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Coating Characterization of Tartaric Sulfuric Acid Anodizing Compared with Chromic Acid Anodizing

by Lindsey Blohm, Scott Grendahl, Scott Howison, and Jack Kelley

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Lindsey Blohm, Scott Grendahl, and Jack Kelley
DEVCOM Army Research Laboratory

Scott Howison
US Army Aviation and Missile Command

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14. ABSTRACT Hexavalent chromium, Cr(VI), is a confirmed human carcinogen that is increasingly regulated; therefore, an urgency to find performance-meeting alternatives has emerged. A program between the US Army Combat Capabilities Development Command Army Research Laboratory and the US Army Missile and Aviation Command Logistics Directorate (G-4) aims to optimize, qualify, and demonstrate Sikorsky’s Tartaric Sulfuric Acid Anodizing (TSAA) as an alternative to Chromic Acid Anodizing (CAA). Thus far, a majority of laboratory testing is complete and reported in this interim report. The majority of the data shows promising results. However, bendability results as well as axial fatigue show that TSAA is not meeting the standard of CAA. Additional results will be forthcoming in a future report; this report provides results and gathers guidance.					
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1. Introduction

1.1 Program Overview

Chromic Acid Anodizing (CAA) of aluminum (Al) is one of the most frequently employed processes at the Corpus Christi Army Depot (CCAD) Advanced Metal Finishing Facility (AMFF) during the depot maintenance of rotary aircraft. Although this process is effective and thoroughly established, it relies on the use of hexavalent chromium, Cr(VI), a known carcinogen and environmental contaminant that is the subject of increasing domestic and international regulatory scrutiny. As such, it has been targeted by the Army for reduction or elimination.

To qualify an alternative, the US Army Combat Capabilities Development Command Army Research Laboratory and the US Army Missile and Aviation Command (AMCOM) Logistics Directorate (G-4) have been tasked to evaluate, test, and demonstrate Tartaric Sulfuric Acid Anodizing (TSAA), a process that was previously selected and optimized by Sikorsky Aircraft Corporation (Sikorsky) as an alternative to CAA. In the current effort, the AMCOM G-4 is working with DEVCOM Army Research Laboratory to test the TSAA process against validated requirements using the current process (CAA) as a control.

The TSAA technology, if accepted, would address all aviation platforms processed at CCAD to include the UH-60, AH-64, and CH-47 helicopters. The Army Environmental Requirements and Technology Assessment PP-2-02-06 would be addressed by eliminating Cr(VI) used for anodized Al. Hexavalent chromium is a confirmed human carcinogen and thus poses a significant the risk to personnel using it. A replacement for CAA must meet fatigue, corrosion, adhesion, and reparability performance requirements. This TSAA change would also support the Future Vertical Lift Cross-Functional Team through qualification as a base for coatings for Army Aviation systems. The increasingly strict worldwide regulatory environment suggests the eventual obsolescence of Cr(VI), as industry is transitioning to alternative products. Also, three tanks in the AMFF-T processing line would be impacted, resulting in significant chromic acid reductions and a reduction in CCAD operation costs.

The intended product is a validated and approved TSAA process with a non-Cr(VI) sealer as an alternative to CAA with plans to meet requirements of MIL-A-8625-F¹ and implement via maintenance engineering orders at CCAD. Testing resulted in subpar performance of TSAA compared with CAA, specifically failures in fatigue and bendability testing. Fatigue is a vital test, particularly for aerospace applications.

1.2 Anodize Process

Different types of anodize properties are preferred for specific outcomes, as shown in Fig. 1,² and they are contradicting one another. For corrosion protection, an anodize should be thick, with small pore diameter and high aluminum oxide (Al_2O_3) content. To protect against fatigue, thin film is preferred with high aluminum hydroxide [$\text{Al}(\text{OH})^3$] content. For ideal adhesion, anodize should have large pores, high $\text{Al}(\text{OH})^3$ content, and high film stability. From these properties, it is evident that a delicate balance is required to produce the ideal pretreatment to meet all performance criteria.

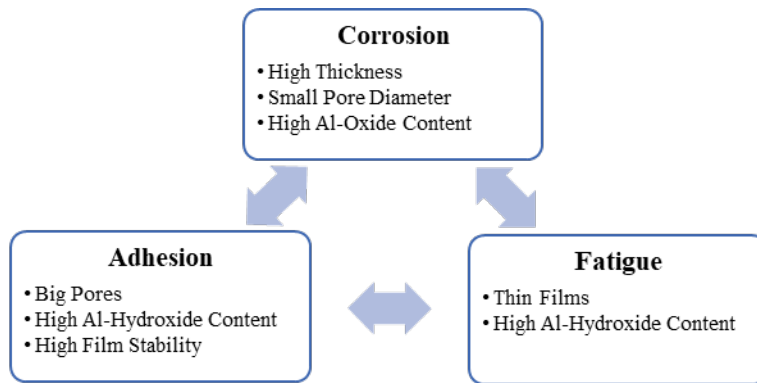


Fig. 1 Contracting requirements of anodizing pretreatments for ideal performance criteria²

Anodic coatings such as CAA and TSAA are typically sealed in a process to reduce the outer pores, forming a less permeable film or causing blockages of pores via inclusion or precipitation of deposited salt.³ In this work, sealers used were trivalent chrome and chrome acid (hexavalent rinse). Historically, MIL-A-8625 Type I¹ coatings have been sealed in hot sodium dichromate solution (near boiling), forming a hydrothermal seal and precipitating chromium oxides into the anodic coating porous structure.³ As a result, the oxide is converted to a more stable boehmite form.³ Note that a conventional trivalent chromium process (TCP) seal, as used in this work, is performed under ambient conditions so as not to impart a dense hydrothermal seal of oxide onto the substrate.³ A potential alternate option is a duplex seal following the TCP immersion and rinse in which the sample is rinsed in hot water to initiate a hydrothermal seal.

2. Experimental Procedure

AMZ Manufacturing Corporation (York, Pennsylvania) supplied all panels tested. The details of the testing performed on these panels and any characterization performed on the coating are outlined in Tables 1 and 2. This test plan was developed in conjunction with the Systems Readiness Directorate (SRD) following work performed by Sikorsky to validate that the optimized TSAA process meets or exceeds the requirements of MIL-A-8625F¹ Type IC for Al 2024-T3 and 7075-T6 substrates.^{4,5} The full test matrix includes coating quality, coating thickness, coating weight, corrosion resistance, coating adhesion (wet/dry/pull-off), fluid compatibility, axial fatigue, and tensile on Al alloys 2024-T3 and 7075-T6. Each alloy was tested with CAA with both chromic acid seal and a trivalent chrome seal (Chemeon TCP). Samples were also tested with TSAA with a chromic acid seal and trivalent chrome seal.

Table 1 Coating characterization matrix (TMR 15-01)

Tests	Methods	Primer	Sample dimensions (inches)	Baseline Type I CAA				TSAA			
				Chromic acid seal		Trivalent chrome seal		Chromic acid sealer		Trivalent chrome seal	
				2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6
Coating quality	MIL-A-8625 ¹	None	3 × 10	all	all	all	all	all	all	all	all
Coating thickness	ASTM B244 ⁶	None	3 × 10	all	all	all	all	all	all	all	all
Coating weight	MIL-A-8625 ⁶	None	3 × 10	5	5	all	all	all	all	all	all
Corrosion resistance	ASTM B117 ⁷	None	3 × 10 4 × 6	5	5	5	5	5	5	5	5
	ASTM G85 ⁸	23377 Type-1 Class N ⁹	3 × 10	5	5	5	5	5	5	5	5
		None	3 × 10	5	5	5	5
Coating adhesion (wet)	FED-STD-141 ¹⁰ (6301), Tape tests	23377 Type-1 Class N ⁹	3 × 10	5	5	5	5
	per ASTM 3359 ¹¹ (Method B)	85582 Type-1 Class N ¹²	3 × 10	5	5	5	5
Coating adhesion (dry)	ASTM D3359 ¹¹ (Method B)	23377 Type-1 Class N ⁹	3 × 10	5	5	5	5	5	5	5	5
Coating adhesion (pull-off)	ASTM D4541 ¹³	23377 Type-1 Class N ⁹	4 × 6 × 0.032	5	5	5	5	5	5	5	5
Bendability	ASTM D522 ¹⁴ Method B (ASTM B117)	None	3 × 10	5	5	5	5
Fluid compatibility	MIL-STD-810G ¹⁵ Method 504.1 Procedure II	None	3 × 5	33	33	33	33

Table 2 Structural integrity matrix (TMR 15-01)

Tests	Method [reference]	Sample	Bare aluminum alloy (no anodize or seal)		Baseline Type I CAA w/chromic acid seal		TSAA w/trivalent chrome seal	
			2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6
Tensile	ASTM B577 ¹⁶	...	3	3	3	3	3	3
Axial fatigue	ASTM E466 ¹⁷	$K_t = 1$	12	12	12	12	12	12
		$K_t = 3$	12	12	12	12	12	12

The process line specifics used to process the panels from Table 1 and 2 are broken down in and detailed in Fig. 2. The performance objectives and success criteria for TSAA are detailed in Table 3. These criteria were used to determine if TSAA met or did not meet criteria set by the CAA baseline.

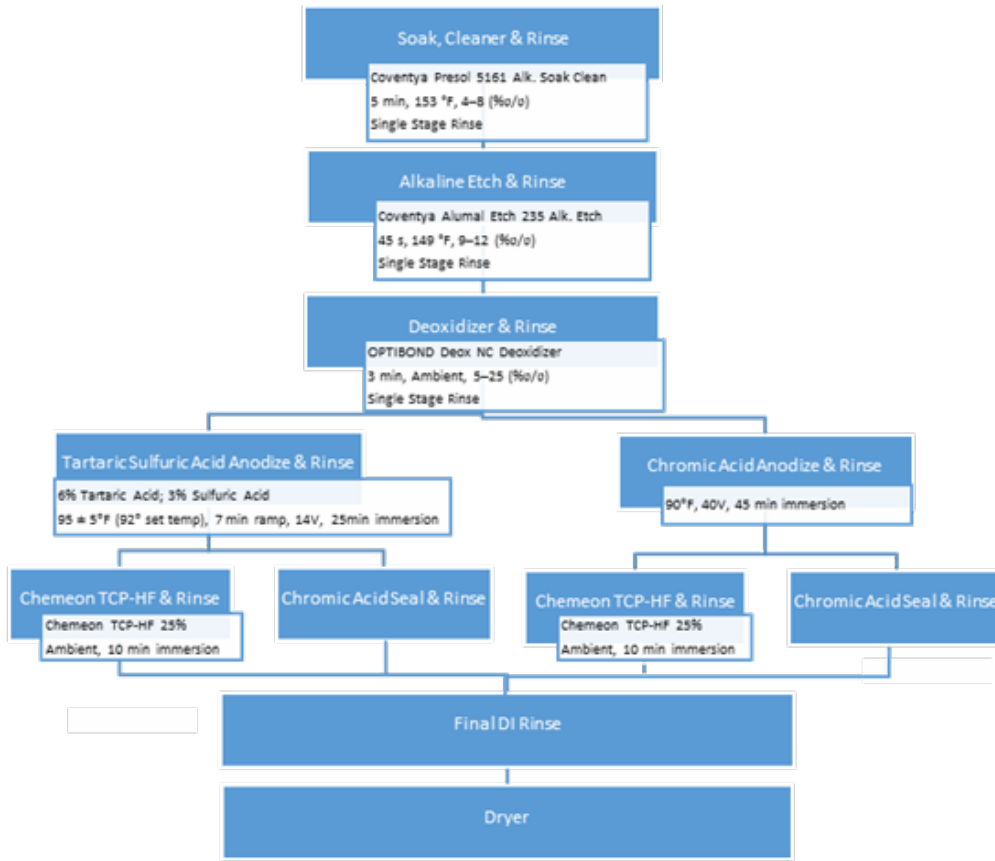


Fig. 2 Anodization process performed by AMZ, as optimized by Sikorsky¹⁴

Table 3 Performance objectives and success criteria for TSAA

Performance objectives	Data requirements	Success criteria
Coating quality	MIL-A-8625 ¹	Anodic coating shall be continuous smooth, adherent, uniform in appearance, and free from powdery areas, loose films, breaks, scratches, and other defects that will reduce the serviceability of anodized samples.
Coating thickness	ASTM B244 ⁶	Within coating thickness range of 0.1 and 0.2 mil for Type I CAA.
Coating weight	MIL-A-8625 ¹	In accordance with MIL-A-8625. ¹
Corrosion resistance	ASTM B117 ⁷	<i>After 336 h of exposure or until failure:</i> Test specimens shall show no more than a total of 15 isolated pits (B117, Section 6.19), none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded.
	ASTM G85 ⁸	Test specimens shall show no more than five isolated pits, none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded.
Coating adhesion (wet)	FED-STD-141 ¹⁰	Adhesion rating better than 4B.
	(6301) Tape tests per ASTM 3359 ¹¹ Method B	No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.
Coating adhesion (dry)	ASTM D3359 ¹¹ Method B	Adhesion rating better than 4B.
		No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.
Bendability	ASTM D522 ¹⁴ Method B (ASTM B117)	Same as corrosion resistance requirements.
Coating adhesion (pull-off)	ASTM D4541 ¹³	Similar to or better than performance of CAA.
Fluid compatibility	MIL-STD-810G ¹⁵ Method 504.1 Procedure II	4.56: Procedure II small items, ambient temperature; applied by immersing. Similar to or better than performance of CAA.
Tensile	ASTM B577 ¹⁶	Equal to or better than CAA.
Axial fatigue	ASTM E466 ¹⁷	Endurance limit equivalent or greater than Type I CAA.

2.1 Characterization of Coatings Test Methods

2.1.1 Quality

Success criteria for quality are the following: Anodic coating shall be continuous, smooth, and adherent, uniform in appearance, and free from powdery areas, loose films, breaks, scratches, and other defects that will reduce the serviceability of anodized samples, as per MIL-A-8625-F.¹

2.1.2 Coating Thickness

AMZ provided two coating thickness measurements per coated panel using ASTM B244-09.⁶ Coating thickness should be in accordance with MIL-A-8625,¹ Table V.

2.1.3 Coating Weight

Coating weight was reported by AMZ as per MIL-A-8625.¹ Weight testing was performed on 10 flat Al test panels, 5 TSAA panels, and 5 CAA panels, all of which were 3.0 × 10.0 × 0.032 inches.

2.1.4 Corrosion Resistance

2.1.4.1 ASTM B117

Corrosion resistance testing using ASTM B117-11⁷ was performed over 2 weeks (336 h) using the following requirements. Test specimens shall show no more than a total of 15 isolated pits, none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded. Test specimens shall show no more than five isolated pits, none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded.

2.1.4.2 ASTM G85

Corrosion resistance testing using ASTM G85-02⁸ was outsourced to Auto Technology Company (Strongsville, Ohio). Samples were tested for 15 days in an Auto Technology Salt Fog Model 22 chamber using the following requirements. Test specimens shall show no more than a total of 15 isolated pits, none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded. Test specimens shall show no more than five isolated pits, none larger than

0.031 inch in diameter, in a total of 30 square inches from one or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded.

2.1.5 Coating Adhesion (Wet)

2.1.5.1 Wet Adhesion

Samples were soaked in deionized water for 24 h per FED-STD-141 (6301).¹⁰ Cross-hatch adhesion testing was performed per ASTM 3359 (Method B).¹¹ Three panels per sample type were tested with four adhesion tests per panel. Results are averaged over the total 20 cross-hatch adhesion tests. Samples must have an adhesion rating better than 4B to meet passing criteria and have no intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.

2.1.5.2 Dry Adhesion

Samples were tested via ASTM D3359 (Method B).¹¹ Five panels per sample type were tested, with six adhesion tests per panel. Results are averaged over the 30 cross-hatch adhesion tests.

2.1.5.3 Pull-Off Adhesion

Samples were tested in accordance with ASTM D4541.¹³ Five panels per sample type were tested, with 25–30 adhesion values per panel set. Results were averaged across the collected values along with the type of adhesion failure mode, as detailed in Table 4.

Table 4 Adhesion failure modes

Failure	Failure description
Glue	No coating on dolly
Adhesive	Coating failure at interface w/other coating
Cohesive	Same coating on dolly and panel
Cohesive + Adhesive	Both cohesive and adhesive failures

2.1.6 Bendability

Panels were bent using a mandrel bend (3/4 inch) test device per ASTM D522¹⁴ (Method B). Subsequently, panels were placed in neutral salt-spray testing (ASTM B117¹³) for 2 weeks (336 h). Due to extenuating circumstances, panels had to be removed from the neutral salt spray mid-test due to a laboratory shutdown. Samples were tested for 243 h, rinsed with deionized water, removed from the chamber, and moved to a neutral location for the duration of the shutdown. When the laboratory

was reopened, samples were put back in salt spray for the remaining 93 h. Passing criteria are the same as corrosion resistance requirements (Section 2.1.4.1)

Following the bendability and neutral salt-spray testing, sample bends were visually inspected using a Keyence VK-X1000 Series 3-D scanning confocal microscope. Laser images were taken with a 100× lens to show more detail as well as perform some mathematical analysis.

Images and micrographs of samples denoted as “bend” were taken in the area depicted in Fig. 3a, and those denoted as “flat” areas of the panel are depicted in Fig. 3b. Stitched images of the 4- × 6-inch panels were compiled: 100× magnification micrographs by the Keyence software for the bend area and 50× magnification for the flat area. These stitched micrographs were collected in the directionality, as shown in Figure 3c (scaling of stitch depicted by red rectangle for reference and not accurate). All micrographs were adjusted to level the laser micrographs, with the bent samples also adjusted for curvature prior to analysis.

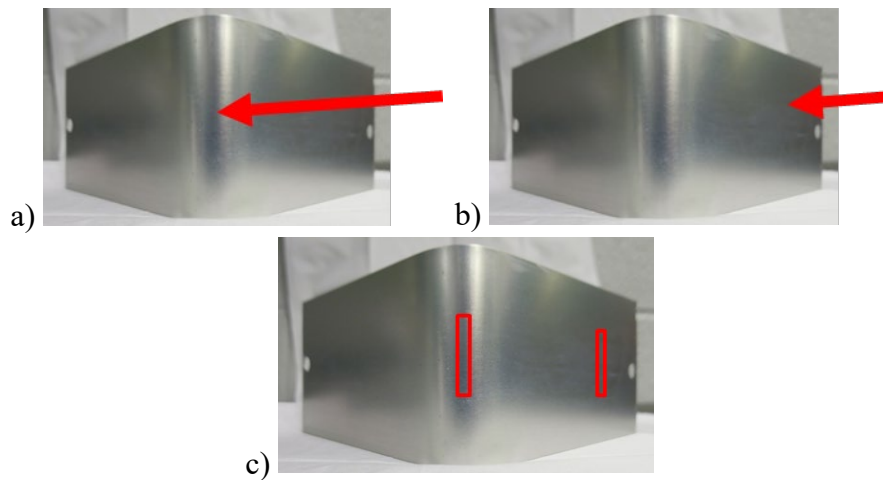


Fig. 3 a) Bend area of samples where images and micrographs were processed, b) flat area of samples where images and micrographs were processed, and c) directionality and location of stitched micrographs

Multiple analyses were performed on the stitched micrographs using the Keyence VK-X10003D laser scanning confocal microscope. Figure 4a shows an example of a singular micrograph at 100× of a TSAA trivalent chrome seal 2024 panel following ASTM B117⁷ taken at the bend. Following the bend, crazing (microfracturing of the anodic layer) appears to have formed; more details are described in the Results section. Figure 4b shows a micrograph at the bend where these microfractures were formed, and the thickness between cracks was measured. Four measurements across the stitched micrographs were taken among four random microfractures and averaged along with the standard deviation taken. Figure 4c shows a representation of crack thickness measurement. Four measurements across

the stitched micrographs taken on four random “craze thicknesses” were averaged along with standard deviation measurements.

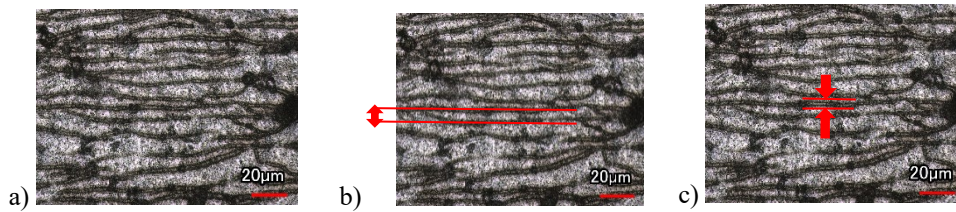


Fig. 4 a) Example micrograph at 100×, b) example “craze” thickness measurement, and c) example “craze” gap measurement

2.1.7 Fluid Compatibility

Samples were tested for fluid compatibility per MIL-STD-810G¹⁵ Method 504.1 Procedure II. Fluids were selected via from EFM 143559¹⁸ as shown in Table 5. Triplicates of each sample type were tested in each fluid.

Table 5 Fluids tested per EMF 143559

Fluid	Fluid per EMF 143559	Fluid used
Fuel	JP-8	F-24 (switch authorized by SRD)
Hydraulic fluid	MIL-PRF-83282 ¹⁹ MIL-PRF-5606 ²⁰	Royco 782
Lubricating oil	MIL-PRF-23669, ²¹ MIL-PRF-7808L, ²² Mobil Aviation Gear Lubricant (AGL)	Eastman Turbo Oil
Cleaner	Isopropyl alcohol	Isopropyl alcohol
	MIL-PRF-85570 ²³ Fuselage cleaner 1:5 water	MIL-PRF-85570
Deicing fluid	Per MIL-STD-810G ¹⁵ /504 Table 1	TKS-Deicing Fluid
Grease	Syntec HMS 20-1155	Syntec NS-4405-FG
Corrosion preventative compound	CorBan 27-L, Cor-Ban 35	Cor-Ban 35

2.2 Structural Integrity Test Methods

2.2.1 Tensile

Tensile testing was conducted to verify the mechanical properties of the alloys and heat treatment used. Table 2 shows the test matrix for each test material. An Instron Model 5964 250-kip mechanical test frame equipped with a 10-kip load cell was used. Testing was conducted in accordance with ASTM B577-19.¹⁶ All tests were conducted in air at room temperature.

2.2.2 Axial Fatigue

Two stress intensities, $K_t = 1$ and $K_t = 3$, were used for the axial fatigue strength assessment. The sample geometry configuration was based not only on the stress intensity requirements but also on the fatigue test-frame capabilities at DEVCOM ARL. Figures 5 and 6 present the schematics for the $K_t = 1$ and $K_t = 3$ specimens used, respectively. These specimen geometries were approved through AMCOM's SRD. Table 2 shows the test matrix for each test material. An Instron Model 1332 100-kip servo-hydraulic test frame equipped with a 10-kip load cell was used. Testing was conducted for at least four different stress levels driving the cycles to failure between 100K and 5M cycles. Tests were performed with sinusoidal oscillation at a frequency of 20 Hz and at an R-ratio (minimum to maximum stress) of 0.1. A Nicolet Model 4094 oscilloscope was used to optimize the conditions of the sinusoidal wave during loop-shaping parameter adjustment of the closed-loop feedback systems on the test-frame hardware. Testing was conducted in accordance with ASTM E466-21.¹⁷ All tests were conducted in air at room temperature. The run-out cutoff was 5M cycles. All run-outs lasted at least this long; however, weekends and holidays were used to their fullest extent so some run-outs were longer.

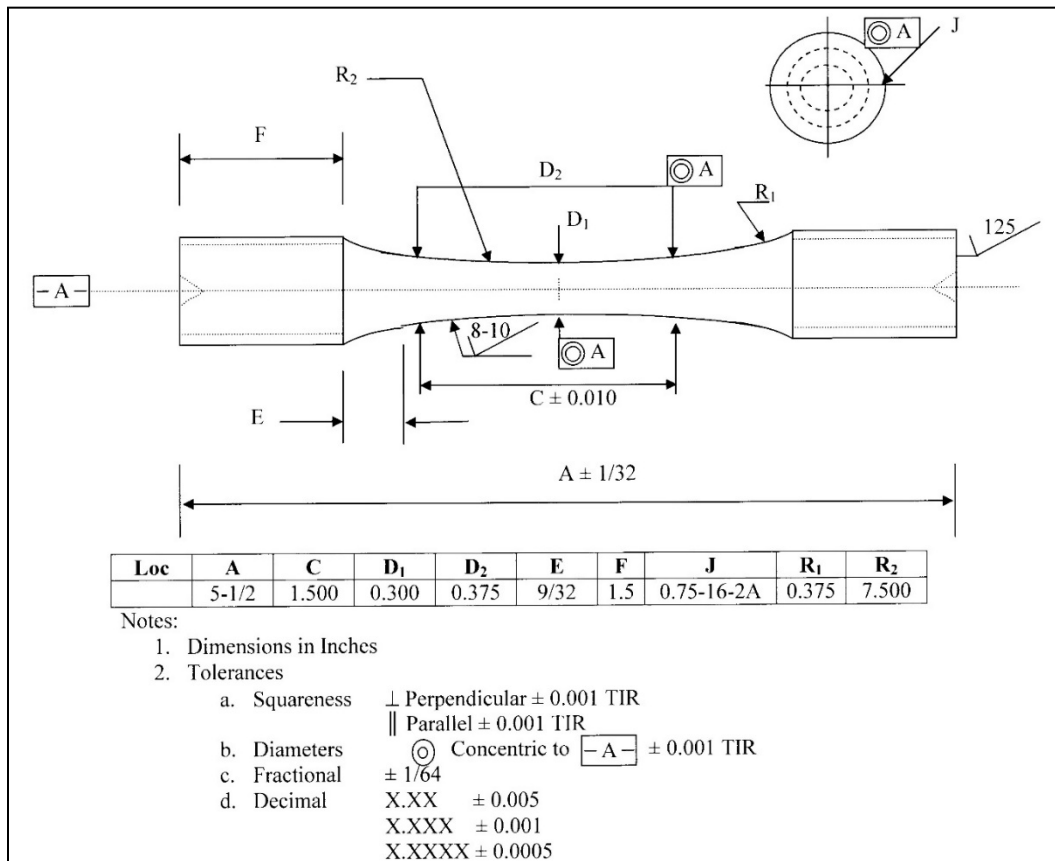


Fig. 5 Schematic of the $K_t = 1$ specimens

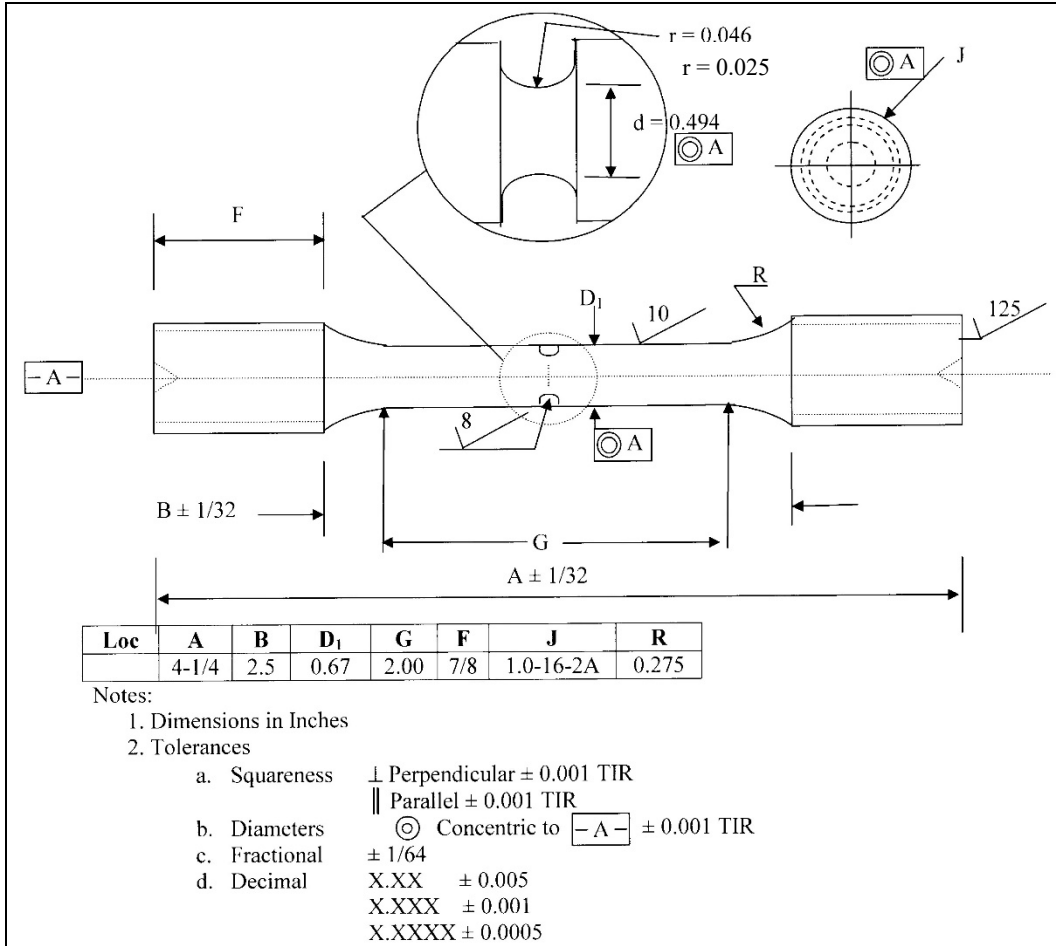


Fig. 6 Schematic of the $K_t = 3$ specimens

3. Results and Discussion

3.1 Characterization of Coating Integrity

3.1.1 Quality

All samples met the success criteria for quality.

3.1.2 Coating Thickness

Coating thickness measurements were performed at 25 min and found to be between 0.1 and 0.2 mil, which meets the requirements as set per MIL-A-8625-F.¹ The averaged coating thickness, in thousandths of an inch, along with the standard deviation for the duplicate sets of panels for each set of panels listed in Table 1 is shown in Fig. 7 for CAA and in Fig. 8 for TSAA, both with trivalent chrome seal (Chemeon TCP-HF) and chromic acid seal.

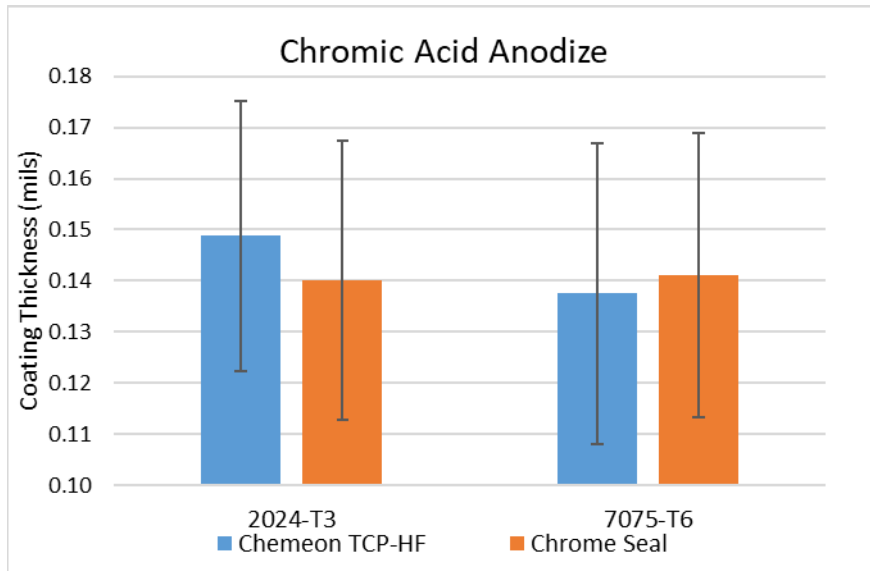


Fig. 7 CAA coating thickness

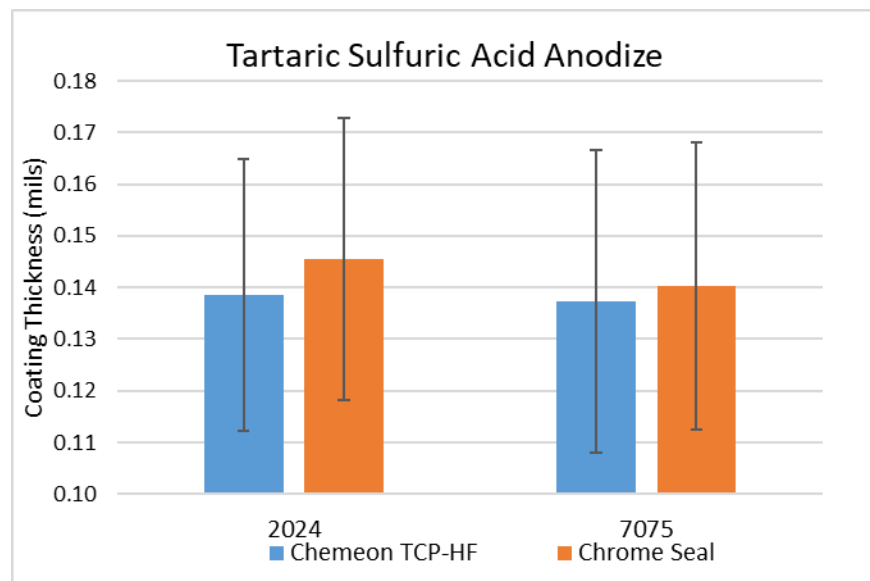


Fig. 8 TSAA coating thickness

3.1.3 Coating Weight

Coating weight measurements were in accordance with MIL-A-8625-F.¹ The anodic coating of all TSAA panels were continuous, smooth, adherent, and uniform in appearance. The TSAA was free from powdery areas, loose films, breaks, scratches, and defects. TSAA and CAA coating weight was tested on 10 flat Al panels (5 TSAA and 5 CAA panels) by AMZ in accordance with test matrix and met the requirements of MIL-A-8625-F,¹ paragraph 3.7.1.1, Table 1, Coating Type I.

3.1.4 Corrosion Resistance

3.1.4.1 ASTM B117

Example panels following ASTM B117⁷ are shown in Fig. 9. Each panel was scanned with a Canon 9000F Mark II at 600 dpi and rated by counting the number of pits per panel, which was averaged across the panels per set. To meet the performance objective, the panels had to have fewer than 15 pits per set of panels and less than 5 pits per individual panel. All panels met the performance objective apart from CAA 2024-T3 panels with a trivalent chrome seal. Upon close inspection of these panels, they failed individually as well as when pits were averaged per set of panels. Example panels of CAA and TSAA with trivalent chrome seal on 2024-T3 are shown in Fig. 9. Pitting was observed on the CAA panels. The difference in panel size results from matrix rearrangement to allow for maximum testing to be performed in this study. The values for the TSAA anodize are listed in Table 6, and those for CAA are listed in Table 7. All panels met the ASTM B117-11⁷ performance objective apart from the CAA 2024-T3 trivalent chrome seal test panels. These panels produced a plethora of pits, far exceeding the limit of 5 pits per panel and an average of 15 pits per set.

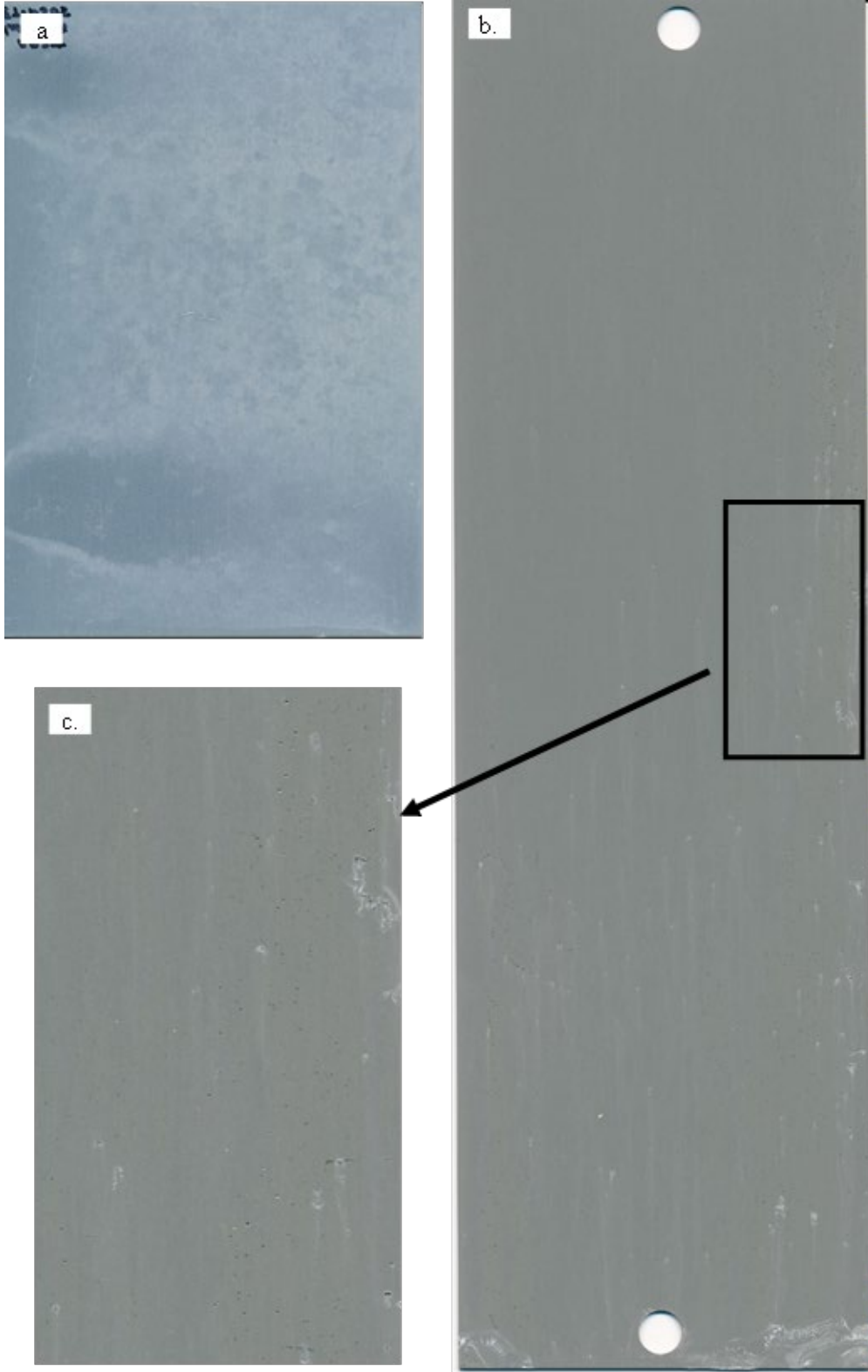


Fig. 9 2024-T3 panels following ASTM B117 a) TSAA, trivalent chrome seal; b) CAA, trivalent chrome seal; and c) close-up showing pitting on CAA, trivalent chrome seal panel

Table 6 TSAA corrosion resistance results

Anodize	Material	Seal type	Average (no. pits)	Standard deviation	<15 Pits/set	<5 Pits/panel
TSAA	2024-T3	Trivalent chrome seal	0	0	Met	Met
		Cr(VI)	0	0	Met	Met
	7075-T6	Trivalent chrome seal	0	0	Met	Met
		Cr(VI)	2	±0.55	Met	Met

Table 7 CAA corrosion resistance results

Anodize	Material	Seal type	Average (no. pits)	Standard deviation	<15 Pits/set	<5 Pits/panel
CAA	2024-T3	Trivalent chrome seal	38.4	±29.56	Not met	Not met
		Cr(VI)	0.0	0	Met	Met
	7075-T6	Trivalent chrome seal	0.2	±0.45	Met	Met
		Cr(VI)	1.0	±1.41	Met	Met

3.1.4.2 ASTM G85

All bare panels tested in accordance with ASTM G85-02⁸ conditions failed (Table 8) and did not meet criteria as laid out in Table 3. Representative images of bare panels following testing are shown in Fig. 10, showing catastrophic failure for both TSAA and CAA. ASTM G85-02⁸ is too aggressive a test for uncoated anodized aluminum. As for samples coated with MIL-PRF-23377⁹ Type I Class N, representative images are shown in Fig. 11 with results in Table 9. The coated TSAA samples met performance requirements in each treatment category. Thus, when coated, the TSAA samples met meet the performance objective for ASTM G85-02⁸ as laid out in Table 3, showing no more than five isolated pits from one or more test pieces. Note that the average number of pits is higher for CAA (5.9) than TSAA (5.7). This is a small difference; however, if the test is performed for a longer duration in future study, lengthier exposure can provide additional insights.

Table 8 Results of bare panels tested under ASTM G85-02⁸

Treatment	Seal type	Material	Primer	Results
CAA	Chromic acid seal	2024-T3	None	Not met
		7075-T6		Not met
TSAA	Trivalent chrome seal	2024-T3		Not met
		7075-T6		Not met

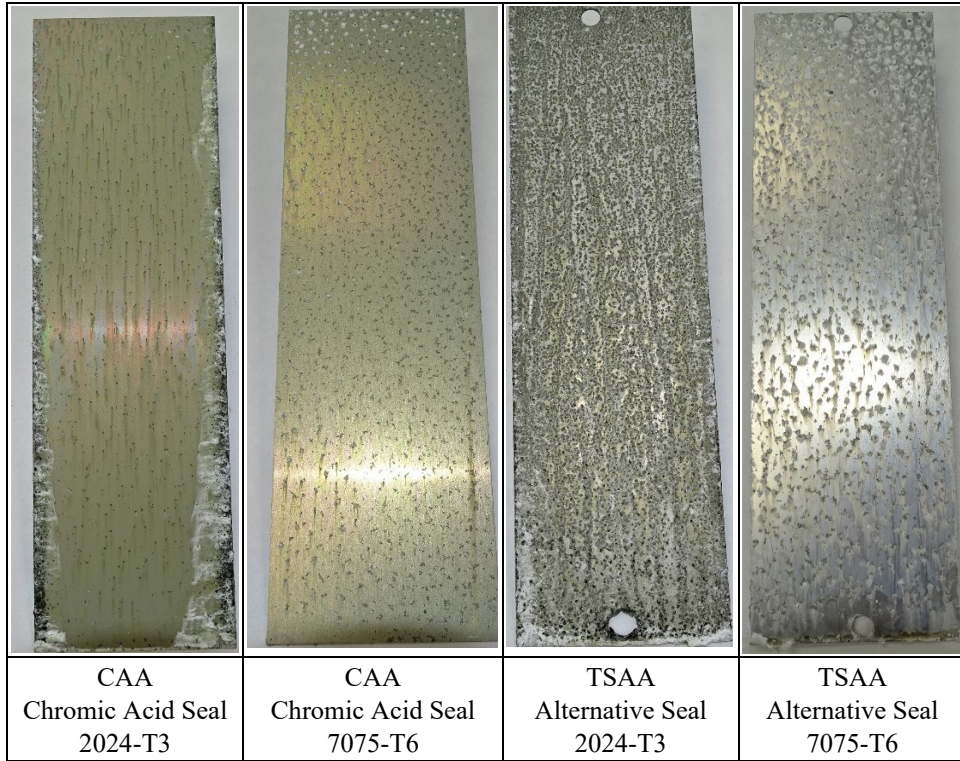


Fig. 10 Examples of bare panels following corrosion-resistance testing (ASTM G85-02⁸)

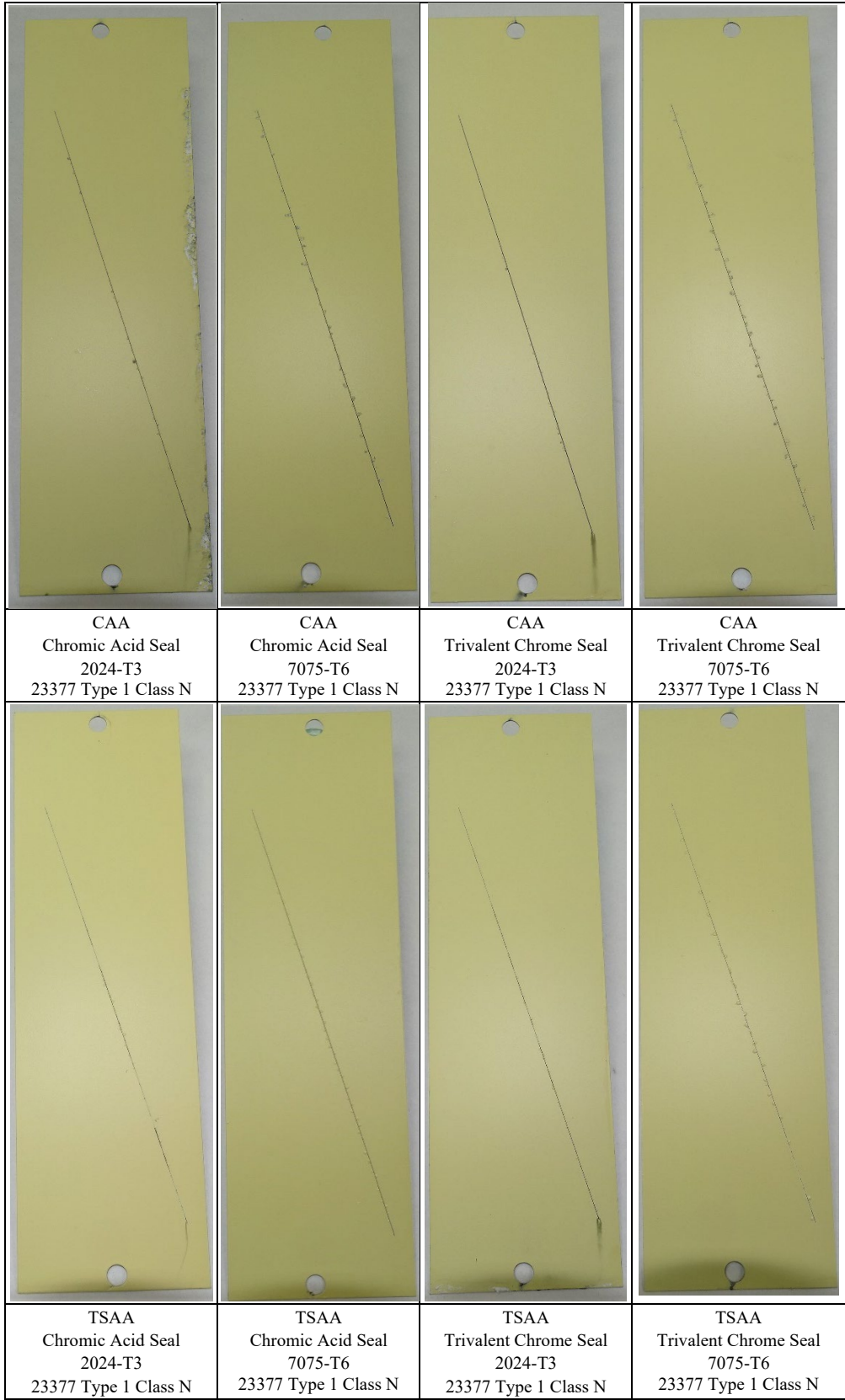


Fig. 11 Examples of primed panels following corrosion-resistance testing (ASTM G85-02⁸)

Table 9 Results of coated panels tested under ASTM G85-02⁸

Anodize	Seal type	Material	Average no. pits	Average rating/set	Met/not met
CAA	Chromic acid seal	2024-T3	1.06	7.3	Met
		7075-T6	2.03	6.3	Met
	Trivalent chrome seal	2024-T3	0.61	8.3	Met
		7075-T6	2.20	6.3	Met
TSAA	Chromic acid seal	2024-T3	0.42	9.0	Met
		7075-T6	1.56	7.0	Met
	Trivalent chrome seal	2024-T3	0.58	8.3	Met
		7075-T6	3.14	6.0	Met

3.1.5 Coating Adhesion

3.1.5.1 Wet Adhesion

Panels for wet coating adhesion were scribed and rated, as shown in Fig. 12. A compilation of the rating results is plotted in Fig. 13. The panels coated in the MIL-PRF-85582¹⁹ Type 1 Class N primer outperformed the MIL-PRF-23377⁹ Type 1 Class N primer. The standard deviation was relatively minimal. Note the TSAA samples had a greater standard deviation for the MIL-PRF-23377 Type 1 Class N primer, and CAA samples had a larger standard deviation for the MIL-PRF-85582 Type 1 Class N primer. Overall, the TSAA performed comparably to CAA in the wet adhesion tests across both alloys and primers. An adhesion rating of 4B is required to meet the performance objective. Only the TSAA samples coated with MIL-PRF-85582 Type 1 Class N primer met this criterion, as seen in Fig. 12, with TSAA; however, 2024 and 7075, coated with MIL-PRF-85582 Type 1 Class N, met an adhesion rating of 4.

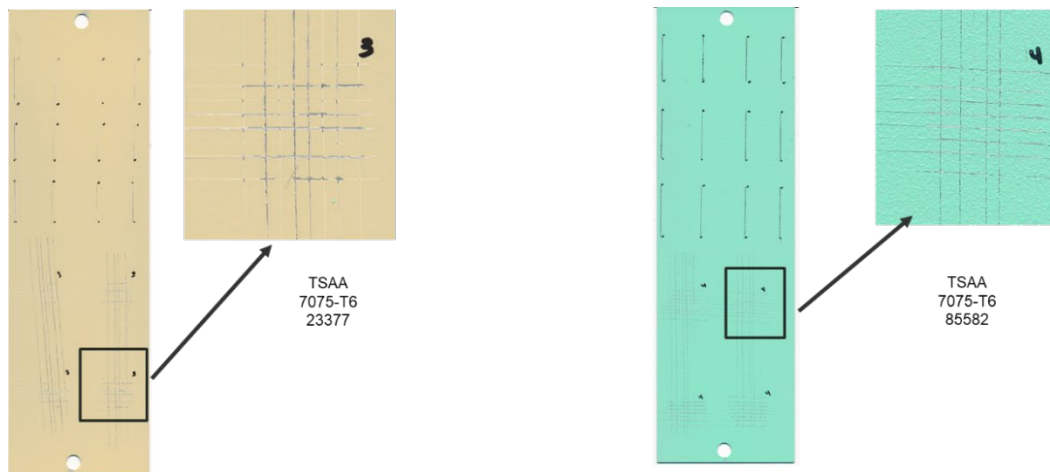


Fig. 12 Examples of panels following wet adhesion testing (FED-STD-141¹⁰ [6301] and ASTM 3359¹¹ [Method B])

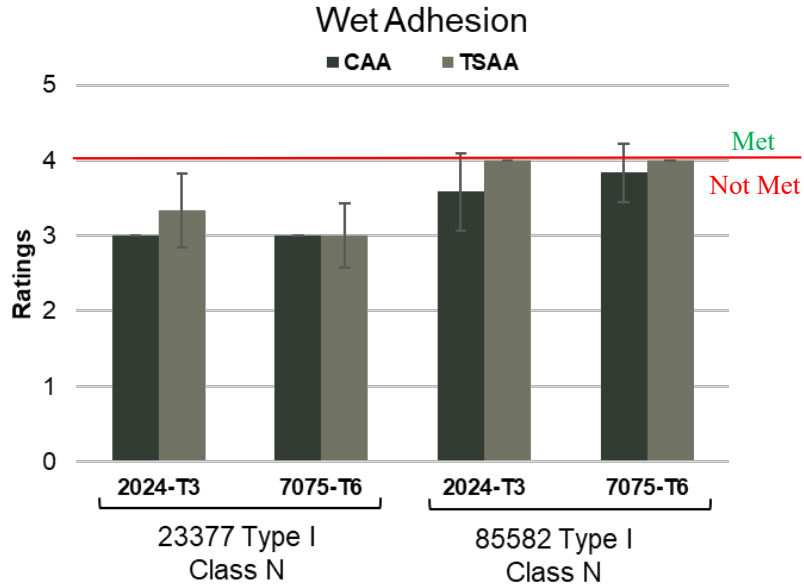


Fig. 13 Wet-coating adhesion rating compilation

Failures may be the result of a long gap between acquisition of panels and testing in the laboratory because of the COVID-19 pandemic, there is a potential that humidity fluctuations in laboratory resulted in minor moisture ingress in panels. Additionally, Shruthi et al. investigated trivalent chromium as a sealant for anodized 2024-T3 and found that smut, consisting of Al, sulfur, and oxygen was on the anodized surface and could be removed with a 20-min ultrapure water soak.³ This step dissolved deposits exposing the porous oxides and subsequently would allow increased adhesion. The test matrix tested herein only required a single stage rinse. An additional, higher quality rinse prior to priming panels could potentially increase adhesion.

3.1.5.2 Dry Adhesion

Dry-coating adhesion panels were scribed and rated, as shown in Fig. 14. A compilation of the rating results is plotted in Fig. 15. All panels performed well with a rating of 3 to 4. The two categories in which the TSAA panels did not meet equivalency of the CAA panels were the 7075-T6 chromic acid seal and 2024-T3 trivalent chrome seal (Chemeon TCP-HF). When the ratings were averaged, none met the passing criteria of 4B.

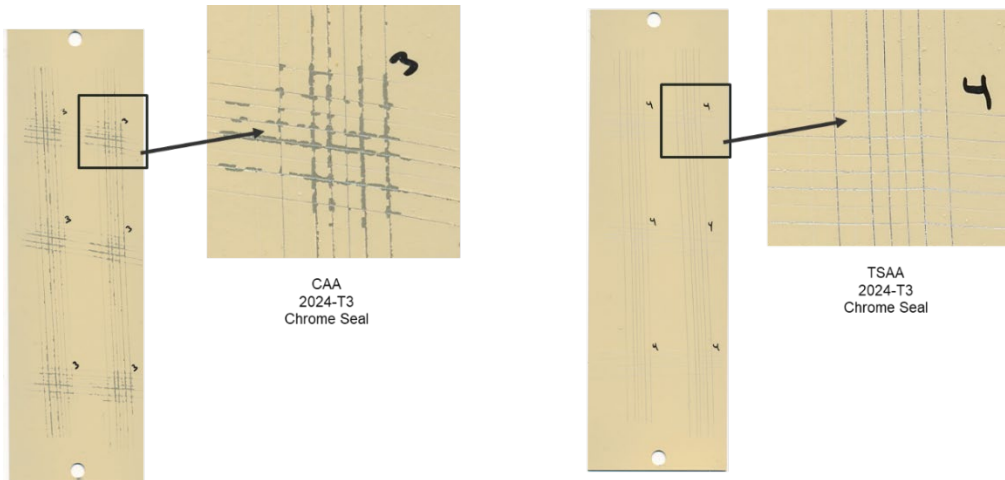


Fig. 14 Examples of panels following dry adhesion testing (ASTM 3359¹¹ [Method B])

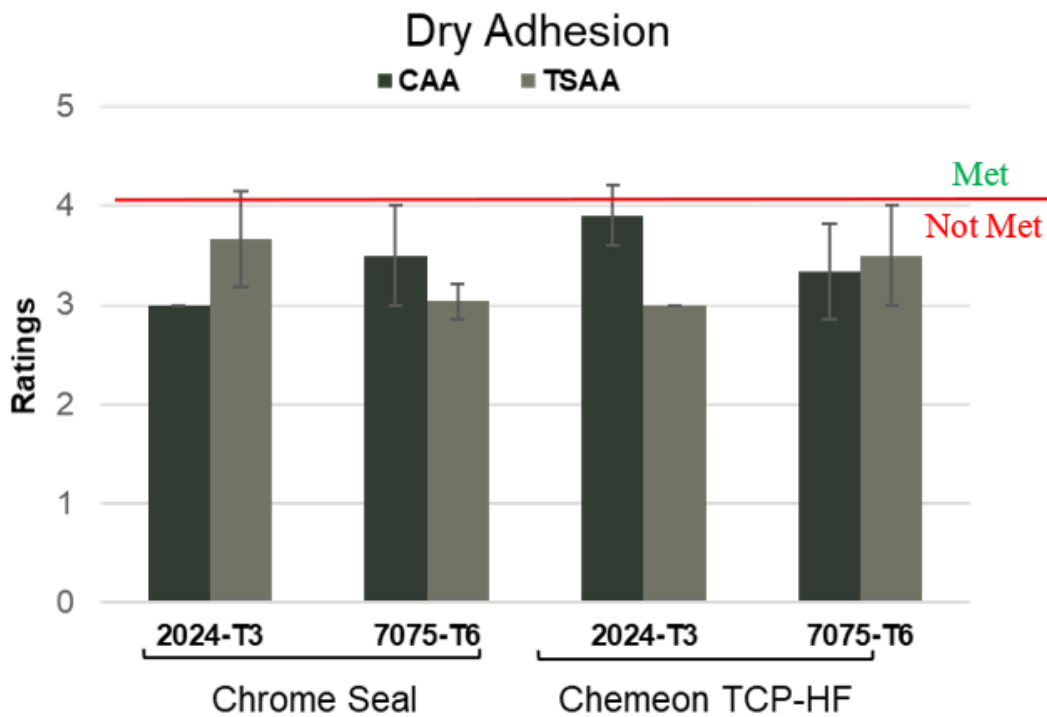


Fig. 15 Dry-coating adhesion rating compilation

3.1.5.3 Pull-Off Adhesion

Coating adhesion values, in pounds per square inch (psi), are shown in Table 10, with adhesion values greater than 1,200 psi deemed passing.²⁴ Values highlighted in blue are glue failures in which no coating remained on the dolly post-pull. The values highlighted in yellow are adhesive failures in which the coating failure occurred at the interface between coatings. Scans of the adhesion panels, using a Canon 9000F Mark II at 600 dpi can be found in the Appendix.

Table 10 Coating adhesion values: pull-off in accordance with ASTM D4541¹³ (psi)

CAA				TSAA											
Chromic acid seal		Trivalent chrome seal		Chromic acid seal		Trivalent chrome seal									
2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6								
886	1308	1611	1788	842	810	1628	1486	1248	2242	1842	2181	1708	1506	1695	2269
881	1754	1753	1100	1731	1661	1522	2060	2441	1929	2238	1840	2328	1421	2030	1769
491	1632	1960	1535	1344	1188	1177	1428	2030	2007	1883	1160	2015	2480	2830	1883
1028	1864	1264	1665	1636	1255	830	2055	1759	1871	1347	1430	1374	1831	2241	2014
1742	1231	2441	2588	1586	1182	1719	1354	1941	1880	1528	1331	1704	1406	1541	2081
812	1436	1211	1406	1554	1403	793	1192	2162	2584	1149	1716	1893	2611	1420	2473
1494	1715	1625	1390	1406	1374	623	1615	2055	1665	2433	1284	645	1085	1465	2160
1417	1021	2333	684	967	986	1533	1234	1231	2197	2034	1431	1870	1329	1312	2108
1120	1468	1515	1572	983	1464	972	932	1399	1778	1624	1798	1204	1734	2052	1620
1334	1754	1631	2115	1399	1042	2335	1024	1439	1775	1961	2653	2368	736	2219	3000+
1608	1207	2299	1907	1323	1262	1327	1237	1677	1023	1877	1534	1837	652	1789	775
838	512	1298	720	1074	1510	1483	2013	2696	1913	975	2168	1075	538	2378	2348
1473	1563	850	782	2593	1197	1574	908	1462	2820	1748	2232	2313	1081	1917	2622
1765	1848	1723	1735	2624	1953	1347	959	2299	1345	1682	2238	2104	450	2967	1673
1351	1834	1448	1409	2604	...	1221	1063	2646	2345	354	1499	1152	516	1784	2136
								1622	1496	813	1578	1292	613	2258	1874
								2400	763	830	2252	1934	594	2287	1381
								1595	...	2379	...	1723	...	1593	...
Avg	1346	1579	1447	1355	1878	1686	1461	1970							
StdDev	394	487	483	412	488	514	624	452							

Note: Values highlighted in blue are glue failures, while values highlighted in yellow are adhesive failures.

3.1.6 Bendability

All samples, upon visual inspection, passed the initial bend test, ASTM D522 (Method B).¹⁴ Samples were then subjected to ASTM B117-11.⁷ Due to extenuating circumstances, samples were removed after 1 week of exposure, rinsed with deionized water, and moved to a neutral location. After 5 months, testing was resumed and completed. The results of the corrosion testing of the bendability samples are shown in Table 11. None of the TSAA 2024-T3 bend panels met the performance objectives following the ASTM B117-11 test. There was severe corrosion on the TSAA 2024-T2 panels in the bend region. The 7075-T6 TSAA, although it did not meet requirements, resulted in one of five panels being the mitigating factor. All CAA panels met the performance objectives following the corrosion testing. Images of some of these panels are shown in Fig. 16. These results led to a further investigation of the bend area to analyze what was happening on the anodize surface.

Table 11 Bendability corrosion results

Treatment	Seal type	Material	Primer	Met/not met
CAA	Chromic acid seal	2024-T3	None	Met
		7075-T6		Met
TSAA	Trivalent chrome seal	2024-T3		Not met
		7075-T6		Not met

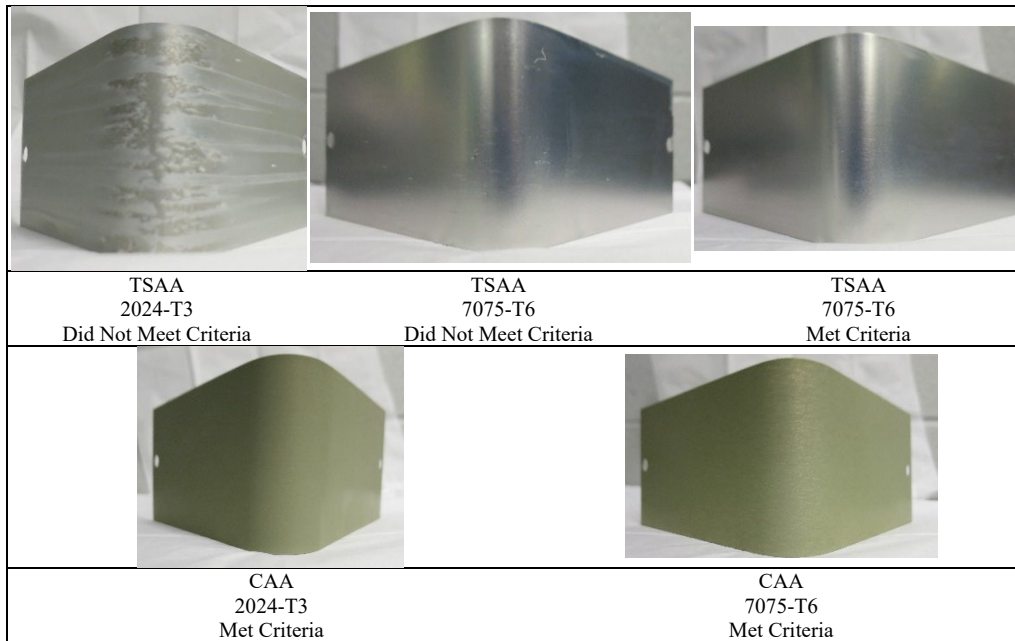


Fig. 16 Bendability panel images following accelerated corrosion testing

To visualize a larger area, Fig. 17 shows stitched micrographs, using a Keyence VK-X10003D laser scanning confocal microscope at 100 \times , of the bend area and the flat area of both the TSAA and CAA panels for 7075-T6 and 2024-T3 panels. The 2024-T3 and 7075-T6 were stitched at different sizes. It is evident that even though there was no damage to the surface treatment following ASTM D522,¹⁴ there is an obvious surface difference between the bent and flat area of the panel. For a better visualization, Fig. 18 shows micrographs of the bend and flat areas of the same panels at 100 \times —unstitched—to allow more detail to be seen easily per micrograph. Unstitched micrographs were used for analysis, as these micrographs can be gathered at a much faster rate using the Keyence software, allowing for larger sample sizes for analysis.

The chromate sealed panels had a yellow-green appearance, while the anodize is gray in color. No visual color change was noticed on the TSAA samples when sealed with TCP. Black spots are present on panels; however, they do not qualify as pits. Looking at Fig. 18, the biggest of these spots is approximately 20 μm , which is 0.0078 inch. In accordance with ASTM B117,⁷ test specimens must have no more than 15 pits greater than 0.031 inch. This shows that the locations imaged do not have quantifiable pits based on ASTM B117.

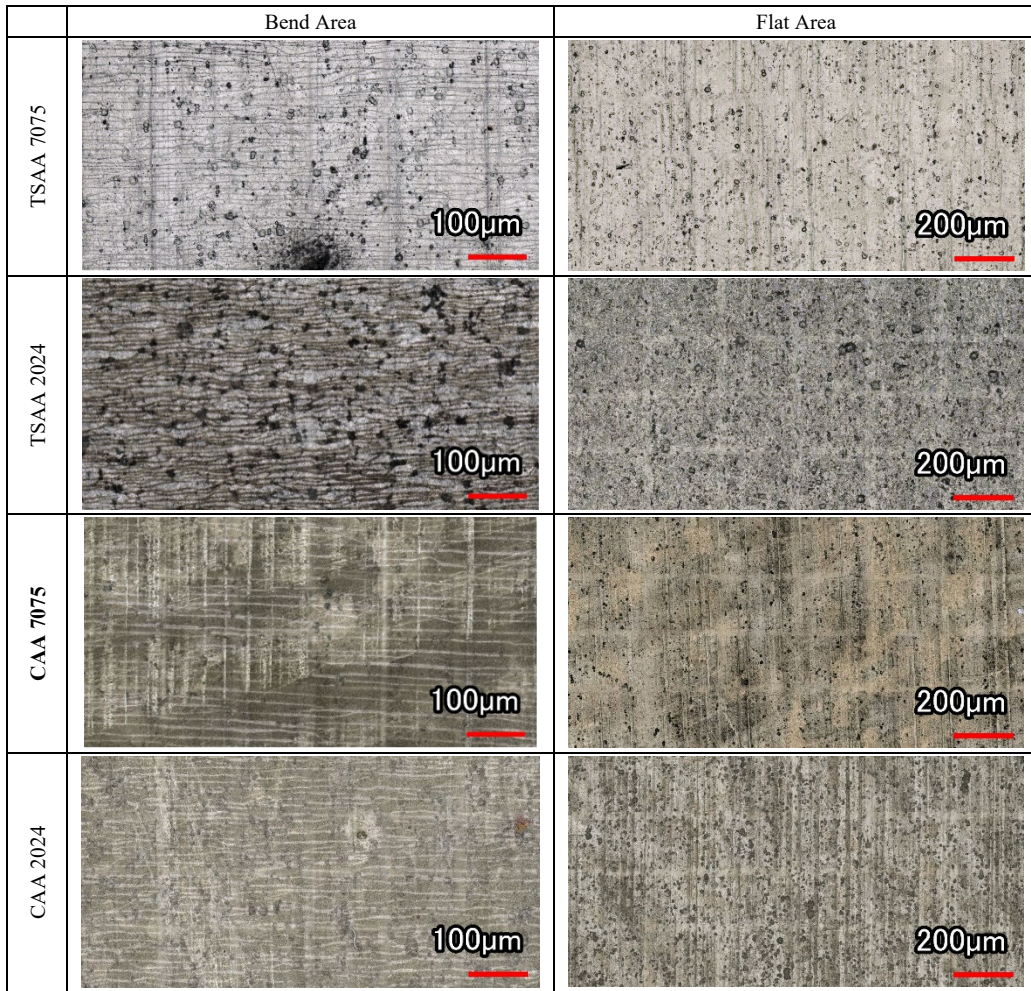


Fig. 17 Stitched micrographs of TSAA and CAA samples at both the bend and flat areas of panels following ASTM B117-11⁷ (100×)

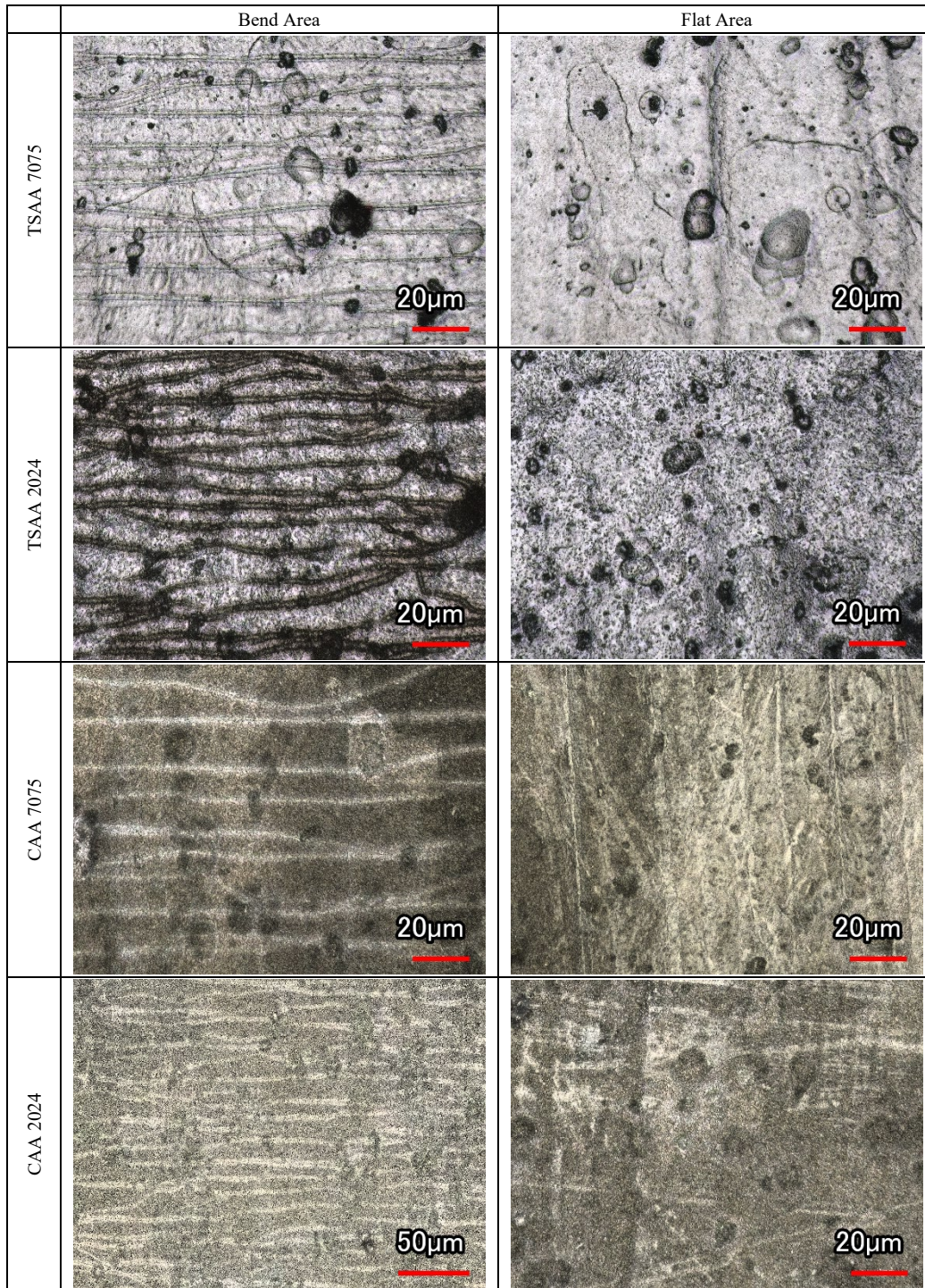


Fig. 18 Micrographs of TSAA and CAA samples at both the bend and flat areas of panels following ASTM B117⁷ (100×)

The average and standard-deviation craze gap distances are shown in Table 12. The average space between craze, when also looking at the standard deviation, is comparable between CAA and TSAA. The average and standard-deviation widths

of the craze are shown in Table 13. This data shows that the TSAA 2024 panel tested had less space between crazing than the other panels. The finer, but more frequent cracks in the anodize coating likely allowed for greater ingress of electrolyte and therefore contributed to the poor observed performance. TSAA 2024 is a lower strength alloy than 7075; it is more easily bent and retains its bend shape. Because 2024 is more malleable, it is likely that the alloy bent further during ASTM D522,¹⁴ resulting in larger thicknesses between the crazing.

Table 12 Craze gap

Sample	Gap	
	Avg (μm)	StdDev (μm)
CAA 7075	1.758	0.28
TSAA 7075	3.613	0.30
CAA 2024	3.742	0.79
TSAA 2024	3.023	0.50

Table 13 Craze thickness

Sample	Thickness	
	Avg (μm)	StdDev (μm)
CAA 7075	18.229	2.84
TSAA 7075	13.912	1.80
CAA 2024	17.670	2.70
TSAA 2024	8.879	1.17

A possible explanation for the observed performance deficit in bendability testing may result from the fact that the oxide layer is porous and brittle and compounded by residual stress added during the anodization process.² In fact, Lee et al. investigated CAA versus Tartaric Acid Anodizing (TAA) panels that were hot water sealed on 7075-T7451 and found that TAA has smooth and round pores versus the irregular pores of CAA.²⁵ This variation allows for increased craze initiation on TAA. This pore formation and brittleness of the anodize can be a causation of the bendability failures.²⁵

3.1.7 Coating Adhesion (Pull-Off)

Coating adhesion values, in pounds per square inch, are shown in Table 14, with adhesion values greater than 1,200 psi deemed passing.²⁴ Values highlighted in blue are glue failures in which no coating remained on the dolly post-pull. The values highlighted in yellow are adhesive failures in which the coating failure occurred at the interface between coatings. Scans of the adhesion panels using a Canon 9000F Mark II at 600 dpi can be found in the Appendix.

Table 14 Coating adhesion values: pull-off in accordance with ASTM D4541¹³ (psi)

	CAA				TSAA										
	Chromic Acid Seal		Trivalent Chrome Seal		Chromic Acid Seal		Trivalent Chrome Seal								
	2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6	2024-T3	7075-T6							
886	1308	1611	1788	842	810	1628	1486	1248	2242	1842	2181	1708	1506	1695	2269
881	1754	1753	1100	1731	1661	1522	2060	2441	1929	2238	1840	2328	1421	2030	1769
491	1632	1960	1535	1344	1188	1177	1428	2030	2007	1883	1160	2015	2480	2830	1883
1028	1864	1264	1665	1636	1255	830	2055	1759	1871	1347	1430	1374	1831	2241	2014
1742	1231	2441	2588	1586	1182	1719	1354	1941	1880	1528	1331	1704	1406	1541	2081
812	1436	1211	1406	1554	1403	793	1192	2162	2584	1149	1716	1893	2611	1420	2473
1494	1715	1625	1390	1406	1374	623	1615	2055	1665	2433	1284	645	1085	1465	2160
1417	1021	2333	684	967	986	1533	1234	1231	2197	2034	1431	1870	1329	1312	2108
1120	1468	1515	1572	983	1464	972	932	1399	1778	1624	1798	1204	1734	2052	1620
1334	1754	1631	2115	1399	1042	2335	1024	1439	1775	1961	2653	2368	736	2219	3000+
1608	1207	2299	1907	1323	1262	1327	1237	1677	1023	1877	1534	1837	652	1789	775
838	512	1298	720	1074	1510	1483	2013	2696	1913	975	2168	1075	538	2378	2348
1473	1563	850	782	2593	1197	1574	908	1462	2820	1748	2232	2313	1081	1917	2622
1765	1848	1723	1735	2624	1953	1347	959	2299	1345	1682	2238	2104	450	2967	1673
1351	1834	1448	1409	2604	...	1221	1063	2646	2345	354	1499	1152	516	1784	2136
								1622	1496	813	1578	1292	613	2258	1874
								2400	763	830	2252	1934	594	2287	1381
								1595	...	2379	...	1723	...	1593	...
Avg	1346	1579	1447	1355	1878	1686	1461	1970							
StdDev	394	487	483	412	488	514	624	452							

Note: Values highlighted in blue are glue failures, while values highlighted in yellow are adhesive failures.

3.1.8 Fluid Compatibility

All samples shown in Table 15 were tested with fluids listed in Table 16. All panels met requirements with no deterioration.

Table 15 Panels tested for fluid compatibility

Treatment	Seal type	Material	Primer	Met/not met
CAA	Chromic acid seal	2024-T3	23377	Met
		7075-T6		Met
TSAA	Trivalent chrome seal	2024-T3		Met
		7075-T6		Met

Table 16 Fluid compatibility results

Fluid	Fluid tested [reference]	Met/not met
Fuel	F-24 (switch authorized)	Met
Hydraulic fluid	Royco 782	Met
Lubricating oil	Eastman Turbo Oil	Met
Cleaner	Isopropyl alcohol	Met
	MIL-PRF-85570 ²³	Met
Deicing fluid	TKS-Deicing Fluid	Met
Grease	Syntec NS-4405-FG	Met
Corrosion preventative compound	Cor-Ban 35	Met

3.2 Structural Integrity Matrix

3.2.1 Tensile

The results of the tensile testing are presented in Table 17. It can be observed that the anodized and control (bare) materials each exhibited similar results. For both 2024-T3 and 7075-T6, TSAA performed as well or better than CAA in meeting performance requirements set in Table 3.

Table 17 Tensile testing

Specimen	0.2% offset YS (ksi)	Avg YS (ksi)	Std Dev	UTS (ksi)	Avg UTS (ksi)	Std Dev	Strain to failure (inches)	Avg strain	Std Dev
2024 Bare #1	56.67	56.56	0.215	72.82	73.01	0.486	0.193	0.194	0.002
2024 Bare #2	56.32			72.64			0.192		
2024 Bare #4	56.71			73.56			0.196		
2024 CAA, CS #5	57.07	57.27	0.343	73.33	73.35	0.424	0.179	0.177	0.008
2024 CAA, CS #8	57.07			72.94			0.168		
2024 CAA, CS #9	57.67			73.79			0.183		
2024 TSAA, TCS #6	56.77	56.41	0.308	72.64	72.42	0.218	0.164	0.171	0.006
2024 TSAA, TCS #7	56.27			72.42			0.172		
2024 TSAA, TCS #3	56.20			72.21			0.176		
7075 Bare #3	77.81	76.42	1.839	83.95	83.91	0.106	0.155	0.163	0.018
7075 Bare #4	74.33			83.99			0.149		
7075 Bare #8	77.10			83.79			0.183		
7075 CAA, CS #1	76.23	76.94	0.640	84.31	84.25	0.157	0.134	0.137	0.003
7075 CAA, CS #5	77.48			84.38			0.138		
7075 CAA, CS #7	77.10			84.08			0.139		
7075 TSAA, TCS #2	77.57	77.05	0.455	84.05	83.73	0.280	0.117	0.122	0.010
7075 TSAA, TCS #6	76.70			83.58			0.134		
7075 TSAA, TCS #9	76.90			83.55			0.116		

Notes: TCS = trivalent chrome seal, CS = chromic acid seal

The 2024-T3 Al demonstrated approximately 73-ksi ultimate tensile strength (UTS) with a yield strength (YS) of approximately 56 ksi. The UTS of CAA had an approximately 0.47% increase from the control, while TSAA had a 0.81% increase. The YS of the CAA increased from the control 1.27%, while the TSAA decreased 0.27%.

The 7075-T6 material exhibited approximately 84-ksi UTS with a yield strength of approximately 76 ksi. These results are typical for the alloys with these heat treatments. The UTS of CAA had an approximately 0.68% increase from the control, while TSAA had a 0.21% increase. The YS of the CAA increased from the control 0.41%, while the TSAA increased 0.82%

3.2.2 Axial Fatigue

The results of the fatigue testing are shown in Figs. 19 and 20. The results are presented with the maximum stress plotted against the cycles to failure. The fatigue program was somewhat limited in scope, using only 12 specimens per group and four stress levels, yielding three data points at each stress level. They are by no means a full characterization of the performance of these anodizing treatments. It would certainly be expected, though, that the trends observed here would carry forward to a more robust test approach. For the $K_t = 1$ stress intensity, it can be observed that the CAA had an approximately 2.5-ksi lower endurance limit for the 2024-T3 material, while the TSAA had an approximately 7.5-ksi lower endurance limit than the base material. This translates to a 7% and 20% difference, respectively. In the 7075-T6 material, it can be observed that the CAA had an approximately 10-ksi lower endurance limit, while the TSAA had an approximately 12.5-ksi lower endurance limit than the base material. This translates to a 22% and 28% difference, respectively. The initial success criteria were for the TSAA group to have equal or better performance than the CAA group. Unfortunately, this was not revealed to a great extent under this program. The TSAA group only faired equal or better compared with the CAA in two out of four instances. The $K_t = 3$ for 7075-T6 would be considered having equal performance and the $K_t = 3$ group for 2024-T3 outperformed the CAA. Although the results for the 7075-T6 material were somewhat closer to the baseline than for 2024-T3, the TSAA fatigue results proved significantly worse than the CAA test group. In the case of 2024-T3 material at $K_t = 1$, it proved drastically worse with a $3\times$ fatigue debit.

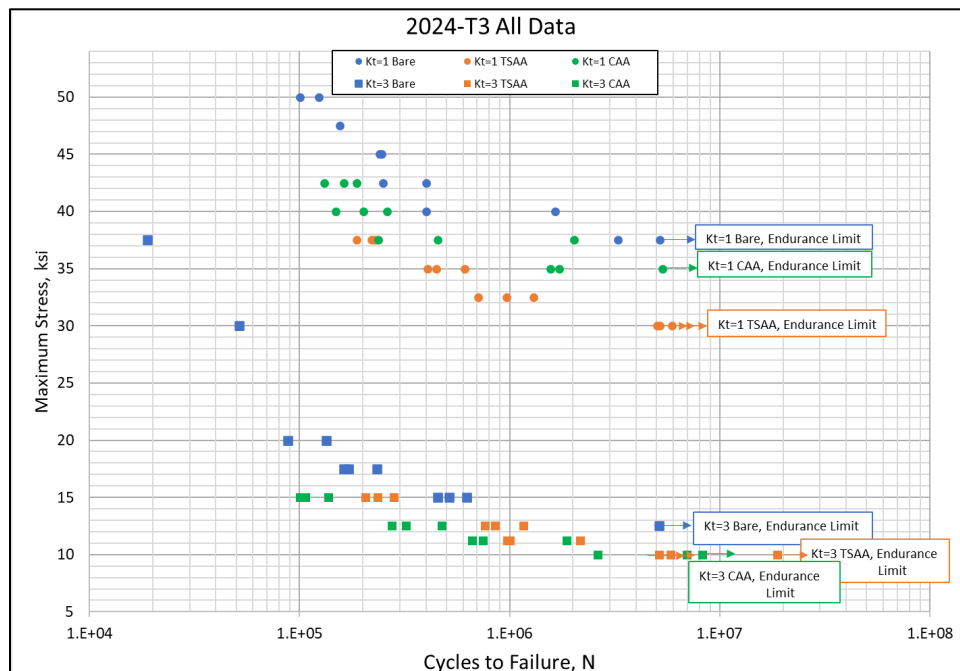


Fig. 19 Fatigue results of the 2024-T3 material

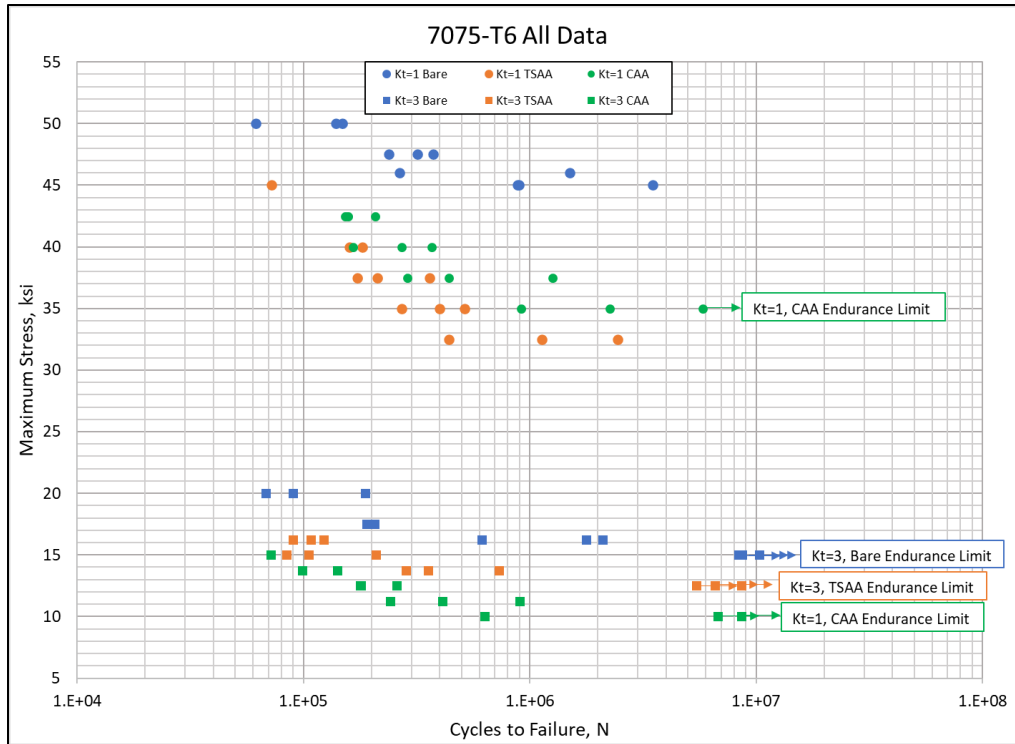


Fig. 20 Fatigue results of the 7075-T6 material

At the $K_t = 3$ stress intensity, the comparative results between the two processes were more similar and generally a favorable result for TSAA. A drastic decrease in performance from the baseline data was not observed. For the 2024-T3 material, the fatigue curves for both processes, CAA and TSAA, showed little difference. Both had an approximate 2.5-ksi reduction from the baseline. For the 7075-T6 material, the TSAA process outperformed the CAA, having only a 2.5-ksi debit from the baseline. The CAA process experienced a 5.0-ksi drop from the baseline, approximately twice as much as the TSAA.

The seemingly conflicting results of the $K_t = 1$ and $K_t = 3$ groups were unexpected. At $K_t = 1$, TSAA demonstrated a weaker performance for both materials, while at $K_t = 3$ it was at least equal if not superior to CAA. Further work is necessary to delineate the data. Overall, the anodizing processes proved detrimental to the baseline material. They showed a decrease in fatigue life compared with the baseline. Unless the detrimental effects of these processes (both CAA and TSAA) are mitigated, these fatigue results might be expected to translate into lower component life if employed on actual rotorcraft components. However, in service, critical components are almost always shot-peened, which can have a normalizing effect on the material fatigue life. Follow-up studies will explore this consideration to assess whether the fatigue debit due to these processes would be realized in service or normalized through shot-peening.

Research has shown that pits formed during pretreatment cause accelerated crack nucleation during fatigue loading.²⁵⁻²⁸ Lee et al. found that the smooth and round pores of TAA versus the irregular pores of CAA seemed to determine the ease of crack initiation and subsequent fatigue behavior on 7075-T7451.²⁵ Hence, pits and the anodize structure of TSAA might be causing subpar fatigue performance.

3.3 Summary of Results and Discussion

To qualify an alternative to CAA, AMCOM-G4 with DEVCOM ARL have tested TSAA against validated requirements, as set forth by SRD. The intended product is a validated and approved TSAA process with a non-Cr(VI) sealer as an alternative to CAA with plans to meet requirements of MIL-A-8625-F¹ and implement via maintenance engineering orders at CCAD. A full summary of the results of the performance requirements and results for the coating characterization matrix are cataloged in Table 18, with structural integrity effects shown in Table 19.

In Table 18, TSAA met more requirements than CAA. TSAA provided slightly better corrosion resistance, specifically in ASTM B117⁷ than CAA with trivalent chrome seal. TSAA system provided better adhesion for MIL-DTL-85582¹²; however, MIL-DTL-23377⁹ did not adhere well to either CAA or TSAA. In bendability testing followed by B117, TSAA did not perform as well, particularly 2024-T3, compared with CAA. In Table 19, for fatigue and tensile properties, the success criteria are equivalent or better than the baseline CAA-coated samples. All of the TSAA samples met requirements for tensile properties. TSAA was only able to meet the fatigue requirement for axial fatigue in one case. Only the TSAA-coated 2024 tested in $K_t = 3$ could achieve a greater endurance limit than the CAA-coated 2024 in $K_t = 3$.

Table 18 Summary of performance objectives for coating integrity

Tests	Methods [reference]	Primer [reference]	Success criteria	CAA				TSAA			
				Chromic acid seal		Trivalent chrome seal		Chromic acid seal		Trivalent chrome seal	
				2024	7075	2024	7075	2024	7075	2024	7075
Coating quality	MIL-A-8625 ¹	None	Anodic coating shall be continuous smooth, and adherent, uniform in appearance, free from powdery areas, loose films, breaks, scratches, and other defects that will reduce the serviceability of anodized samples.	Met	Met	Met	Met	Met	Met	Met	Met
Coating thickness	ASTM B244 ⁶	None	Within coating thickness range of 0.1 and 0.2 mil for Type I CAA.	Met	Met	Met	Met	Met	Met	Met	Met
Coating weight	MIL-A-8625 ¹	None	In accordance with MIL-A-8625. ¹	Met	Met	Met	Met	Met	Met	Met	Met
Corrosion resistance	ASTM B117 ⁷	None	<i>After 336 h exposure or until failure:</i> Test specimens shall show no more than a total of 15 isolated pits (see 6.19), none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces. Areas within 0.062 inch from identification markings, edges, and electrode contact marks remaining after processing shall be excluded.	Met	Met	Not met	Met	Met	Met	Met	Met
			23377 ⁹ Type 1 Class N	Test specimens shall show no more than five isolated pits, none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces. Areas within 0.062 inch from identification markings, edges and electrode contact marks remaining after processing shall be excluded.	Met	Met	Met	Met	Met	Met	Met
	ASTM G85 ⁸	None	Test specimens shall show no more than five isolated pits, none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces. Areas within 0.062 inch from identification markings, edges and electrode contact marks remaining after processing shall be excluded.	Not met	Not met	Not met	Not met
Coating adhesion (wet)	FED-STD-141 ¹⁰ (6301), Tape tests per ASTM 3359 ¹¹ (Method B)	23377 ⁹ Type 1 Class N	Adhesion rating better than 4B.	Not met	Not met	Not met	Not met
		85582 ¹² Type 1 Class N	No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.	Not met	Not met	Met	Met
Coating adhesion (dry)	ASTM D3359 ¹¹ (Method B)	23377 ⁹ Type 1 Class N	Adhesion rating better than 4B. No intercoat separation between the paint system and anodic coating or the anodic coating and the base metal.	Not met	Not met	Not met	Not met	Not met	Not met	Not met	Not met
Coating adhesion (pull-off)	ASTM B4541 ¹³	23377 ⁹ Type 1 Class N	Similar to or better than performance of CAA.	Met	Met	Met	Met	Met	Met	Met	Met
Bendability	ASTM D522 ¹⁴ Method B (ASTM B117 ⁷)	None	Same as corrosion resistance requirements.	Met	Met	Not met	Not met
Fluid compatibility	MIL-STD-810G ¹⁵ Method 504.1 Procedure II	23377 ⁹ Type 1 Class N	Similar or better than performance of CAA.	Met	Met	Met	Met

Table 19 Summary of performance objectives for fatigue and tensile properties

Tests	Method [reference]	Sample	Success criteria	Baseline Type I CAA with chromic acid seal		TSAA with trivalent chrome seal	
				2024	7075	2024	7075
Axial fatigue	ASTM E466 ¹⁷	$K_t = 1$	Endurance limit equivalent or greater than Type I CAA	Met	Met	Not met	Not met
		$K_t = 3$		Met	Met	Met	Not met
Tensile	ASTM B557 ¹⁶	...	Equal to or better than CAA	Met	Met	Met	Met

4. Conclusions and Recommendations

Both CAA and TSAA coatings met the coating quality requirements, including thickness, weight, and appearance. This indicates that the process controls used for TSAA were adequate for producing coatings of similar density to the CAA.

The trivalent sealer did not provide adequate corrosion protection. Chromates are very efficient in healing defects following coating damage be it from bending or stress. Chromate sealing of anodize coatings is performed at elevated temperatures, which provides a dense hydrothermal seal of the anodize. Trivalent chromium seal alone does not hydrothermally seal the oxide layer because it is performed under ambient conditions. Additionally, trivalent chrome is not as successful as hexavalent chromium at migrating to protect exposed aluminum following substrate exposure. This leads to the potential for additional sealing processes to protect the substrate and allow for enhanced protection.

The path forward includes two parts. First, retest fatigue of TSAA and CAA, as well as Thin-Film Sulfuric Acid Anodizing, with various sealing processes. If these combinations are still unable to meet the fatigue requirement, alternate options to anodizing will be investigated.

5. References

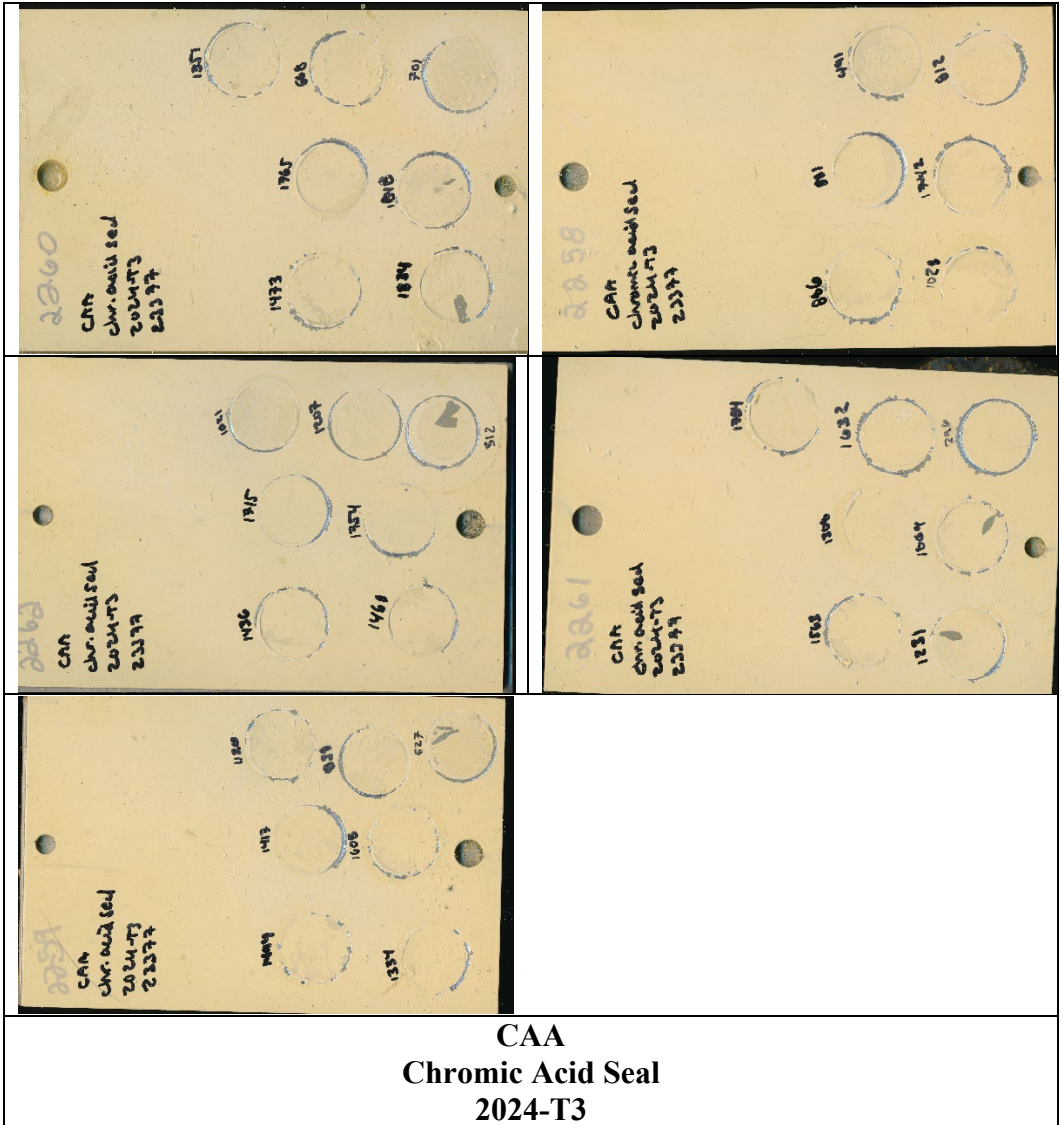
1. MIL-A-8625-F, Anodic coatings for aluminum and aluminum alloys. Naval Air Engineering Center; 2003.
2. Martínez-Viademonte MP, Abrahami S, Hack T, Burchardt M, Terryn HA. A review on anodizing of aerospace aluminum alloys for corrosion protection. *Coatings*. 2020;10(11):1106.
3. Shruthi TK, Walton J, McFall-Boegeman S, Westre S, Swain GM. Investigation of the trivalent chromium process conversion coating as a sealant for anodized AA2024-T3. *J Electrochem Soc*. 2020;167.
4. Iwu K. Tartaric sulfuric acid anodizing final report. Sikorsky Aircraft Corporation; 2017.
5. AMZ Manufacturing Corp. Optimization of tartaric sulfuric acid anodizing for aluminum alloys. AMZ Manufacturing Corp; 2019.
6. ASTM B244-09. Standard test method for measurement of thickness of anodic coatings on aluminum and of other nonconductive coatings on nonmagnetic basis metals with eddy-current instruments. ASTM International; 2014.
7. ATSM B117-11. Standard practice for operating salt spray (fog) apparatus. ASTM International; 2013.
8. ASTM G85-02. Standard practice for modified salt spray (fog) testing. ASTM International; 2018.
9. MIL-PRF-23377K. Primer coatings: epoxy, high solids. Naval Air Warfare Center Aircraft Division; 2012.
10. FED-STD-141. Method, paint, varnish, lacquer and related materials: methods of inspection, sampling and testing. General Services Administration; 2001.
11. ATSM D3359. Standard test methods for measuring adhesion by tape test. ASTM International; 2010.
12. MIL-PRF-85582E. Primer coatings: epoxy, waterborne. Naval Air Warfare Center Aircraft Division; 2012.
13. ASTM D4541-17. Standard test method for pull-off strength of coatings using portable adhesion testers. ASTM International; 2017.
14. ASTM D522. Mandrel bend test of attached organic coatings. ASTM International; 2001.

15. MIL-STD-810G. Environmental engineering considerations and laboratory tests. Army Developmental Test Command (US); 2008.
16. ASTM B577-19. International, standard test methods for detection of cuprous oxide (hydrogen embrittlement susceptibility) in copper. ASTM International; 2019.
17. ASTM E466-21. Standard practice for conducting force controlled constant amplitude axial fatigue tests of metallic materials. ASTM International; 2021.
18. Kane MJ. Memorandum for AMSAM-ENVI-TI (Mr Glenn Williams). Revise TN 137858 in accordance with revisions suggested by Sikorsky and accepted by AEF to support the continued development of a program Statement of Work (SOW), TN 143599. 2015 Feb 20. p. 6.
19. MIL-PRF-83282. Hydraulic fluid, fire resistant, synthetic hydrocarbon base, metric. NATO Code Number H-537; 1997.
20. MIL-PRF-5606. Hydraulic fluid, petroleum base; aircraft, missile, and ordnance. Naval Publication and Form Center; 2018.
21. MIL-PRF-23669G. Lubricating oil, aircraft turbine engine, synthetic base. NATO Code Number O-156; 2014.
22. MIL-PRF-7808L. Lubricating oil, aircraft turbine engine, synthetic base. Naval Publications and Form Center; 1997.
23. MIL-PRF-85570. Cleaning compounds, aircraft, exterior. Naval Publication and Form Center; 2002.
24. Kelley JV, Braswell T. Demonstrating nonhexavalent chrome steel conversion coatings on Stryker high hard armor steel hatches. Army Research Laboratory (US); 2017. Report No.: ARL-TR-6789.
25. Lee E, Jeong Y, Kim S. S-N fatigue behavior of anodized 7050-T7451 produced in different electrolytes. *Metall Mater Trans A*. 2012;43(6).
26. Shahzad M, Chaussumier M, Chieragatti R, Mabru C, Rezai-Aria F. Influence of anodizing process on fatigue life of machined aluminum alloy. *Procedia Eng*. 2010;2(1).
27. Savas T, Earthman J. Surface characterization of 7075-T73 aluminum exposed to anodizing pretreatment solutions. *J Mater Eng Perform*. 2008;17:674–681.

28. AL-Sudani IM, Al-Rabii SA, Al-Fattal DS. The effects of anodizing process on the corrosion rate and fatigue life of aluminum alloy 7075-T73. Eng Tech J. 2020;38(1):34–42.
29. Lieb N. US Army toxic metal reduction program: demonstrating alternatives to hexavalent chromium and cadmium in surface finishing. (Presentation). ASETSDefense. 2014 Nov 18. <https://apps.dtic.mil/sti/pdfs/ADA617080.pdf>.

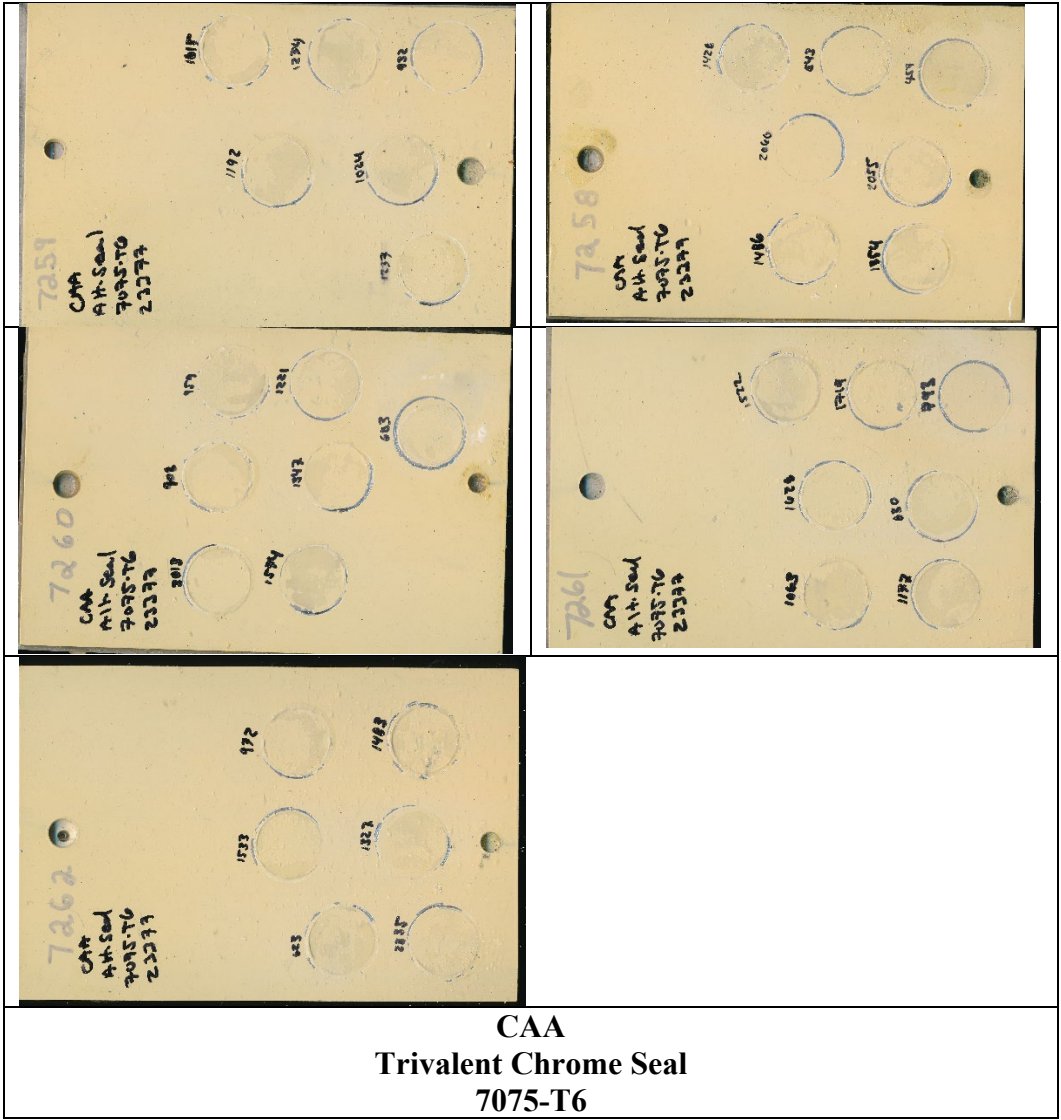
Appendix. Pull-Off Adhesion Scans

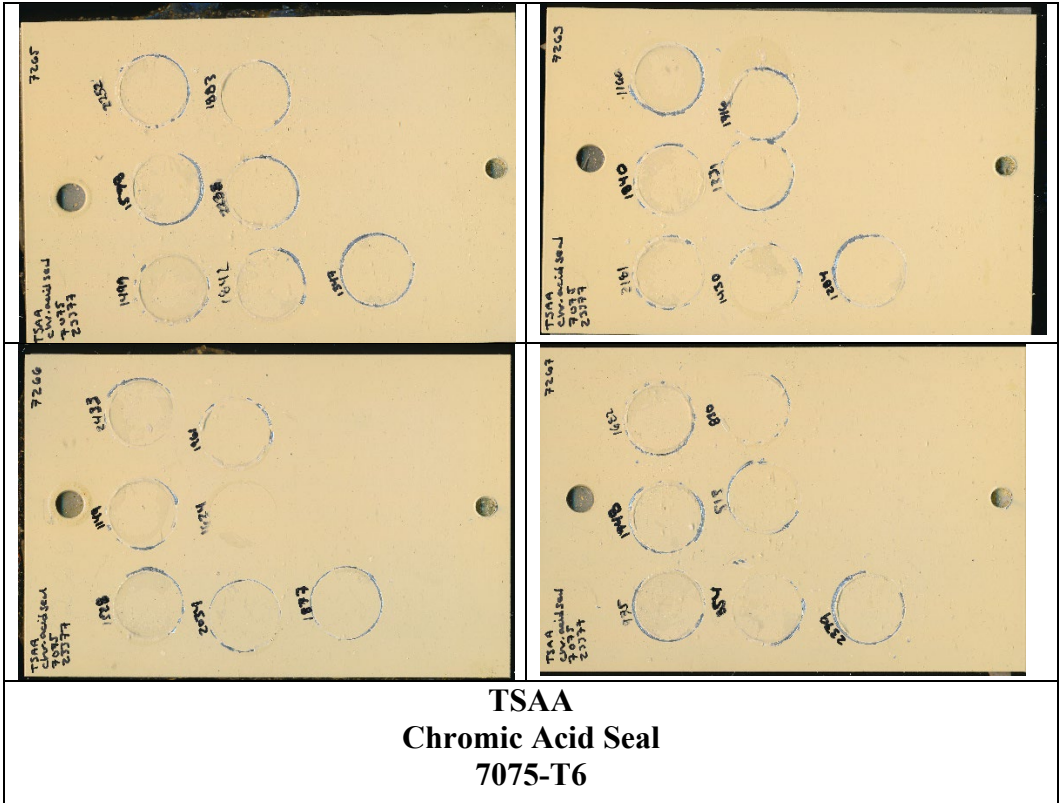
This appendix contains scans of pull-off adhesion panels (3.1.7) using a Canon 9000F Mark II at 600 dpi. Samples include both Chromic Acid Anodize (CAA) and Tartaric Sulfuric Acid Anodized (TSAA).

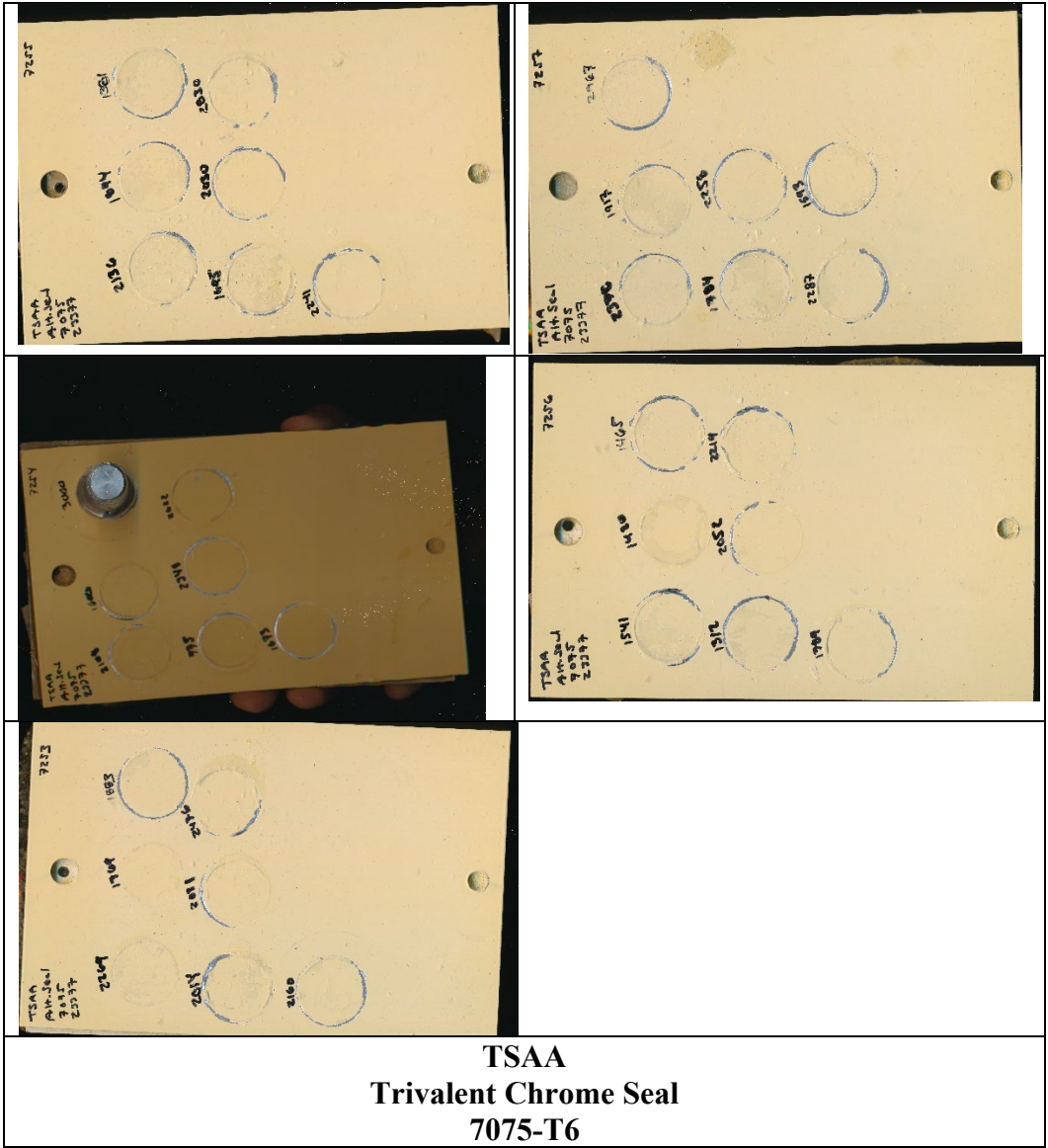


CAA
Chromic Acid Seal
2024-T3

<p>2248 CAA A14 Seal 2024-T3 23379</p> <p>80 1403 1461 1887 2257</p>	<p>2249 CAA A14 Seal 2024-T3 23379</p> <p>1574 1494 1486 1042 2264</p>
<p>2252 CAA A14 Seal 2024-T3 23379</p> <p>1404 1495 1465 1466 1523 1410 1483</p>	<p>2251 CAA A14 Seal 2024-T3 23379</p> <p>1482 1576 1574 1574 1574 1574</p>
<p>2250 CAA A14 Seal 2024-T3 23379</p> <p>1481 1481 1481 1481 1481 1481 1481 1481</p>	
<p>CAA Trivalent Chrome Seal 2024-T3</p>	







TSAA
Trivalent Chrome Seal
7075-T6

List of Symbols, Abbreviations, and Acronyms

3-D	three-dimensional
AGL	Aviation Gear Lubricant
Al	aluminum
AMCOM	US Army Missile and Aviation Command
AMFF	Advanced Metal Finishing Facility
ARL	Army Research Laboratory
CAA	Chromic Acid Anodizing
CCAD	Corpus Christi Army Depot
Cr	chromium
Cr(VI)	hexavalent chromium
DEVCOM	US Army Combat Capabilities Development Command
G-4	Logistics Directorate
Sikorsky	Sikorsky Aircraft Corporation
SRD	Systems Readiness Directorate
TCP	Trivalent Chromium Process
TFSAA	Thin-Film Sulfuric Acid Anodizing
TSAA	Tartaric Sulfuric Acid Anodizing
UTS	ultimate tensile strength
YS	yield strength

1 DEFENSE TECHNICAL
(PDF) INFORMATION CTR
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J FENYAK

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