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Demonstration of Chrome-Free Pretreatments at Corpus Christi Army Depot

by Daniel Pope, Thomas Considine, Fred Lafferman,
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NOTICES

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14. ABSTRACT

Recent changes in regulations are driving the need for chrome-free coating and treatments on DOD assets. Recent work in the laboratory has identified aluminum surface treatments that can replace legacy chrome conversion coatings in spray and immersion processes at military repair depots. These treatments needed to be applied and validated in a depot setting to establish viability as an alternative to legacy treatments. Two demonstrations, using three different chrome-free surface treatments and the legacy system, were completed at Corpus Christi Army Depot encompassing spray and immersion processes for applying conversion coatings on aluminum substrates. The parts and panels received the aviation stackup of primer and topcoat after the surface treatments were applied. The parts and panels were tested in various ways including laboratory and static outdoor exposures. The successful demonstrations showed that non-chrome aluminum surface treatments can be used as part of depot processes and perform on the same level expected from legacy hexavalent chrome-containing conversion coatings.

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Contents

List of Figures

List of Tables

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 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 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 technologies 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 nonCr^{6+} pretreatment coatings:

1) OSHA regulation 1910.1026[2]: Regulatory requirements and allowable exposures to Cr^{+6}

2) DOD policies[3] minimizing the use of 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 Information[5]

    4.1) *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 Cr^{+6} or the use of Cr^{+6} 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 April 2009, regardless of the place of performance.

    4.2) *Exceptions (223.7304)*: The prohibition in 223.7303 does not apply if the use of Cr^{+6} 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 Cr^{+6}. However, alternatives to Cr^{+6} 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[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 Command[8]

8) US Army Environmental Requirements and Technology Assessment (AERTA) requirement, AERTA PP-2-02-04, *Toxic metal reduction in surface finishing of Army weapon system*s, specifically the requirement for an alternative to Cr^{6+} conversion coating[9]

This testing supporting US Army Toxic Metal Reduction Program for Cr^{6+}-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 system. This includes limiting the waste stream generated from the application and removal of existing legacy pretreatments from operating depot and corrosion repair locations. Previous work laboratory tested multiple chrome-free pretreatments as possible replacements for hexavalent and trivalent chromium containing conversion coatings.[10] This effort identified three products to demonstrate at Corpus Christi Army Depot (CCAD) as possible direct replacement to the Cr^{+6} conversion coating that is currently used as part of the depot's processes.

The report details the demonstrations of chrome-free pretreatments at CCAD. The first was to demonstrate pretreatments with spray application as replacement for mop-on Cr^{+6} conversion coating. The second was to demonstrate immersion application pretreatments to replace the Cr^{+6} conversation coating baths in the plating shop.

2. Technical Approach

Zirconium pretreatments were tested and evaluated through depot 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 fewer 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 Cr^{6+} by immersion technology.

Zirconium pretreatments were applied via spray and immersion to bare test coupons and beyond economical repair (BER) parts per manufacturer's recommendations. Spray and immersion demonstrations were completed at different times. Once pretreated, the parts and panels completed the depot painting process receiving their standard primer and topcoat used in other repair operations. Once coated, the panels were tested in laboratory and at static outdoor sites. The performance of the zirconium pretreatments was compared to the Cr^{6+} conversion coating currently used at CCAD for both immersion and spray pretreatment applications.

3. Experimental Procedure

3.1 Products

Table 1 lists the products selected for testing. The products include zirconium pretreatments from Henkel Corporation (Düsseldorf, Germany), MacDermid Inc. (Waterbury, Connecticut), and PPG Industries, Inc. (Pittsburgh, Pennsylvania). The controls selected are approved products on the DOD's Qualified Products Database for MIL-DTL-81706.[11] The Type I material was Henkel's BONDERITE (formerly Alodine) 1200 and is a Cr6+ conversion coating.

Table 1 Products used in demonstrations

Vendor	Product	Application	Primer window
Henkel	BONDERITE 1200 (baseline)	Spray	Dry–168 h
MacDermid	Iridite 14-2 (baseline)	Immersion	24–96 h
Henkel	BONDERITE 5200/5700	Spray and immersion	24–96 h
MacDermid	Iridite NCP	Spray	Dry–1 day (possibly longer)
PPG	11-TGL-27 (renamed Desoprep 3000)	Spray	Dry–168 h

3.2 Coatings

The surface treatments in the test are meant to be part of a coating stackup, not providing similar standalone corrosion performance as the legacy Cr^{6+} materials; the zirconium-based products are not intended for such applications. To simulate what would be applied on an Army aviation asset that is painted at CCAD, a Cr^{6+}-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 demonstration

Specification	Details
MIL-PRF-23377 Class N	Primer: Cr^{6+}-free, high solids, solvent-based epoxy
MIL-DTL-53039 Type IX	Topcoat: solvent-based urethane

3.3 Application

There were two separate application demonstrations to capture the two application methods of conversation coating at CCAD. In January 2016, a spray application demonstration was completed to identify replacements for the current mop on Cr^{6+} conversion coating process. Observations were made to capture process and processing time.

In June 2016, an immersion demonstration was completed to replacements for the current immersion Cr^{6+} conversion coating process. Observations were made to capture process and processing time. Both demonstrations included 2024-T3 aluminum panels and BER parts.

3.4 Adhesion

This test was done in accordance with ASTM D3359 Method B.[12] Using a cutting-wheel-style tool with six blades, a lattice pattern was cut through the coating down to the substrate with the parallel scribes 2 mm apart. After the lattice had been cut, the testing area was gently brushed to remove loose particles, and a certified, nonexpired, pressure-sensitive tape was placed over the lattice. The tape was rubbed with even pressure using a pencil eraser to ensure complete adhesion. After 90 ± 30 s, the tape was removed by pulling the tape straight back at as close as possible to 180° in a single motion. The test area was inspected and given a rating based upon comparison with the paint removal classifications illustrated in the test method.

3.5 Corrosion

Cyclic corrosion testing was completed in accordance with GMW14872.[13] Testing occurred in a calibrated Autotechnology Cyclic Test Chamber, Model NC90 (Fig. 1) for a duration of 21 cycles. Fog deposition rates were recorded daily by chamber operators, and temperature/humidity data are recorded internally by the chamber. A premixed, certified salt solution (sodium chloride [NaCl] 0.9%, calcium chloride [$CaCl_2$] 0.1%, and sodium bicarbonate [$NaHCO_3$] 0.075%) was used during spray cycles, and the humidity cycles used laboratory-supplied deionized water (DI), conforming to ASTM D1193[14] Type IV. Chamber operation was validated using standard mass-loss coupons.

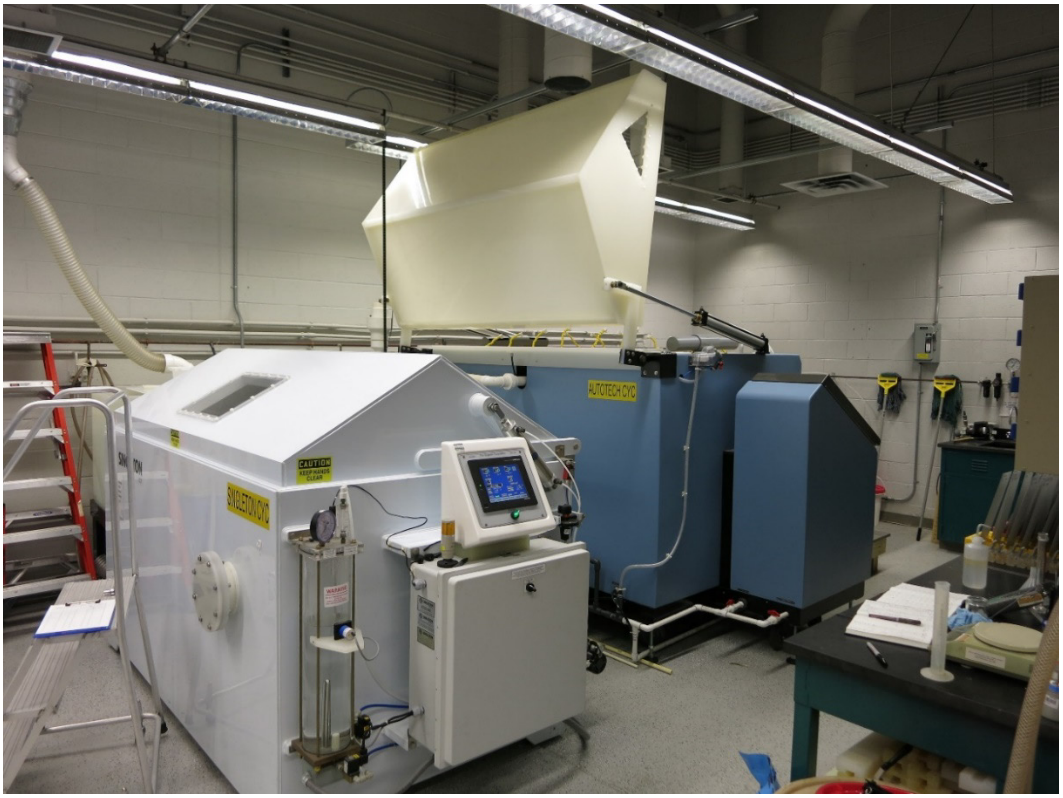

Fig. 1 Autotechnology cyclic test chamber, Model NC90

Galvanic panels (Fig. 2) were used for this testing, which use the 2024-T3 panels with titanium and stainless steel fasteners installed after coating. One set of fasteners were installed over the as-coated surface and the others were installed over an area that was scribed. The galvanic panels were oriented at a 15° incline and exposed for a total of 21 cycles.

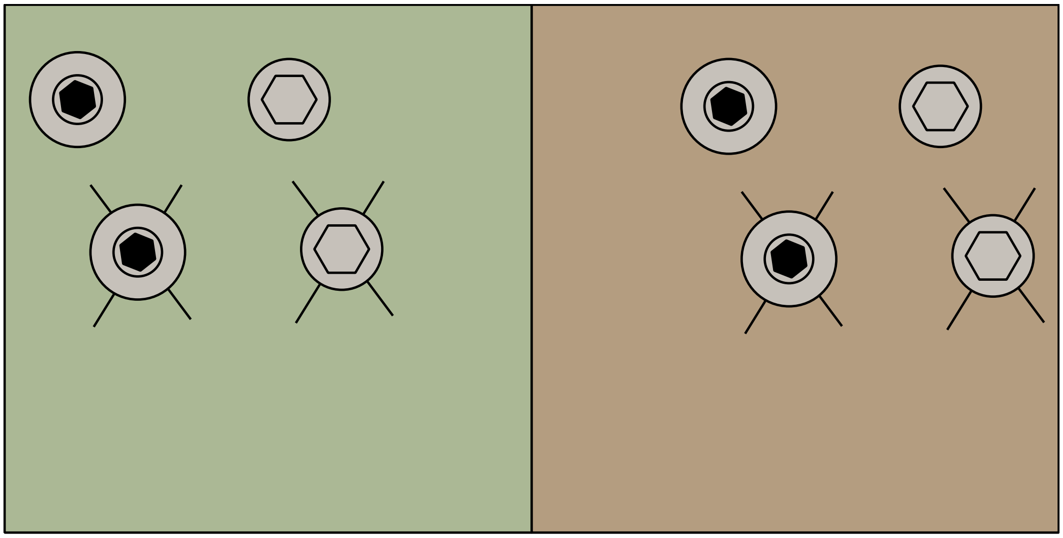

Fig. 2 Sketch of galvanic test samples, primer only (left) and primer and topcoat (right)

Inspections were made at the end of the exposure and were visual in nature. A measuring optical magnifier was used to examine the panels. Each panel was rated on the primer-only side and the primer with topcoat side. Areas away from the fasteners and scribes were rated for blisters in field (BIF) in accordance with Table 3. This rating captured all blisters and other defects present after the exposure that could not be directly related to the galvanic corrosion potential created by the fasteners.

Table 3 Rating for unscribed areas with color coding: green (acceptable), yellow (borderline, fail), and red (failure)

Area failed (%)	Rating number
No failures	10
>0 to 1	9
2 to 3	8
4 to 6	7
7 to 10	6
11 to 20	5
21 to 30	4
31 to 40	3
41 to 55	2
56 to 75	1
Over 75	0

Each fastener and surrounding area received two ratings for corrosion. The first represented the maximum growth of blisters radially from the washer interface. These ratings were based upon the rating scale from ASTM D1654-05[15] Procedure A and presented in the column labeled "Blister Rating". When blisters were present, the length of contact with the washer was measured and presented in the column "AMT (mm)," which has a maximum possible length of 30 mm. The scribed areas were rated maximum creep from scribe was captured in accordance with ASTM D1654 Procedure A, which rates performance on a 0 to 10 scale (0 being 16 mm or more creep, 10 being no creep).

3.6 Atmospheric Exposure at CCAFS

Select parts and panels (flat and galvanic) from the demonstrations were shipped from CCAD to Florida for outdoor testing at the US Army Combat Capabilities Development Command (CCDC) Army Research Laboratory (ARL)/Tank Automotive and Armaments Command (TACOM) Outdoor Exposure Site at Cape Canaveral Air Force Station (CCAFS). Cape Canaveral is considered one of the most corrosive environments in the continental United States. The corrosion rate observed by ASTM International is 5.17 mil per year (mpy) on standard steel mass-loss coupons at 55 m inland. For this reason, CCDC Army Research Laboratory selected this outdoor exposure facility for much of its outdoor testing.

The ARL corrosion racks are set at approximately 170 and 220 m inland and parallel to the ocean, facing southeast (Fig. 3). The average corrosion rate in mil per year observed by ARL since 2011 on standard mass loss coupons is 5.4 mpy at 170 m inland (confirming corrosion rates reported for similar exposure by ASTM International). Prior to exposure, the test panels were scribed in accordance with ASTM D1654[15] and held in place on wood or composite racks with nylon standoffs and SS fasteners (Fig. 4). The coupons are inspected at each individual fastener and evaluated quarterly in accordance with ASTM D1654 using the same methods for the cyclic corrosion testing.

Fig. 3 Satellite image of the CCAFS/TACOM outdoor exposure site in relation to the ocean

Fig. 4 Racks at the CCAFS/TACOM outdoor exposure site with galvanic panels on the top three rows

3.7 Atmospheric Exposure at CCAD

Large parts from the spray demonstration and select parts from the immersion demonstration were placed in a secure storage areas at CCAD located approximately 460 m from the Corpus Christi bay. Figure 5 shows the layout of the parts from both demonstrations with the mass loss coupons placed on the inside of the fence facing toward the Corpus Christi bay. The large nacelles from the spray demonstration were strapped to pallets and placed on the concrete pad. The smaller parts from the immersion demonstration were installed onto custom racks that were built onsite to secure the parts, with the parts secured to the racks using zip ties. The use of pallets to expose the nacelles and the exposure racks allow them to be removed in case of hurricanes of other extreme weather events. Figure 6 shows the mass loss data collected from the CCAD site compared to CCAFS. Strictly looking at mass loss, the CCAD site was half as of aggressive as the CCAFS exposure site. Despite this, CCAD is still considered a very corrosive site for exposure.

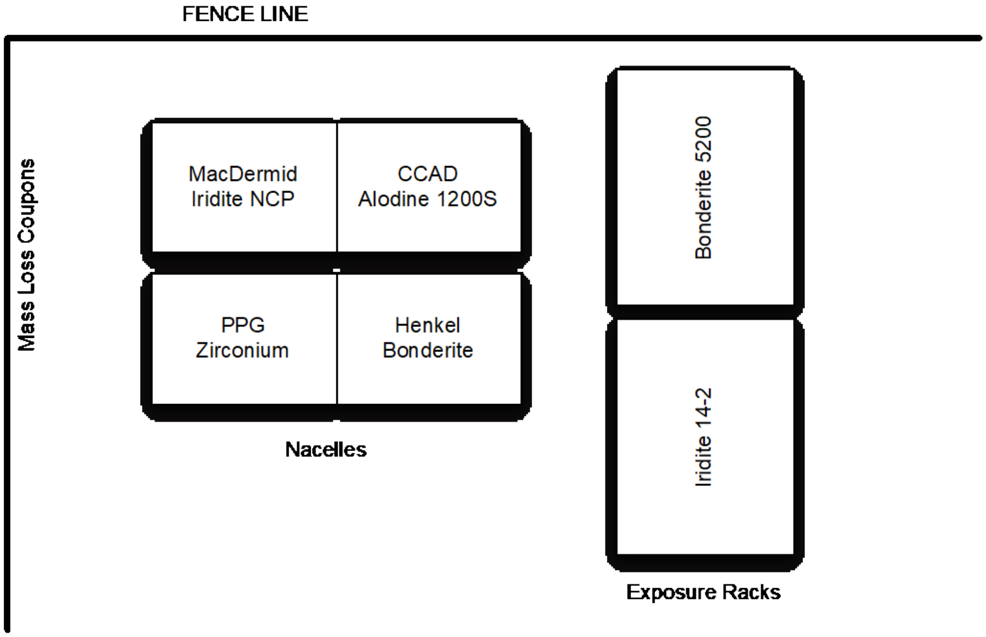

Fig. 5 **CCAD exposure layout**

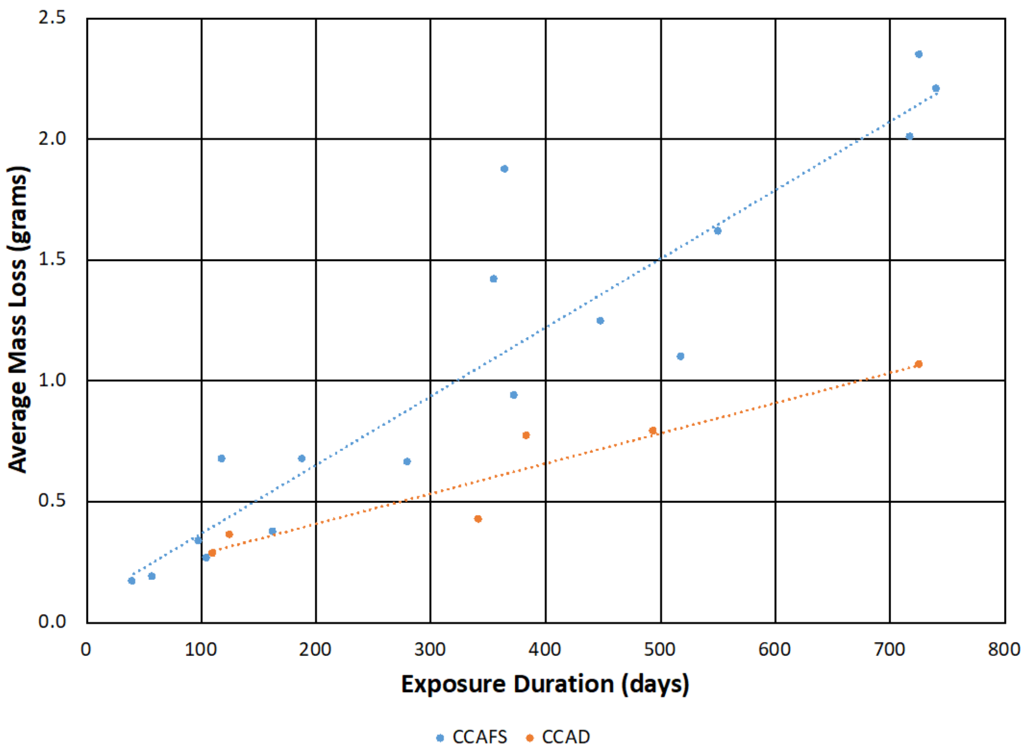

Fig. 6 Mass loss for sites at CCAD and CCAFS

4. Results

4.1 Spray Application Demonstration

During the week of 25 January 2016, a demonstration was held at CCAD for spray-on alternatives to Cr^{6+} pretreatments. CCAD agreed to participate in a demonstration using three alternatives to their chromate conversion coating process. The three products were the following:

- Henkel BONDERITE M-NT 5700 (BONDERITE)
- PPG 11-TGL-27 Spray-on Rinse-off Zirconium (Zirconium)
- MacDermid Iridite NCP (Iridite)

All products were applied by representatives from the respective vendor companies. CCAD personnel applied the Alodine 1200S chromate conversion coating using their current process. The application was performed on the following parts and panels (per system):

- Parts
    - half of an AH-64 engine nacelle
    - four hatches and covers from these nacelles
- 12 panels
    - 2024 and 7075 aluminum

The parts were representative of a repair item at CCAD, which had been prepared for rework per their normal process by plastic media blasting (PMB), although no specific details were provided. This resulted in parts that had some remaining (adherent) paint and Cr^{6+} conversion coating. The panels were virgin aluminum (2024), which were cleaned and processed using the procedures for each pretreatment.

Table 4 compares the general process steps based on the preliminary information provided by each vendor. Generally, these were adhered to during the demonstrations.

Table 5 shows the elapsed time during each process step for treating the parts (half nacelle, hatches, and covers); only one person performed the process steps for each demo. The total time for each process is summarized for each vendor as well as the active minutes, which excludes dwell times and drying periods where active work was not being performed.

Table 4 General process steps for each system

Step	Henkel – BONDERITE	PPG – Zirconium	MacDermid – Iridite	CCAD – Alodine 1200S
1	Spray assembly with 25% mixture of BONDERITE C-AK 298.	Solvent wipe with methyl ethyl ketone or acetone and a DI water rinse (< 20 µS/cm).	Spray Isoprep 50LLF (5% by volume) at 100F for 2 min.	Solvent wipe with methyl n-propyl ketone (MPK).
2	Allow assembly to soak 2–5 min while abrading to activate the surface (do not allow to dry).	Spray RECC 1043 deoxidizer at room temperature using high-volume, low-pressure (HVLP) equipment completely covering the part with RECC 1043 so all surfaces are thoroughly wetted.	Rinse with room temp DI water for 2 min.	Brush apply Alodine 1200S to all surfaces.
3	Rinse with water.	Keep surfaces saturated for 1 min, reapply RECC 1043 as needed.	Spray Isoprep 184 (5% by volume) at room temp for 2 min (good ventilation is needed).	DI rinse all surfaces.
4	Inspect for water break areas.	Allow surfaces to air dry for 7 min, but less than 4 hours (dab areas where solution puddles of blow off areas using clean compressed air).	Rinse with room temp DI water for 2 min.	Allow to air dry.
5	Use abrasive pad to clean areas that do not achieve a water break.	Spray apply 11-TGL-27 zirconium using HVLP equipment at full strength, making sure all surfaces are thoroughly wetted.	Spray Iridite NCP (5% by volume) at 100F for 2 min.	. . .
6	Re-rinse with water.	Allow the 11-TGL-27 zirconium to dwell for 5-min to complete the zirconium deposition.	Rinse with room temp DI water for 2 min.	. . .
7	Inspect for water break free surface, repeat 5 through 7 if.	Rinse with DI water to removal all unreacted necessary treatment.	Blow dry.	. . .
8	Spray BONDERITE M-NT 5700 (as received) from top to bottom.	Allow surface to dry completely under ambient conditions before painting (minimum of 1 h).	. . .	. . .
9	Allow BONDERITE M-NT 5700 to dwell for 2–4 min (do not allow to dry).	. . .	. . .	. . .
10	Moderate (low-pressure, low-volume) rinse with water.	. . .	. . .	. . .

Table 5 Process times for each pretreatment demonstration

Step	Henkel – BONDERITE 5200/5700	PPG – Zirconium	MacDermid – Iridite NCP	CCAD – Alodine 1200S
START	26 January 2016 at 0900	27 January 2016 at 0932	28 January 2016 at 1001	29 January 2016 at 0826
1	Initial cleaning – 5 min Second cleaning – 5 min	Solvent wipe – 7 min	Cleaning – 2 min	Solvent wipe – 6 min
2	Dwell concurrent with application	Spray deoxidizer – 10 min	Rinse – 3 min	Brush application – 5 min
3	Initial rinse – 5 min Second rinse – 2 min	Dwell concurrent with application	Initial acid etch – 3 min Second acid etch – 1 min	Rinse – 3 min
4	Inspection concurrent with rinse	Air dry – 31 min	Rinse – 1 min	Air dry – not timed
5	Initial scrub concurrent with rinse Second scrub – 3 min	Pretreatment – 4 min	Initial pretreatment – 5 min Second pretreatment – 1 min	…
6	Re-rinse time not recorded	Dwell – 8 min	Rinse – 3 min	…
7	Scrub inner surface – 3 min	Initial rinse – 2 min Second rinse – 6 min	Blow dry – not timed	…
8	Pretreat outer surface – 2 min Pretreat inner surface – 4 min	Air dry – not timed	…	…
9	Dwell concurrent with application	…	…	…
10	Rinse outer surface – 4 min Rinse all surfaces – 3 min	…	…	…
END	**26 January 2016 at 0949**	**27 January 2016 at 1120**	**28 January 2016 at 1029**	**29 January 2016 at 0849**
TOTAL	**49 min (36 active min)**	**118 min[a] (29 active min)**	**28 min[b] (19 active min)**	**23 min (14 active min)**

[a] Includes 30 min of downtime between solvent wipe and deoxidizer steps while correcting air fitting issue.

[b] Excludes 96 min of downtime at the start of the demonstration while assembly adjusting pH and heating solutions.

The active times for each alternative process were compared to the active time for the Alodine 1200S:

- Henkel BONDERITE: 2.57 times the CCAD process (157% increase)

- PPG Zirconium: 2.07 times the CCAD process (107% increase)
- MacDermid Iridite: 1.36 times the CCAD process (36% increase)

All of the processes took longer than the Alodine 1200S. The shortest process was the MacDermid Iridite, although this did not include the time necessary for pH adjustment and solution heating, which would be necessary before application.

In addition to the process times, other observations were made with respect to the alternative pretreatment products:

- Henkel: BONDERITE
    - Powdery buildup observed on aluminum and titanium components 40 min after final rinse (no notes were made as to whether or not this was removed prior to painting).
    - Difficult to observe color shift on 7075 samples, readily observed on 2024.

  Images from the BONDERITE 5200/5700 demonstration are shown in Figs. 7–11. For the demonstration, the vendor completed the work utilizing spray bottles (similar to those used for household cleaners). The vendor said this product can be applied with any low-pressure method including a wand sprayer for larger surface areas. For the demonstration, the spray bottles produced a finish that was mostly consistent and covered the entire substrate. No harsh chemical irritants were detected by people witnessing the demonstration. For rinsing, lower pressure, similar to what would come from a garden hose, was used.

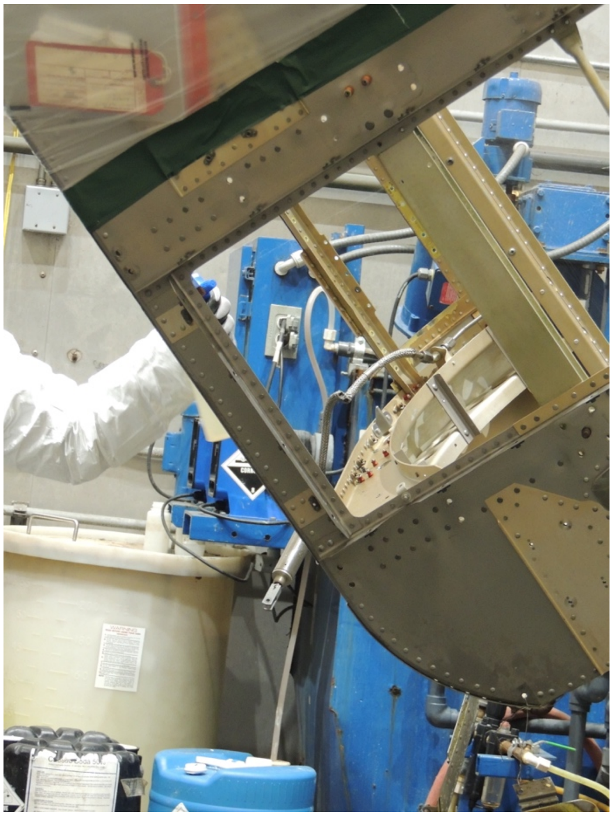

Fig. 7 Cleaning for the BONDERITE 5200/5700 treatment

Fig. 8 Rinse following the cleaning step for the BONDERITE 5200/5700 system

Fig. 9 Deoxidizer for the BONDERITE 5200/5700 system

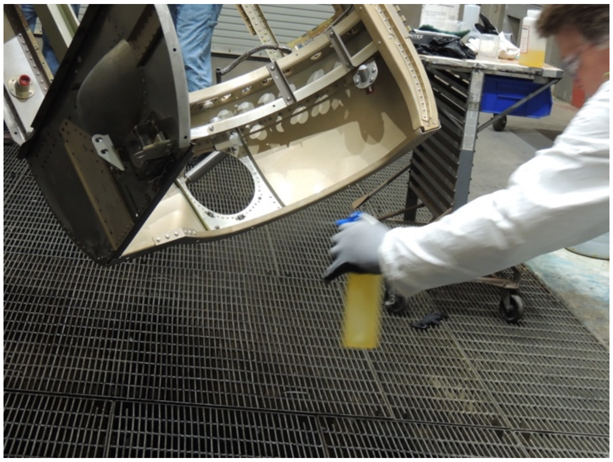

Fig. 10 Application of the BONDERITE 5200/5700 system on the nacelle

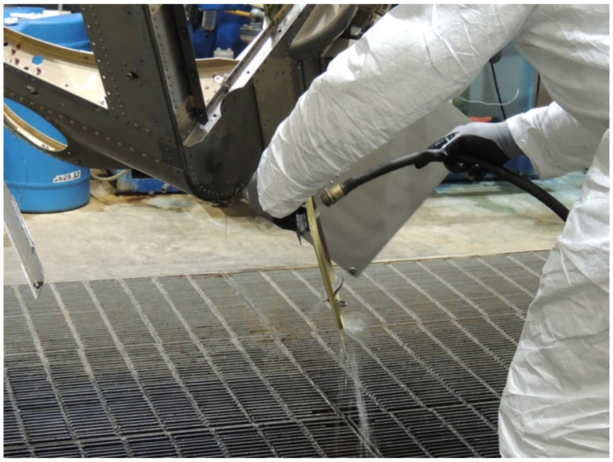

Fig. 11 Final rinse for the BONDERITE 5200/5700 system

- PPG 11-TGL-27
    - RECC 1043 deoxidizer was noted to irritate nose and throat in area near application, alleviated with a half-face respirator.
    - The titanium parts did not achieve a water-break free surface (uncertain if there could be residual contaminants the solvent wipe was unable to remove).
    - Dark powdery residue observed on titanium sections; can be removed with a tech wipe.
    - Slight blue tint on pretreated areas (easier to observe near intact chromate conversion coating)

Images from the PPG 11-TGL-27 demonstration are shown in Figs. 12–14. The vendor used a HVLP spray gun for the demonstration of this product. This application method cause all materials to be fully atomized. It ensured full and proper coverage. At the same time, it cause chemical irritants to become airborne, thus requiring the use of a half-face respirator when using the deoxidizer. The vendor later was asked if the material could be applied using a wand sprayer. This was tested at a later date and found to be effective for application and reduced the amount of airborne irritants. When applied, the PPG 11-TGL-27 left an orange peel appearance that made it very easy to determine what areas were properly coated. The final rinse for this product required additional pressure than is available from a garden hose for rinsing. For the demonstration, a garden hose with a sprayer nozzle was used.

Fig. 12 RECC 1043 deoxidizer (90 °F) application to the nacelle

Fig. 13 11-TGL-27 zirconium pretreatment application

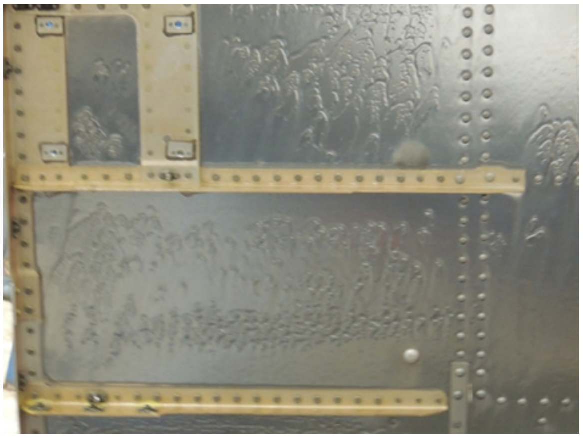

Fig. 14 As-applied appearance of 11-TGL-27 zirconium pretreatment

- MacDermid Iridite
    - Isoprep 50LLF required to be at a pH of 5 before application.
    - Isoprep 50LLF and Iridite NCP required application at 100 °F.
    - Per onsite representatives, the maximum overcoat window is 24 h after pretreatment.
    - Slight yellow/blue color, easier to see when compared to untreated, virgin aluminum

Images from the MacDermid Iridite NCP demonstration are shown in Figs. 15–20. The surface treatment was applied with a wand sprayer that applied the material evenly. There was more prep work required to get the treatments ready for application than compared to other products. Additional tools and training would be needed to implement this material at CCAD. Similar to the PPG product, the deoxidizer was an airborne irritant. The treatments required a rinse with greater pressure than is provided by a garden hose. For the demonstration, a garden hose with a spray nozzle was used.

Fig. 15 Final DI rinse

Fig. 16 pH adjustment of Iridite NCP

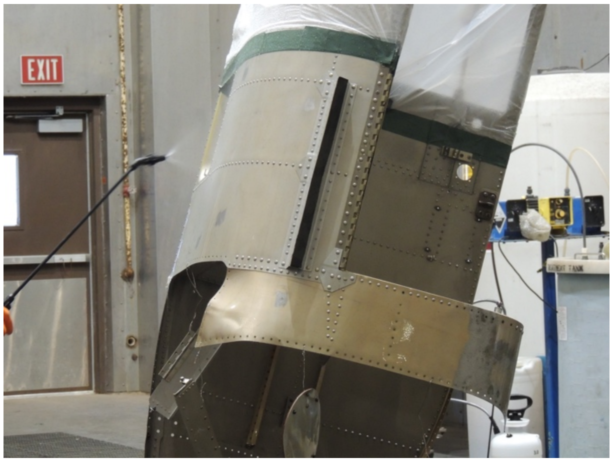

Fig. 17 Isoprep 184 acid etch application to the nacelle

Fig. 18 DI rinse of the nacelle

Fig. 19 Iridite NCP pretreatment (100 °F) applied to the nacelle

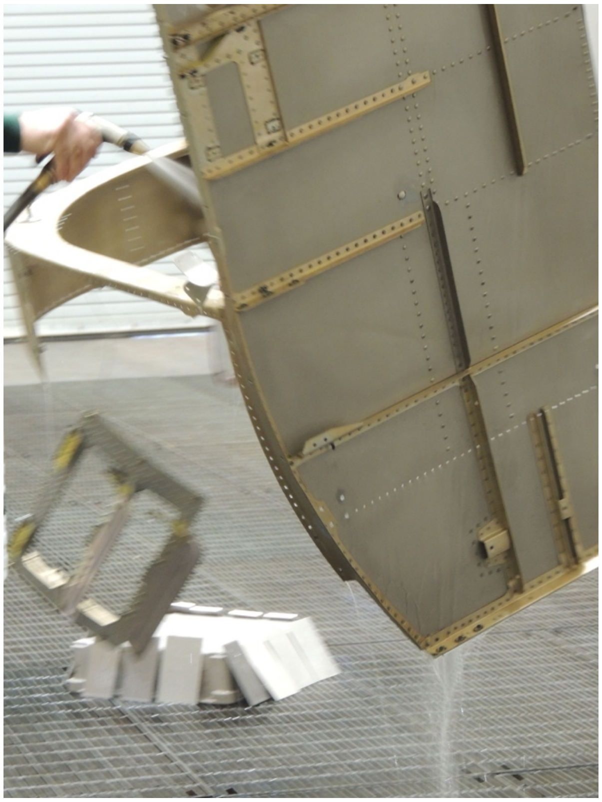

Fig. 20 Final DI rinse of the nacelle

Images from the Alodine 1200S baseline demonstration are shown in Figs. 21–23. The brush and mop application of this product leaves a streaky, inconsistent finish on the substrate. Due to local regulations, the material cannot be sprayed because of the Cr^{6+} in the system. Once brushed on, it was rinsed off with a garden hose.

Fig. 21 Solvent wipe with MPK

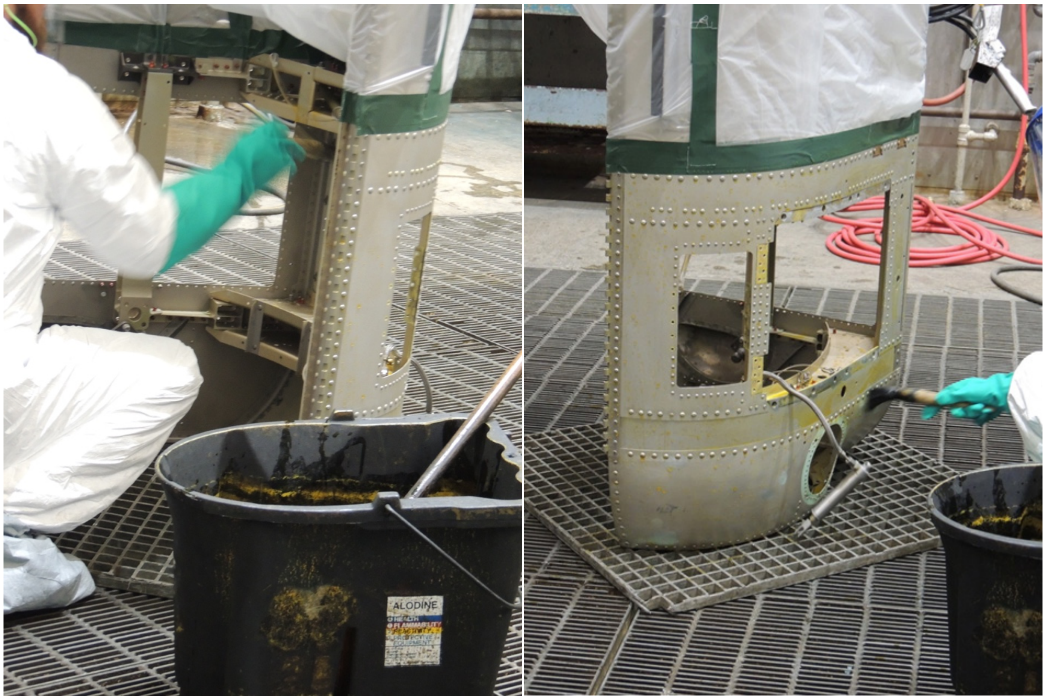

Fig. 22 Brush application with Alodine 1200S

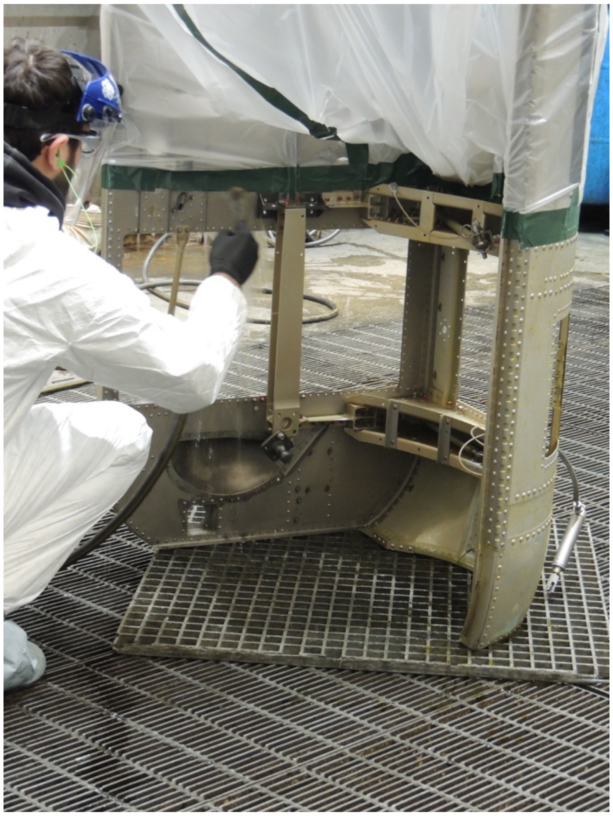

Fig. 23 Final DI rinse for the Alodine 1200S process

After pretreatment, CCAD applied their standard coating system (Hentzen MIL-PRF-23377 Class N primer and solvent-based MIL-DTL-53039 topcoat). Panels and parts were returned to ARL for testing. Nacelles were exposed at CCAD along with mass loss coupons for natural exposure testing. These were exposed within a controlled access lot on 10 February 2016.

4.2 Immersion Application Demonstration

The BONDERITE M-NT 5200 was applied by a representative from the vendor and ARL personnel. CCAD personnel performed chromate conversion coating using their current immersion process, which uses MacDermid Iridite 14-2 (generically referred to at CCAD as “Alodine”). The application was performed on the following parts and panels (per system):

- Parts
    - 10 parts of various sizes
    - General characteristics were flat parts with holes, rivets and fasteners.

    - One box was also coated.
- Panels
    - 24; 3 inch by 6 inch by 1/4 inch
    - 12; 10-inch by 10-inch thin gage
    - 1; 6-inch by 12-inch thin gage

The parts were representative of repair items at CCAD, which had been prepared for rework per their normal process by glass-bead blasting, although no specific details (operating pressure, media size, etc.) were provided. Visually, the parts appeared to be clean and free of any coating materials. The panels were virgin 2024 or 7075 aluminum, which were cleaned and processed using the procedures for each pretreatment.

Table 6 compares the process steps based on the information provided onsite by Henkel (Kristina Tkacz) and CCAD personnel. Generally, these were adhered to during the demonstrations.

Table 6 Process steps for pretreatment demonstrations

Step	Henkel – BONDERITE M-NT 5200	CCAD – Iridite 14-2
1.	Immerse in 9.5% solution of BONDERITE C-AK 212 (9.5 pH) for 2 min at 155 °F.	Abrasive blast/shot peen surface.
2.	Immerse in DI water rinse for 30 s to achieve a water-break free surface (longer immersion allowed).	Immerse in conversion coating bath for 30 to 180 s, checking part frequently.
3.	Immerse in 2.25% solution of BONDERITE C-IC 357 for 1 min at 105 °F.	Rinse.
4.	Immerse in DI water rinse for 30 s to achieve a water-break free surface (longer immersion allowed).	Allow to air dry.
5.	Immerse in a 3% solution of BONDERITE M-NT 5200 (3-3.6 pH) for 1.5 min at ambient.	. . .
6.	Immerse in DI water rinse for 30 s to achieve a water-break free surface (longer immersion allowed).	. . .
7.	Allow to air dry.	. . .

Note: The CCAD immersion process includes steps for degreasing, glass bead blast, alkaline cleaning, rinse, deoxidize, rinse, conversion coating and final rinse. Per the operator these steps were not followed, and parts proceeded straight from glass bead blasting to conversion coating. Process Standard B.00 lists the degreasing, cleaning, and deoxidizing steps as optional.

Table 7 provides the Henkel solution temperatures, concentrations, and pH as-mixed and reported by their onsite representative just prior to the start of the immersion demonstration. The BONDERITE C-AK 212 and C-IC 357 concentrations were higher than the targets, but acceptable to the onsite representative. The temperature of the BONDERITE C-AK 212 was lower than desired, as a result the Henkel representative increased the immersion time in the alkaline cleaner to 3 min. Fig. 24 shows the portable setup of the BONDERITE 5200 in the wash bay.

Table 7 As-mixed BONDERITE solution temperature, concentration, and pH

Solution	Temperature (°F)	Concentration (%)	pH
BONDERITE C-AK 212	105	10.5%	9.5
BONDERITE C-IC 357	105	3%	. . .
BONDERITE M-NT 5200	85 (ambient)	. . .	3.5

Fig. 24 Immersion tanks for the Henkel BONDERITE M-NT 5200 demonstration

At the completion of the demonstration the BONDERITE C-AK 212 was 110 °F and the BONDERITE C-IC 357 was 105 °F.

Table 8 shows the times measured for the first set of panels and the last set of parts to be processed through the BONDERITE M-NT 5200 immersion process.

Table 8 Process times for the BONDERITE pretreatment demonstration and total elapsed time

Step	Henkel – BONDERITE M-NT 5200 (mm:ss)		
	First set – panels	**Second set – parts**	**Difference**
START	**15 June 2016 at 1249**		
1.	3:01	3:35	0:34
2.	0:32	0:48	0:16
3.	1:01	1:30	0:29
4.	0:31	0:41	0:10
5.	1:31	1:31	0:00
6.	0:31	0:54	0:23
Process time	**7:07**	**8:43**	**1:38**
END	**15 June 2016 at 1443**		
TOTAL ELAPSED TIME	**1 h and 54 min**		
Average Process Time	**7 min and 55 s**		

As described, the current CCAD chromate conversion coating process has a single step, immersion in Iridite 14-2 for 4 min followed by a rinse step (assumed to be 30 s). Comparatively, the Henkel BONDERITE M-NT 5200 (on average) requires an additional 3 min, 25 s. However, the B.00 Process Standard provides additional process steps that are listed as being optional, which mirror the steps of the BONDERITE M-NT 5200 process. Fig. 25 replicates the process steps for each material and shows the times for each process step and total overall process times.

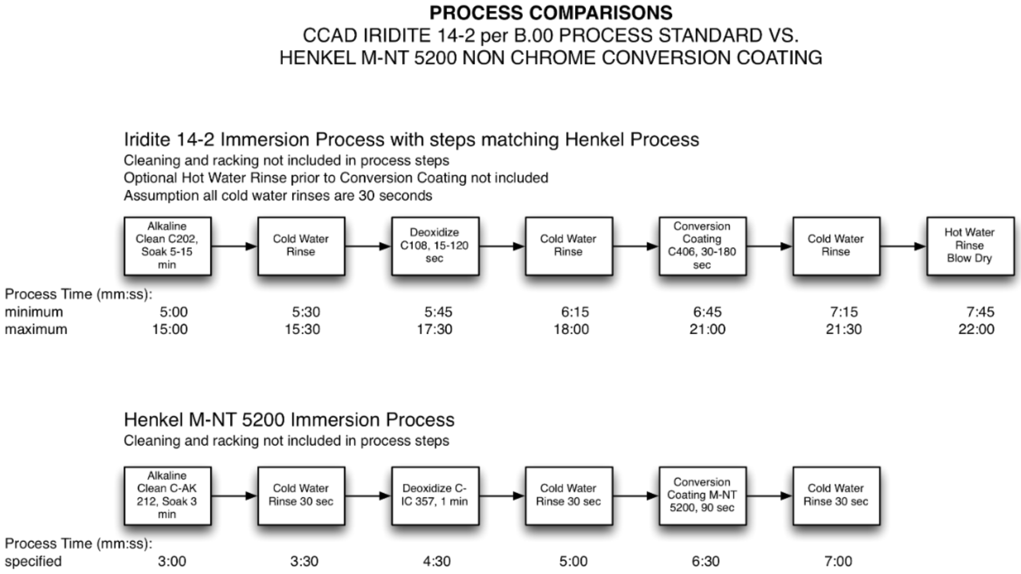

Fig. 25 Comparison of equivalent CCAD Iridite 14-2 and Henkel M-NT 5200 immersion processes

Considering the optional steps, the BONDERITE M-NT 5200 is comparable to the Iridite 14-2 immersion process (Iridite being 15 s [3.5%] longer than BONDERITE).

- Comparison of equivalent processes
    - BONDERITE M-NT 5200: 7:00 (mm:ss)
    - Iridite 14-2: 7:15 (mm:ss)

During the BONDERITE M-NT 5200 immersion demonstration, the following observations were made:

- Dew (moisture) was observed to form on thicker aluminum panels when first placed in the demonstration area. As these samples reached ambient temperature (and after wiping dry), the dew did not reform.
- Foaming of the cleaner was observed, but was attributed to the agitation provided by the mixers (a speed controller was not available).
- No significant color shift was observed on the samples after the pretreatment process.

During this site visit, Henkel and ARL attendees toured the current chromate conversion coating immersion process used at CCAD (Iridite 14-2). The following observations were made/information were obtained:

- The process line has 21 tanks, but is used for hard chrome anodizing and chromate conversion coating.
- Although not used, there are tanks for alkaline cleaning, desmutting (deoxidizing), and rinse tanks. There is also a tank for degreasing, as required.
- Per the CCAD personnel providing an overview of their current process, they bead blast components then within 1–2 h immerse in the chromate conversion coating for 4 min.

After pretreatment, CCAD applied their standard coating system (Hentzen MIL-PRF-23377 Class N primer and solvent-based MIL-DTL-53039 topcoat). These were scheduled for priming the morning of 17 June by the first shift painters, with the topcoat to be applied during the evening of 17 June by the second shift painters. Parts exposed at CCAD were installed onto racks within a controlled access lot February 2017.

4.3 Adhesion

Cross hatch adhesion results can be found in Table 9. Overall, results were all passing with all of the demonstrated products doing as well if not better than the baselines on both 2024 and 7075 aluminum substrates.

Table 9 Adhesion results

Panel	On 2024- T3	On 7075 T6
Spray		
Alodine 1200S	4B	4B
BONDERITE 5200/5700	4B	5B
PPG 11-TGL-27	4B	4B
MacDermid	4B	4B
Immersion		
MacDermid 14-2	4B	4B
BONDERITE 5200/5700	4B	4B

4.4 Corrosion

Corrosion results after 21 cycles of GMW14872 are reported in Table 10. Overall, the results for the demonstration products were on par with the results from the baseline.

Table 10 Corrosion results after 21 cycles GMW14872.

Panel	Field	Titanium bolt					Stainless steel bolt				
		Washer creep (mm)	Radial rating (1654)	Scribe creep (1654)	Scribe washer creep (mm)	Scribe radial rating (1654)	Washer creep (mm)	Radial rating (1654)	Scribe creep (1654)	Scribe washer creep (mm)	Scribe radial rating (1654)
Alodine 1200S	10	1	8	6	9.5	7	4.5	5	6	12	5
BONDERITE 5200/5700	10	0	10	7	2	8	1.5	7	6	3	7
PPG 11-TGL-27	10	0	10	5	13	5	0	10	5	8	5
MacDermid	10	0	10	8	0	10	0	10	5	9	6

Images for the panels can be found in Fig. 26. Visually, all of the system are comparable after the exposure. The demonstration surface treatments look on par with the baseline.

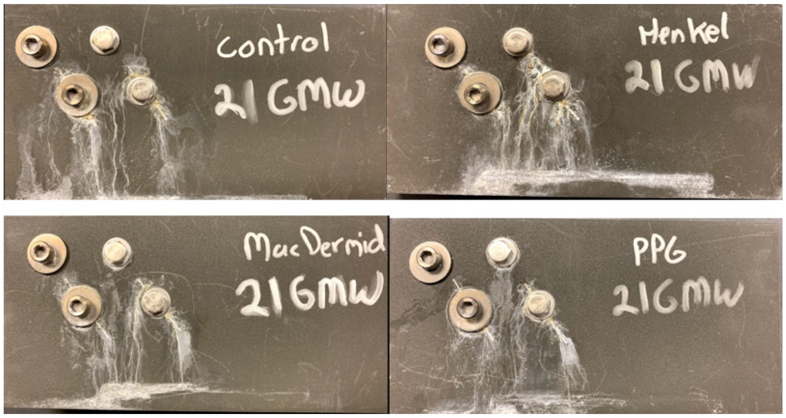

Fig. 26 Panels after 21 cycles

4.5 Atmospheric Exposure

Results for the galvanic panels after 2 years exposure at CCAFS can be found in Table 11. Images for these panels can be found in Fig. 27. Overall, the corrosion buildup on the panels around the fastener were somewhat similar. Corrosion from the scribe was very similar as well. The MacDermid Iridite NCP had some delamination along the scribe the occurred when the panel was scribed.

Table 11 Corrosion results after 2 years at CCAFS

Panel	Sample	Scribe	Field	Titanium bolt					Stainless steel bolt				
				Washer creep (mm)	Radial rating (1654)	Scribe creep (1654)	Scribe washer creep (mm)	Scribe radial rating (1654)	Washer creep (mm)	Radial rating (1654)	Scribe creep (1654)	Scribe washer creep (mm)	Scribe radial rating (1654)
Alodine 1200S	1	5	10	11	6	6	17	3	6	6	4	32	3
	2	6	10	1.5	8	5	21	4	2.5	8	4	24	3
BONDERITE 5200/5700	1	4	10	22	4	4	32	3	16	4	4	26	3
	2	5	10	0	10	5	0	10	26	3	1	26	1
PPG 11-TGL-27	1	5	10	2.5	8	5	10.5	4	13.5	5	5	19	4
	2	5	10	0	10	7	20	6	21	5	7	16	5
MacDermid Iridite NCP	1	4	10	0	10	8	18.5	4	16	4	4	13	4
	2	4	10	0	10	5	0	10	0	10	4	20	4

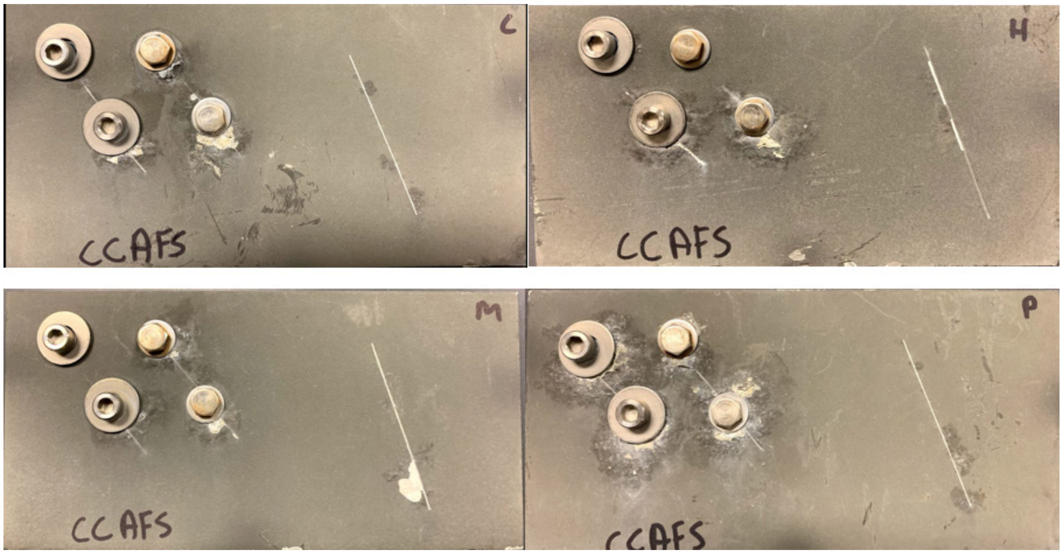

Fig. 27 Galvanic panels after 2 years at CCAFS. Top left: Alodine 1200S, Top right BONDERITE 5200/5700, Bottom left MacDermid Iridite NCP, Bottom right PPG

Images for the nacelles and parts that were exposed at CCAD are shown in Figs. 28–32. Overall, there was no noticeable difference between the demonstrated pretreatments and the baselines. After 3 years of exposure at CCAD, the nacelles were in good condition with no visible corrosion on the body of these parts. There was corrosion (red rust) visible on the steel clips of the surfaces pretreated with the MacDermid Iridite, CCAD Alodine, and Henkel BONDERITE products. This can be seen in Fig. 29. This corrosion was on the interior surfaces and within the crevices of these parts, which were likely not well coated during painting. After 2 years of exposure at CCAD, the immersion parts were in good condition with no visible corrosion on the body of these parts. The parts had some coating loss where the zip ties made contact with the parts. This was witnessed on both the BONDERITE 5200 and baseline parts and can be seen in Fig. 32.

Fig. 28 Engine nacelles with spray demonstration pretreatments after 2 years

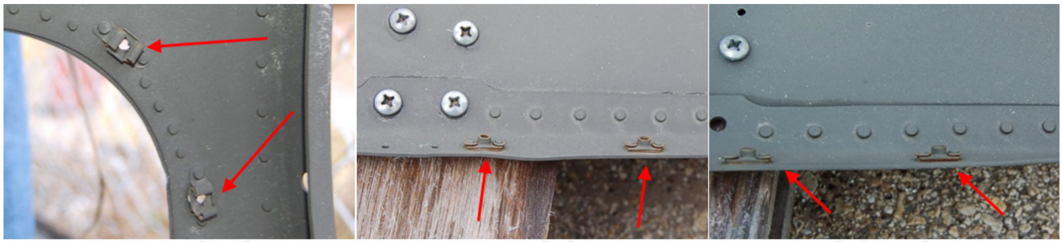
MacDermid Iridite CCAD Alodine Henkel Bonderite

Fig. 29 Red rust on ferrous clips

Fig. 30 Immersion demonstration samples as-installed (Iridite 14-2 on left, BONDERITE 5200 on right)

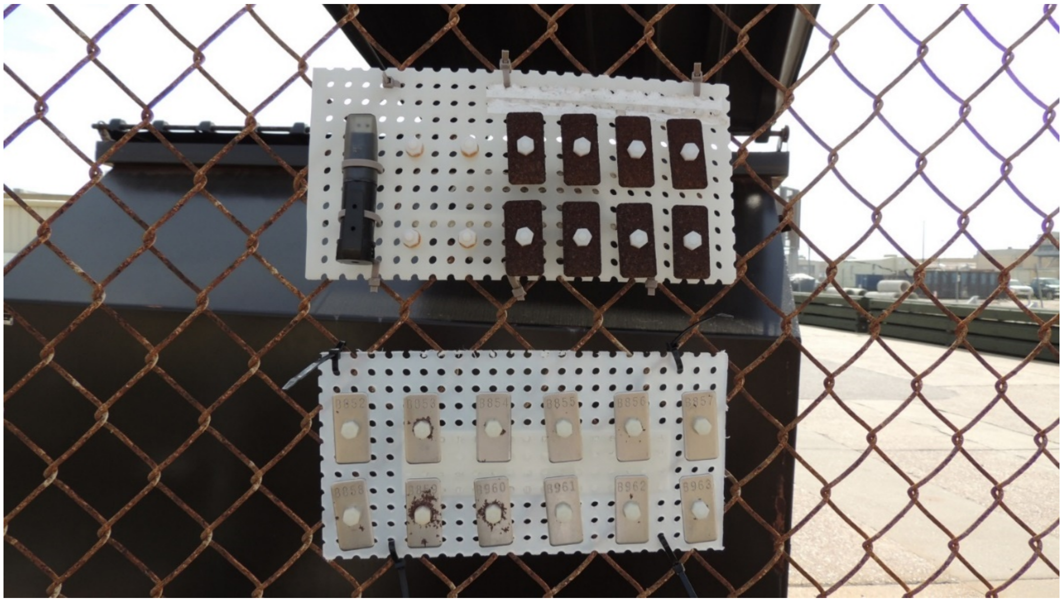

Fig. 31 Mass loss coupons onsite at CCAD

CCAD Iridite Henkel Bonderite

Fig. 32 Parts from immersion demonstration. Coating loss from zip ties

5. Conclusions

After completing two demonstrations at CCAD, the demonstrated products from Henkel, MacDermid, and PPG have shown that they can be applied at the depot and perform on par with the Cr^{6+} conversion coating that is currently used as part of a CARC coating stackup for aviation equipment. All of the demonstrations utilized a solvent-based, chrome-free primer, thus showing that desirable performance can be achieved in a totally chrome-free stackup system. Moving from Cr^{6+} as part of the coating system has positive long-term effects on waste streams without affecting performance in the field and cuts exposure risks to the heavy metal to asset the maintenance community: Solider, civilian, and contractor.

Using processes that were not fully optimized, these demonstrations showed that parts can be processed with chrome-free pretreatments in similar times to the current Cr^{6+} conversion coating. For immersion, the processing time should be similar to the current MacDermid 14-2 surface treatment, but allow for a larger timeframe after pretreatment for the application of primer on parts that have been protected from contaminates. For the spray products, although the processes shown were longer than that for the Cr^{6+} baseline, it is believed that with refinement and experience with the product, one of more of the processes could be optimized to be a similar or shorter duration than the Alodine 1200 process.

6. Path Forward

These materials would have to be written into specifications and production documents to be transitioned to the field for use. The additional laboratory and demonstration work will assist in developing the requirements that need to be included in the specification. At this point, the most appropriate specification for these types of materials would be MIL-DTL-81706. Then process specifications would have to be updated to call out the new chrome-free pretreatments. Also, facilities transitioning to these chrome-free pretreatments will have to address cleaning methods to ensure they are robust to ensure the chrome-free pretreatment will protect as documented.

7. References

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List of Symbols, Abbreviations, and Acronyms

AERTA	US Army Environmental Requirements and Technology Assessment
ARL	Army Research Laboratory
BER	beyond economical repair
BIF	blisters in field
CARC	chemical agent resistant coating
CCAD	Corpus Christi Army Depot
CCAFS	Cape Canaveral Air Force Station
CCDC	US Army Combat Capabilities Development Command
CFR	Code of Federal Regulations
Cr^{+6}	hexavalent chromium
DI	deionized water
DOD	Department of Defense
DTM	Directive-Type Memorandum
EU	European Union
FZA	fluorozirconic acid
HVLP	high-volume, low-pressure
OSHA	Occupational Safety and Health Administration
PMB	plastic media blasting
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
TACOM	Tank Automotive and Armaments Command

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