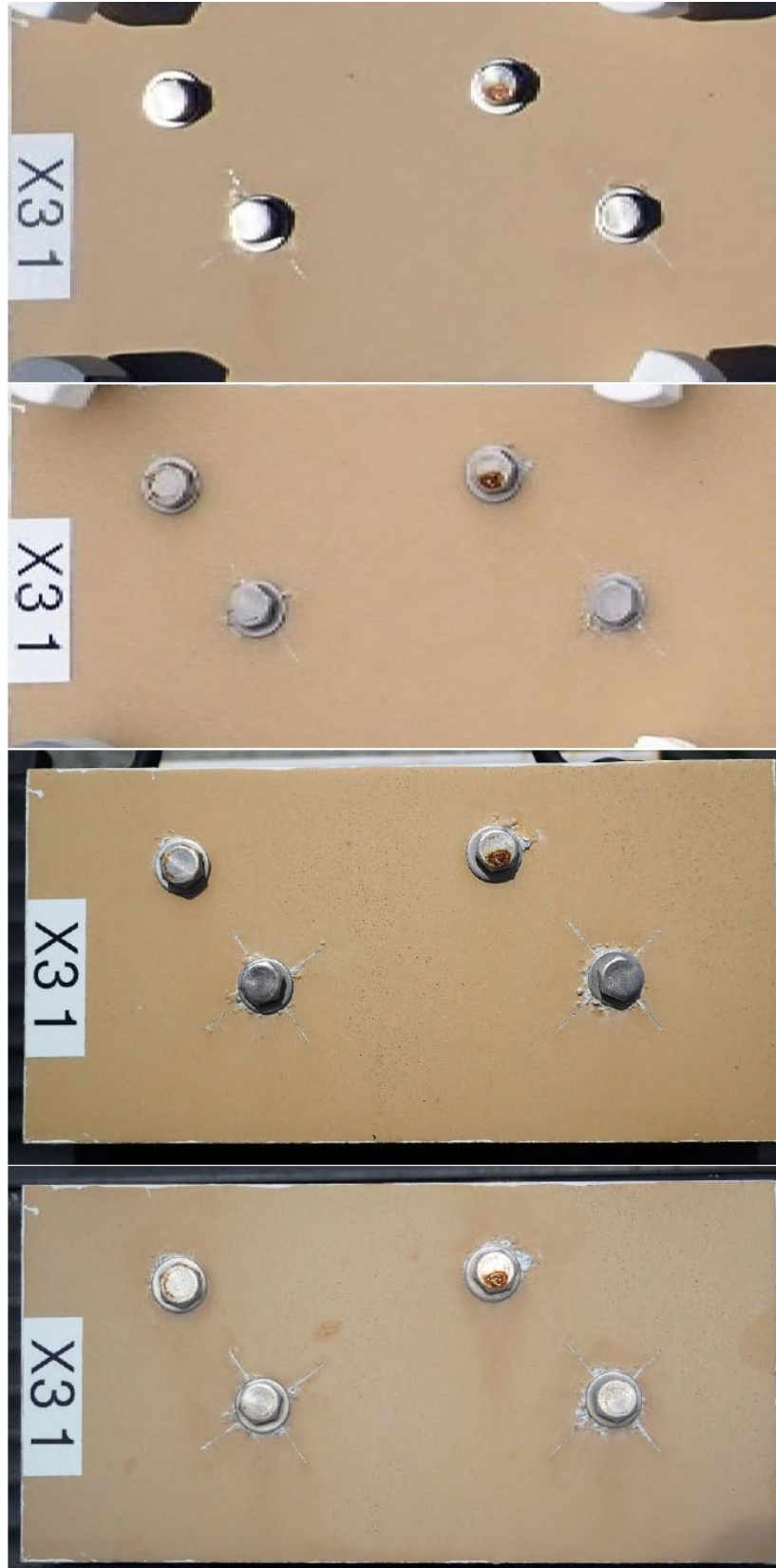


Fig. 12 Panel X3-1 top-bottom: 3-, 6-, 9-, and 12-month inspection images

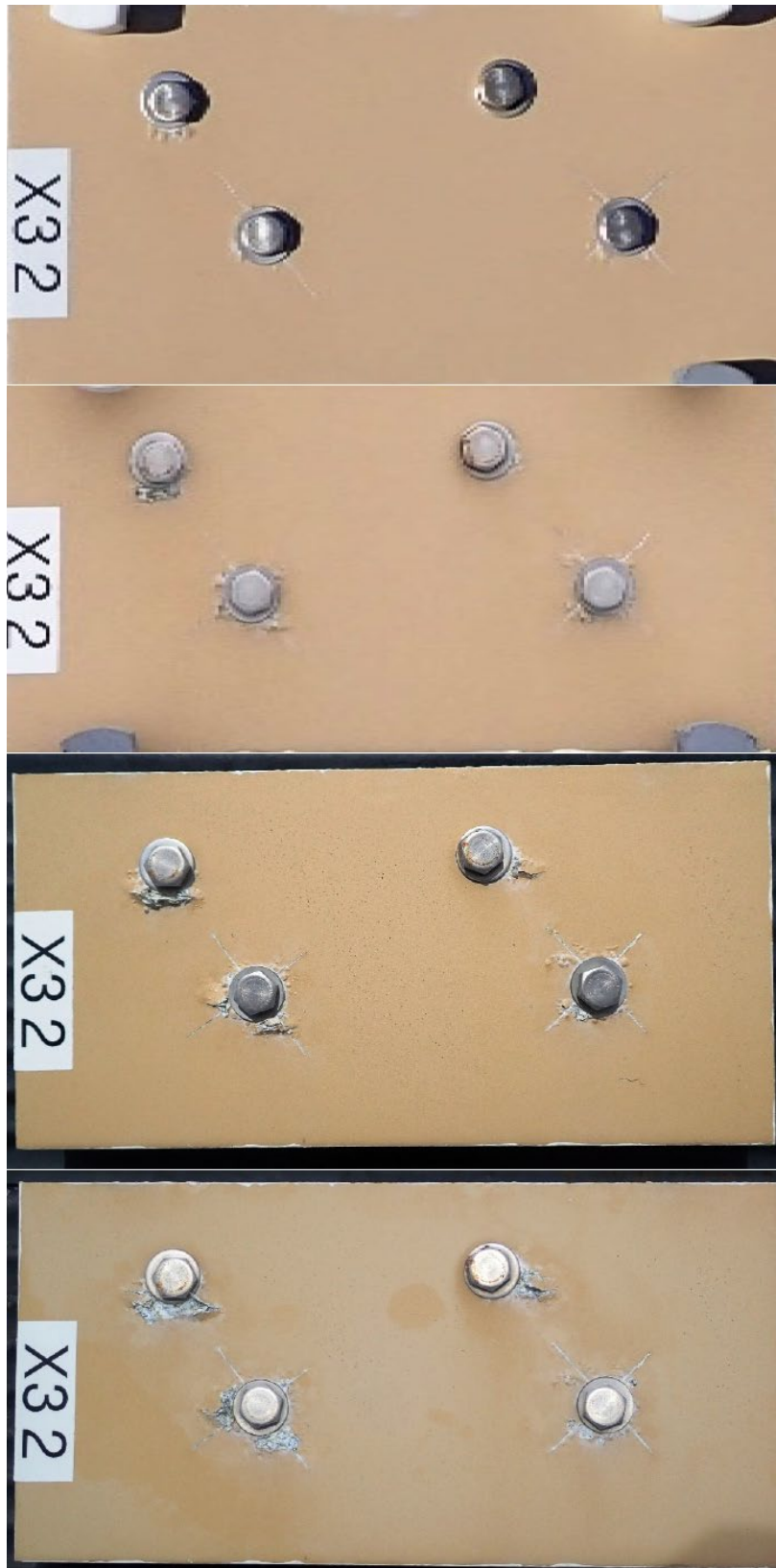


Fig. 13 Panel X3-2 top-bottom: 3-, 6-, 9-, and 12-month inspection images



Fig. 14 Panel X3-3 top-bottom: 3-, 6-, 9-, and 12-month inspection images

The averages of the ratings for the images in Figs. 3–14 are in Table 10. The trivalent chromium conversion coating, SurTec 650, had the lowest average for fasteners installed over “X” scribes. Both zirconium-based products, Bonderite 5200 and X-Bond 4000, had similar rating averages during the 12 months. After 12 months, areas rated on the Cr⁶⁺ conversion coating, Bonderite 1200, had the best average ratings when the fastener was installed over an unscribed area. When installed over an “X” scribed area, the average results for the zirconium pretreatments and the Cr⁶⁺ conversion coating were almost identical.

Table 10 Average ratings of each pretreatment at 3, 6, 9, and 12 months

Pretreatment	Scribed or unscribed	Month			
		3	6	9	12
Bonderite 1200	Unscribed	9.33	9	8.83	7.83
	Scribed	7.33	5.5	5.33	4.5
SurTec 650	Unscribed	9.83	8.33	3.33	1.16
	Scribed	4	1.67	0	0
Bonderite 5200	Unscribed	8.16	6.5	5.16	4.83
	Scribed	7.5	6	4.16	4.16
X-Bond 4000	Unscribed	7.83	6.33	5.16	4.67
	Scribed	6.5	5.33	4.83	4.16

5. Discussion

Testing at the KSC Beachside Atmospheric Corrosion Test Site showed that the zirconium-based products performed better than the trivalent chromium-containing conversion coating, but not at the level of Cr⁶⁺-containing conversion coating under a nonchrome primer. The corrosion witnessed on the zirconium-based Bonderite 5200 and X-Bond 4000 were more in line with the results from the Cr⁶⁺ conversion coating than the trivalent chromium conversion coating. Areas away from the fasteners showed no visible corrosion on the samples treated with Cr⁶⁺ conversion coating—Bonderite 5200 and X-Bond 4000. Corrosion was witnessed on the panel edges of the samples treated with trivalent chromium conversion coating. This testing showed that zirconium pretreatments can perform better than trivalent chromium conversion coatings as part of a CARC stack-up as specified in MIL-DTL-53072; and because this testing was completed at an outdoor facility, these samples were exposed to all the elements that the coatings would be exposed to when used on fielded equipment.

The use of a test panel with dry-installed stainless steel fasteners effectively accelerated corrosion on the 2024 aluminum alloy surface. The galvanic corrosion potential between the stainless steel and 2024 aluminum causes the aluminum substrate to corrode at a high rate if not properly protected with coatings. In the field, fasteners would be installed wet with some type of sealant to help slow this galvanic potential. Installing fasteners dry allowed the failures to happen quickly, but consistent with failures witnessed in the field as the sealant degrades.

6. Conclusion and Future Efforts

The results indicate that both zirconium pretreatments, Bonderite 5200 and X-Bond 4000, performed better than trivalent chromium conversion coating, but not quite as well as the Cr⁶⁺ conversion coating currently approved to MIL-DTL-81706 on galvanic panels with a full CARC stack-up system espoused at KSC's Beachside Atmospheric Corrosion Test Site. Using the zirconium pretreatment did not add any additional time to the panel preparation and can be used as a direct replacement for conversion coating on aluminum substrates that will receive an epoxy primer with no additional time or temperature requirements. The use of these zirconium pretreatments with a MIL-PRF-23377 Class N primer provides a chrome-free stack-up system that can be used as a replacement to Cr⁶⁺ conversion coating on aviation assets that performs better in corrosive environments than currently fielded trivalent chromium conversion coating with MIL-PRF-23377 Class N primer.

All of this work was completed as a full stack-up coating system. Current corrosion requirements in MIL-DTL-81706 require chamber corrosion testing to be completed on the pretreatment with no primer or topcoat. Hexavalent and trivalent chromium conversion coatings can pass this requirement whereas zirconium-based pretreatments have not shown they can pass in this condition. Work will have to be done to revise the MIL-DTL-81706 specification to update qualification requirements to allow high-performing zirconium-based pretreatments to be qualified as part of a stack-up coating system.

7. References

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List of Symbols, Abbreviations, and Acronyms

AERTA	US Army Environmental Requirements and Technology Assessment
CARC	Chemical Agent Resistant Coating
CFR	Code of Federal Regulations
Cr ⁶⁺	hexavalent chromium
DOD	Department of Defense
DTM	directive-type memorandum
EU	European Union
FZA	fluorozirconic acid
KSC	Kennedy Space Center
NASA	National Aeronautics and Space Administration
NAVAIR	Naval Air Systems Command
NR	not rated
OSHA	Occupational Safety and Health Administration
pH	potential hydrogen
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals

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