Performance Validation of Thin-Film Sulfuric Acid Anodization (TFSAA) on Aluminum Alloys

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Chromic acid Anodization (CAA) is still prevalent in the finishing of Al alloys when corrosion inhibition and paint adhesion are needed on fatigue-sensitive parts. NAVAIR has been pursuing replacements to CAA because of the environmental and health hazards associated with use of chromates. Boric-sulfuric acid Anodization (BSAA), a proprietary Boeing product that requires license fees, is NAVAIR's only fully implemented alternative to CAA where corrosion resistance, paint adhesion, and fatigue resistance are required. TFSAA is available as an alternative, but has limited implementation by NAVAIR because of prior performance problems with paint adhesion and corrosion resistance on test specimens with low coating weights. Bell Textron has developed an improved, non-proprietary TFSAA process that meets the performance criteria of MIL-A-8625F. The process produces films that perform as well as CAA films with low coating weights in paint adhesion and corrosion resistance. The improved process has been evaluated by NAVAIR researchers for bare corrosion, paint adhesion, acid resistance, abrasion resistance and wedge crack adhesive bonding with positive results. Those results, as well as work done to verify a full-scale TFSAA process for bare corrosion, paint adhesion and adhesive bonding, and evaluation of TFSAA brush repair and fatigue impact of the process will be discussed. NAVAIR has recently developed a trivalent chromium-based sealer, TCP, which has shown promising results and potential as a technically equivalent replacement to hexavalent chromium. All the tests to evaluate TFSAA as a CAA replacement include evaluation of TCP as a sealer replacement for chromate-based anodize sealers. The evaluation of TCP will be included in the discussion of TFSAA validation.

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Introduction

Chromic acid anodization is still prevalent in the finishing of aluminum alloys when corrosion inhibition and paint adhesion are needed on fatigue-sensitive parts. NAVAIR has been pursuing replacements to CAA because of the environmental and health hazards associated with use of chromates. Boric-sulfuric acid anodization (BSAA), a proprietary Boeing product that requires license fees, is NAVAIR's only fully implemented alternative to CAA where corrosion resistance, paint adhesion, and fatigue resistance are required. TFSAA is available as an alternative but has limited implementation by NAVAIR due to prior performance problems with paint adhesion and corrosion resistance on test specimens with low coating weights.

Bell Textron has developed an improved, non-proprietary TFSAA process that meets the performance criteria of MIL-A-8625F, "Anodic Coatings for Aluminum and Aluminum Alloys," for coating weights of their interest. The process produces films that perform as well as CAA films with low coating weights in paint adhesion and corrosion resistance.

The improved TFSAA process has recently been evaluated by NAVAIR researchers for bare corrosion, paint adhesion, acid resistance, abrasion resistance and wedge crack adhesive bonding with positive results. Those results, as well as work done to verify a full-scale TFSAA process for bare corrosion, paint adhesion and adhesive bonding, and evaluation of TFSAA brush repair and fatigue impact of the process will be discussed.

Multiple processing and environmental benefits are available for NAVAIR depot facilities and OEMs with use of TFSAA. For brush anodizing, where no alternative to CAA is available and approved, TFSAA is potentially a full replacement for bare and painted applications. For tank applications, TFSAA offers a non-proprietary alternative to BSAA. In addition, TFSAA has shown potential as an alternative to CAA and PAA for structural adhesive bonding applications.

Sealed anodic coatings

Alongside the search for CAA alternatives is the pursuit of chromate-based sealer alternatives. For optimum corrosion resistance all anodized aluminum coatings require a post treatment, or sealer, that is typically based on hexavalent chromium compositions. In addition to being harmful to human health and the environment, chromate sealers are typically applied at 200°F.

NAVAIR has been actively searching for replacements to chromate-based sealers for anodized aluminum. To date, non-chromate sealers have been generally inferior to hexavalent chromium in at least one performance aspect (example, corrosion resistance). However, NAVAIR has recently developed a trivalent chromium-based sealer, TCP, which has shown promising results and potential as a technically equivalent replacement to hexavalent chromium. TCP eliminates use of hexavalent chromium, dramatically reduces the amount of total chrome used, and is generally applied at ambient temperature.

Recent Investigations

NAVAIR recently performed several investigations to study the potential of TFSAA as BSAA and CAA alternatives, and to determine the potential of TCP as a chromate seal alternative. Investigation #1 evaluated the paint adhesion performance and corrosion, abrasion, and acid resistance of sealed and unsealed TFSAA and BSAA. In Investigation #2 TCP post treatment immersion time was optimized for corrosion resistance and paint adhesion on TFSAA test specimens.

A previously published NAVAIR investigation to determine the potential of TFSAA in adhesive bonding applications evaluated the adhesive bond performance of unsealed and TCP sealed TFSAA, BSAA, and phosphoric acid anodize (PAA)[1]. The results showed that unsealed TFSAA and TCP sealed PAA performed as good as the unsealed PAA control. Subsequent work to optimize TCP post treatment immersion time and temperature for adhesive bond performance on PAA test specimens is presented as Investigation #3.

Background

Anodic coatings are applied to aluminum and aluminum alloys to provide corrosion resistance and improve paint adhesion and abrasion resistance. Detailed requirements for anodic coatings used by the Department of Defense are given in Military Specification MIL-A-8625F, "Anodic Coatings for Aluminum and Aluminum Alloys." The specification classifies anodic coatings as Type I, conventional chromic acid anodize; Type IB, low voltage chromic acid anodize; Type IC, non-chromic acid anodize (example: boric-sulfuric acid anodize); Type II, conventional sulfuric acid anodize; Type IIB, thin film sulfuric acid anodize; and Type III, hard anodize. MIL-A-8625F states: Types I, IB, and II anodic coatings are intended to improve corrosion resistance under severe service conditions or serve as a base for paint systems; Types IC and IIB anodic coatings provide non-chromate alternatives to Type I and IB coatings where corrosion resistance, paint adhesion, and fatigue resistance is required; and Type IC and IIB may be substituted for Type I and IB coatings only where approval of the procuring activity is granted.

Anodic coatings are porous oxide films, and it is essential to close, or seal, the pores after anodizing. If the pores are not sealed then the anodic coating is easily subject to attack by chemicals and environmental conditions encountered by military aircraft. As a result, MIL-A-8625F states that Types I, IB, IC, II, and IIB anodic coatings must be sealed unless the procuring activity requests otherwise, and that the sealing medium may be any suitable chemical solution that seals the pores and ideally enhances corrosion resistance. Chromate-based sealers applied at elevated temperature are commonly used. Boiling water is an environmentally preferable alternative to chromate-based sealers, but does not provide comparable corrosion resistance.

Performance requirements given in MIL-A-8625F for non-dyed Type I, IB, IC, II, and IIB anodic coatings include coating weight, corrosion resistance, and paint adhesion.

Coating weights must be met as given in Table 1.

Table 1: Unsealed anodic coating weight requirements per MIL-A-8625F

Anodic Coating Type	Required coating weight (mg/sqft)
I and IB	≥ 200
IC	200 to 700
II	≥ 1000
IIB	200 to 1000

MIL-A-8625F requires that corrosion resistance provided by sealed anodic coatings be determined after test specimens are exposed to ASTM B 117 salt spray test for 336 hours. After salt spray exposure all test specimens must not have more than 5 pits per 30 square inches, and pits must not be larger than 0.031 inch in diameter. Although MIL-A-8625F requires 336 hours of salt spray exposure, the joint service aerospace materials community has generally agreed that any candidate coating replacement should perform as good as or better than the coating to be replaced. In most cases anodic coatings currently in use provide adequate corrosion protection well beyond 336 hours of salt spray exposure. Therefore, as a general rule, candidate anodic coatings should be exposed to at least 1,000 hours of salt spray, and the resulting corrosion protection performance be directly compared to the performance of the coating to be replaced.

Paint systems applied to anodic coatings must meet minimum performance requirements. MIL-A-8625F requires no intercoat separation between the paint system and the anodic coating or between the anodic coating and the base metal when the test specimen is subjected to the wet tape adhesion test. The wet tape adhesion test consists of anodized/painted test specimens immersed for 24 hours in room temperature deionized water. After immersion the specimen is tested in accordance with ASTM D 3359, "Standard Test for Measuring Adhesion by Tape Test" Test Method A, where an X-cut is scribed through the paint and tape is applied and removed over the cut. Additional tape adhesion tests routinely used by the joint services to discriminate among coating systems are dry tape X-cut, dry tape cross hatch, four-day wet tape X-cut (96-hr immersion in 120°F deionized water), and seven-day wet tape X-cut (168-hr immersion in 150°F deionized water). Acceptance criteria for these additional tape adhesion tests is given in the joint services developed "Joint Test Protocol (JTP) for Validation of Non-Chromate Aluminum Pretreatments (NCAP)."[2] The JTP states that all wet tape adhesion test specimens shall have no peel away, at least 4A rating per ASTM D 3359, and no blistering of unscribed coating area. Dry tape adhesion cross hatch test specimens should have loss of no more than two complete primer squares or maximum paint loss less than the control, according to the JTP.

Paint blistering is not a performance requirement in MIL-A-8625F, but is often evaluated as part of paint adhesion testing. After immersion in water painted test specimens may develop blisters. ASTM D 714, "Standard Test Method for Evaluating Degree of Blistering of Paints," is used to rate blister size and frequency.

Performance requirements for abrasion resistance are specified for Type III anodic coatings in MIL-A-8625F. In Investigation #1 of this study test specimens with Types IC, II, and IIB anodic coatings were subjected to the abrasion resistance test to determine their relative hardness. ASTM D 4060, "Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser," is used to determine the wear index of each coating system.

In addition to the performance tests specified in MIL-A-8625F, the researchers performed acid dissolution and adhesive bonding tests. The purpose of the acid dissolution test is to determine the chemical resistance that sealers provide for anodic coatings. The test method is described in ASTM B 680, "Standard Test Method for Seal Quality of Anodic Coatings on Aluminum by Acid Dissolution." Although there are no acid dissolution performance criteria specified in MIL-A-8625F the results for each anodic coating and sealer system are compared relative to each other.

Adhesive bonding tests are performed to determine the bond strength durability of a bond primer and adhesive system adhered to a coating. Typically, CAA is used for fatigue sensitive adhesive bonding applications where corrosion resistance is required. PAA is commonly used for fatigue sensitive adhesive bonding applications where corrosion resistance is not required. ASTM D 3762, "Standard Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test)," is used in this study to prescreen anodic coating and sealer systems to identify potential alternatives to CAA.

Experimental

Anodic Coating Application

Test specimens of aluminum alloys 2024-T3 and 7075-T6 were prepared and anodized as follows:

1. Immersed in alkaline cleaner at 120°F to 160°F for 15 minutes or until water-break free, then double rinsed in warm tap water.
2. Immersed in deoxidizer solution at room temperature for 2 minutes for alloy 7075 and 15 minutes for alloy 2024, then double rinsed in ambient deionized water.
3. Anodized, then thoroughly rinsed in cool tap water.
   - Type IC, Boric-sulfuric: per proprietary Boeing Aircraft Process Specification.
   - Type II, Sulfuric: anodized in 15wt% sulfuric acid solution by ramping 5 volts per minute to 17 volts then 20 minutes at 17 volts (20 minutes at 17 volts specified); solution temperature ranged 70°F to 82°F (74°F to 78°F specified).
   - Type IIB, Thin Film Sulfuric: anodized in 5wt% sulfuric acid solution by ramping 3 volts per minute to 15 volts then 20 minutes at 15 volts (19 to 21 minutes at 15 volts specified); solution temperature ranged 72°F to 89°F (75°F to 85°F specified).)
   - Phosphoric: per ASTM D 3933.
4. Immersed in sealer solution while specimens still wet from water rinse.

Sealer Application

- Dichromate: immersed for 25 minutes in 5% dichromate solution at 190°F to 210°F, thoroughly rinsed in cool tap water.
- Boiling water: immersed for 25 minutes in deionized water at 200°F to 208°F, thoroughly rinsed in cool tap water.
- TCP: immersed for 2, 5, 10, and 20 minutes in TCP5B3 solution at room temperature, thoroughly rinsed in cool tap water.
- TCP+hot water: immersed for 2, 5, 10, and 20 minutes in TCP5B3 solution at room temperature, rinsed thoroughly in cool tap water, immediately immersed for 25 minutes in deionized water at 200°F to 208°F, thoroughly rinsed in cool tap water.

Paint Application

Epoxy primers MIL-PRF-23377G (chromated, solvent-based), MIL-PRF-85582C Class C (chromated, water-based) and MIL-PRF-85582C Class N (non-chromated, water-based) were applied after anodized test specimens dried in ambient conditions overnight. Painted test specimens cured in ambient conditions for 14 days before tape adhesion tests were performed.

Coating Weight Test

Test specimen coating weights were determined in accordance with MIL-A-8625F. One unsealed test specimen from each rack of anodized panels was tested.

Corrosion Resistance Test

Two to three replicates of each coating system were exposed to ASTM B 117 neutral salt spray for 1,000 hours to test corrosion resistance. Three-inch by ten-inch panels of aluminum alloys 2024-T3 and 7075-T6 were secured in plastic racks at a 6° incline. After exposure the panels were gently rinsed with deionized water to wash away salt residue and were dried in ambient conditions. Dry panels were rated for evidence of corrosion per ASTM D 1654.

Observations, including number of pits, presence of tails and white and black corrosion product, were recorded.

Paint Adhesion Test

To determine paint adhesion performance one replicate of each anodize/primer coating system was prepared for each of four tape adhesion tests. Three-inch by five-inch test specimens of aluminum alloys 2024-T3 and 7075-T6 were used for dry and wet tape adhesion tests. Wet tape adhesion specimens were fully immersed in containers of deionized water, with each specimen separated to ensure painted surfaces were in contact with water, and covered tightly with foil. Respective test sets were held at ambient conditions for one day, in a 120°F oven for four days, and a 150°F oven for seven days. Immediately after one, four, and seven day water immersions, the specimens were tested and rated in accordance with ASTM D 3359 Test Method A and ASTM D 714. Dry and one-day wet adhesion tests were performed on the same specimens, with the dry adhesion test performed before one-day water immersion.

Abrasion Resistance Test

Three replicates of each coating system on four-inch by four-inch panels of aluminum alloys 2024-T3 and 7075-T6 were abraded in accordance with ASTM D 4060 to determine abrasion resistance. Panel weight and conductivity were measured after every 1,000 revolutions. Conductivity was measured to determine when breakthrough to the base metal occurred. The panel weight used to determine coating weight loss was the final panel weight recorded prior to breakthrough.

Acid Dissolution Test

Three replicates of each coating system on three-inch by ten-inch panels of aluminum alloys 2024-T3 and 7075-T6 were tested for acid resistance per ASTM B 680. Dichromate sealed anodic coatings are generally not resistant to acid attack, and therefore are usually not subjected to this test. In this study, however, the researchers chose to test dichromate sealed specimens for comparative purposes.

Adhesive Bonding Test

For the wedge crack adhesive bonding tests two test panels of each coating system were prepared. Six-inch by six-inch by 0.125-inch aluminum 2024-T3 test panels were prepared with PAA, TFSAA, and BSAA. PAA panels were immersed into a solution of TCP for 20 minutes at ambient conditions, and the BSAA and TSAA panels were immersed in TCP for 5 minutes at ambient conditions.

Bonding Procedure: Standard aerospace adhesion techniques were used to prepare wedge crack test specimens. The bond primer used for this test was BR 127 and was spray applied in the target range of 0.0001 to 0.0004 inches. Primed panels were hot air oven cured for 30 minutes at 250°F. The adhesive was AF-163-2 OST (one side tacky) film with a weight of 0.06 psf (pounds per square foot). Bonding procedures were performed in accordance with manufacturer's instructions, with a heat up rate of 7°F per minute and a cure time of 1 hour at 250°F under a 40 psi atmosphere. The twelve sets of test panels were adhesively bonded in the same autoclave processing cycle.

Wedge Crack Extension Test Method: One-inch wide specimens were cut from each of the bonded panels. In the test only two specimens were prepared and tested from each panel. The edges of the test specimens were polished prior to testing to more accurately determine crack growth. Wedges were inserted and testing was performed on the 1-inch wide specimens in accordance with ASTM D 3762. Wedges are 0.125 inches thick and measure 0.750 inches from top edge of wedge to shoulder. Crack length readings were taken on both sides of each specimen after exposures of 0, 4, 24, 48, 168 and 504 hours in a humidity chamber at 100 % relative humidity and 140°F.

Results and Discussion

Coating Weight

Anodic coating weights applied to panels during Investigations #1 and #2 are given in Table 2. Using BSAA and TFSAA process specifications, coating weights for alloys 2024 and 7075 met the requirements of MIL-A-8625, but did not approach the minimum requirement for each process. The minimum coating weights achieved using the process specifications for BSAA and TFSAA were 100 mg/sqft greater than the minimum coating weight required by MIL-A-8625F. As a result, no corrosion resistance, paint adhesion, or adhesive bonding data was generated for coating weights near the MIL-A-8625F minimum coating weight. As such, use of either BSAA or TFSAA below 300 mg/sqft should be approached with caution unless data is presented that show similar corrosion and paint adhesion performance to coatings of 300 mg/sqft and above.

Table 2: Anodic Coating Weights of Test Specimens

Anodic coating type	Alloy type	Minimum coating weight (mg/sqft)	Maximum coating weight (mg/sqft)	Average coating weight (mg/sqft)	MIL-A-8625F coating weight requirement (mg/sqft)
Type IC (BSAA) Investigation #1	2024	291	392	334	200 to 700
	7075	472	625	532	
Type IIB (TFSAA) Investigation #1	2024	298	438	367	200 to 1000
	7075	491	696	607	
Type IIB (TFSAA) Investigation #2	2024	360	594	432	
	7075	589	880	747	

Corrosion Resistance

Figure 1 depicts corrosion data generated during Investigation #1. The data show that the 20-minute TCP immersion and 20-minute TCP followed by 25-minute hot water immersion sealers generally performed as good as or better than the standard dichromate sealer for all anodize/sealer combinations for both alloys. Hot water sealer provided significantly less corrosion protection than any other sealer, and unsealed test specimens became fully corroded after less than 1,000 hours of exposure. TFSAA performed as good as or better than BSAA except when the hot water sealer was used.

The photos in Figures 2 and 3 show the appearance of BSAA and TFSAA test panels post treated with 20-minute TCP ambient immersion and standard hot dichromate and hot water sealers after exposure to 1,000 hours of ASTM B 117 salt spray.

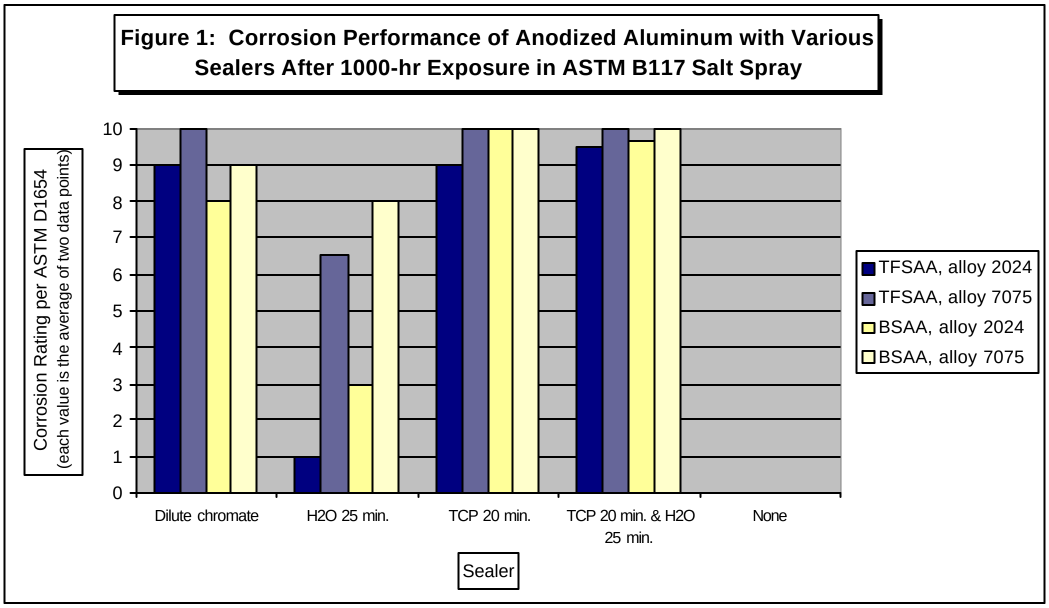


Figure 1: Corrosion Performance of Anodized Aluminum with Various Sealers After 1000-hr Exposure in ASTM B117 Salt Spray

Figure 2: BSAA with various sealers on 2024-T3 aluminum after exposure to 1,000 hours of ASTM B 117 salt spray

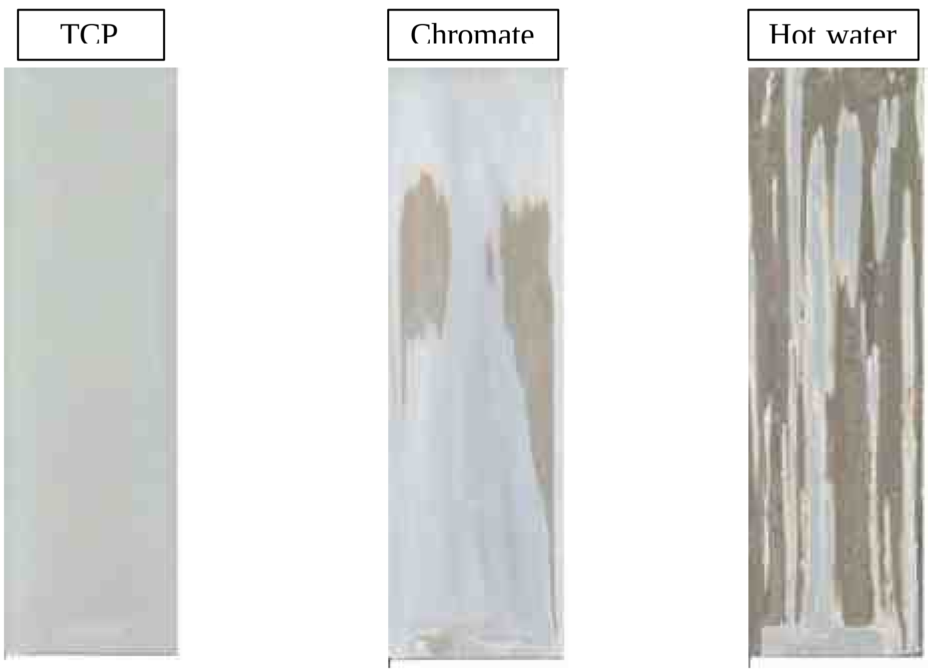


Figure 3: TFSAA with various sealers on 2024-T3 aluminum after exposure to 1,000 hours of ASTM B 117 salt spray

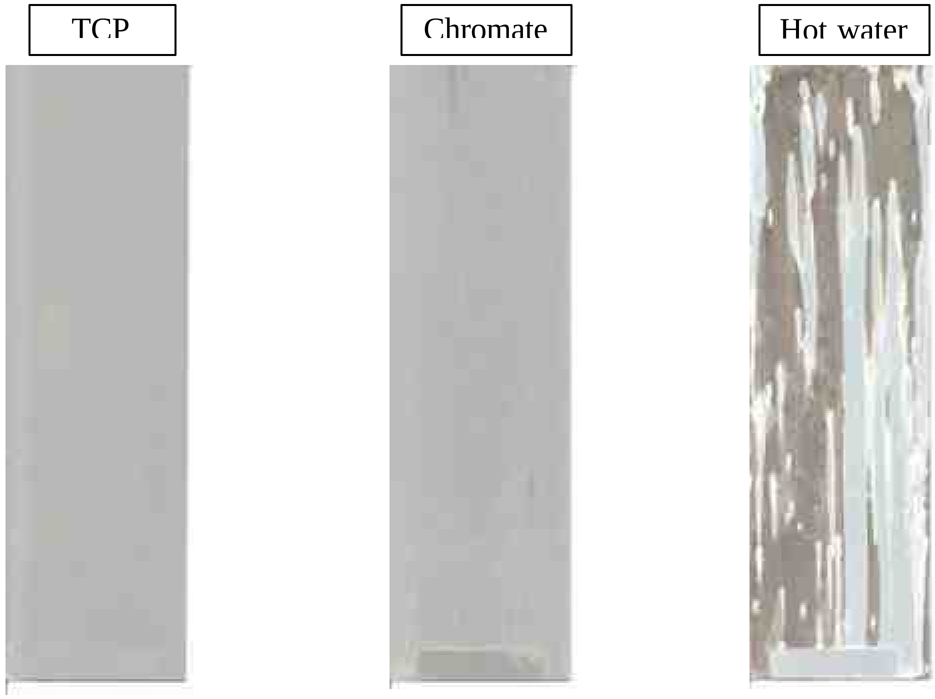


Figure 4 depicts corrosion data generated during Investigation #2. Each rating is the average of three specimens. In this investigation TCP sealer immersion times were varied at 2, 5, 10, and 20 minutes. Test specimens were also prepared at each TCP immersion time followed immediately by a 25-minute immersion in hot water. The results show that all coatings rated 9 or better for both alloys, with the exception of 2-minute TCP immersion followed by 25-minute hot water immersion on alloy 7075. For absolute corrosion protection of TFSAA, all combinations of TCP immersion and hot water seal are acceptable except 2-minute TCP immersion followed by 25-minute hot water immersion on alloy 7075. Immersions of 20 minutes tended to yield slightly powdery coatings. This is expected to reduce paint adhesion. The TCP process appears robust and offers a wide processing range to obtain very good corrosion resistance.

In previous work presented at the 2002 Triservice Corrosion Conference and subsequent work presented here as Investigation #3 the corrosion performance of PAA with and without TCP sealer was studied. Figure 5 shows the resulting corrosion performance of unsealed and TCP sealed PAA after exposure to 72 and 1,000 hours of ASTM B 117 neutral salt fog. The initial work proved that 20-minute ambient TCP immersion adds significant corrosion protection to the PAA coating. Further work was done in Investigation #3 to optimize the TCP immersion process for corrosion protection and adhesive bonding performance. The results presented in Figure 6 show that corrosion protection is optimized with 20-minute TCP immersion at 85°F. Although Figure 13 shows relatively low crack growth rates for those specimens, they exhibited more cohesive failure than other specimens with similar crack growth rates. 10-minute TCP immersion at 100°F and 40-minute immersion at ambient conditions (68°F to 70°F) provide similar corrosion protection without significantly impacting adhesive bonding performance.

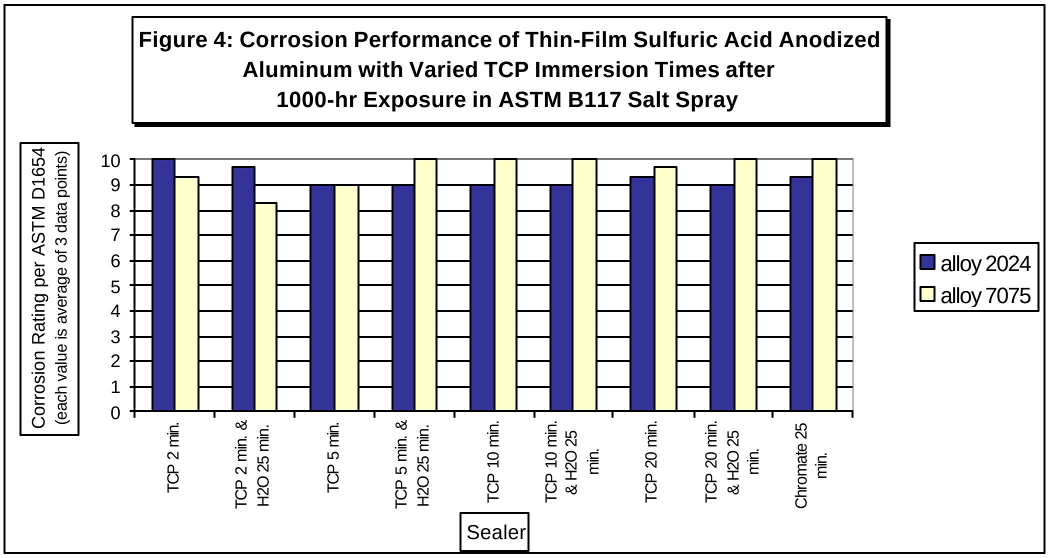
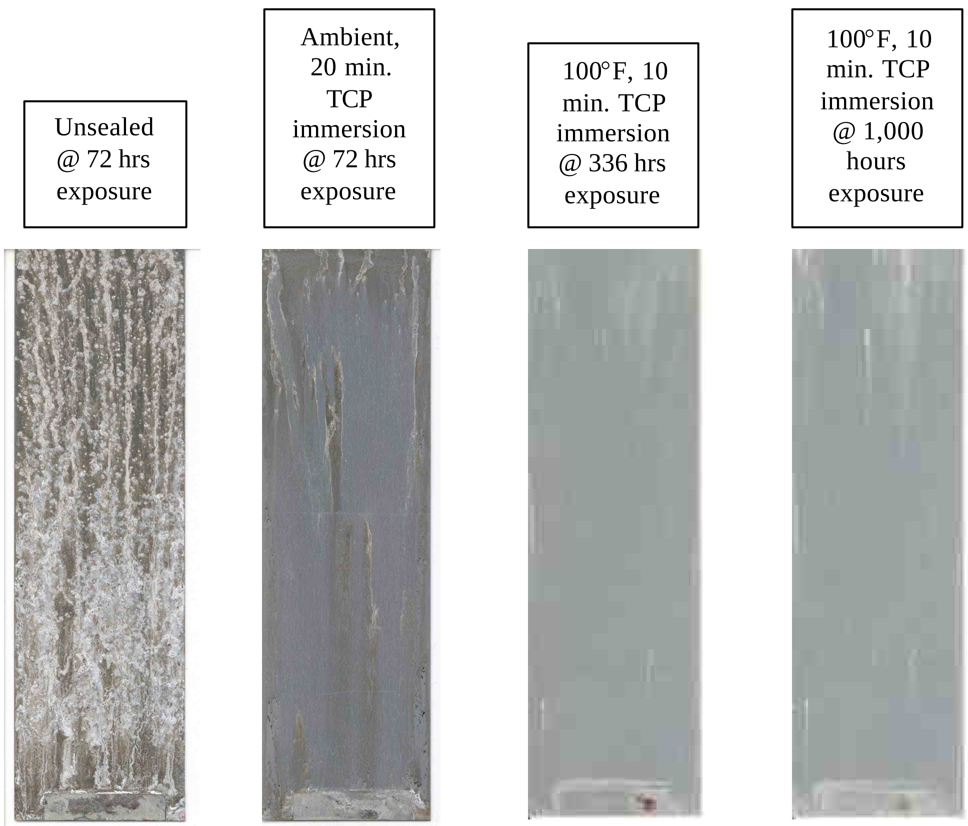
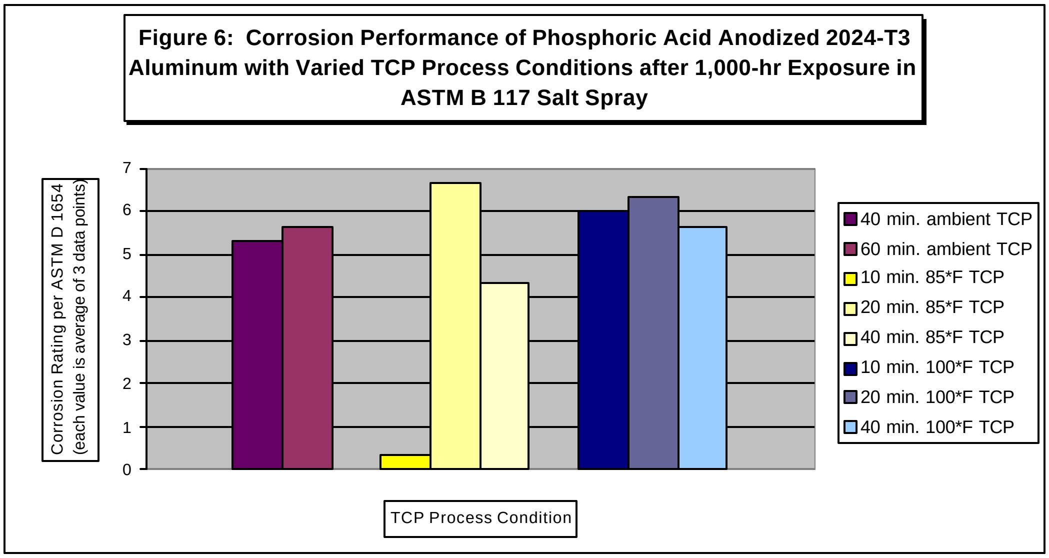


Figure 4: Corrosion Performance of Thin-Film Sulfuric Acid Anodized Aluminum with Varied TCP Immersion Times after 1000-hr Exposure in ASTM B117 Salt Spray

Figure 5: Corrosion performance of TCP sealed PAA on 2024-T3 aluminum after ASTM B 117 neutral salt fog exposure





Paint Adhesion

Paint adhesion data generated during Investigation #1 is presented in Figures 7 and 8. 20-minute TCP immersion and 20-minute TCP immersion followed by 25-minute hot water immersion were compared to standard hot dichromate, hot water and unsealed specimens. 20-minute TCP immersions produced slightly powdery coatings.

The results show the dichromate sealer provided better paint adhesion performance than either of the TCP sealers for both alloys. In general, 20-minute TCP immersion followed by 25-minute hot water immersion performed as good as or better than the hot water sealer. The paint adhesion performance of TFSAA was generally as good as or better than BSAA for all sealer/primer combinations. As a result of the marginal paint adhesion results for 20-minute TCP immersion, Investigation #2 was planned to identify the optimum TCP immersion time that yields maximum paint adhesion and corrosion resistance for a variety of alloys and coating systems.

Two unexpected results are shown in the data. First, unsealed specimens should have provided superior paint adhesion performance over all sealers. In this test, however, the unsealed specimens performed the worst for primer 85582C. Since the dichromate and hot water sealers performed relatively well, the poor performance of unsealed specimens could possibly be explained by poor rinsing. Second, all specimens coated with primer 85582N blistered in the four-day and seven-day wet tape tests, indicating a problem with the primer.

Paint adhesion data generated during Investigation #2 is presented in Figure 9. Overall, 5- and 10-minute TCP immersions and 5- and 10-minute TCP immersions with subsequent 25-minute hot water immersions provided outstanding paint adhesion for all coatings. Both paint adhesion and corrosion performance are optimized with 10-minute TCP immersion as can be seen from Figures 4 and 9.

Figure 7: Paint Adhesion Performance of Anodized Aluminum with Various Sealers - alloy 7075

TFSAA

Primer	85582c1				85582n2				23377c1			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
Dilute chromate	5	5	5	5	5	5	5	5	5	5	5	3
H2O 25 min.	5	4	5	4	5	5	5	5	5	5	5	4
TCP 20 min.	4	2	5	5	3	1	5	5	4	5	4	4
TCP 20 min. & H2O 25 min.	4	4	5	5	3	2	5	5	2	3	5	5
None	5	3	2	0	5	5	5	5	5	5	5	5

BSAA

Primer	85582c1				85582n2				23377c1			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
Dilute chromate	5	4	5	4	5	5	5	5	4	5	5	5
H2O 25 min.	5	3	5	4	5	4	5	4	5	5	5	5
TCP 20 min.	2	2	5	5	3	1	4	5	3	5	5	5
TCP 20 min. & H2O 25 min.	5	5	5	5	4	3	5	5	3	4	5	5
None	5	1	1	0	5	5	5	5	5	5	5	4

Key

adhesion rating	0	1	2	3	4	5
blister rating	dense	med dense	med	few	none	

Note: discounted blisters when along panel edge only

Figure 8: Paint Adhesion Performance of Anodized Aluminum with Various Sealers - alloy 2024

TFSAA

Primer	85582c1				85582n2				23377c1			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
Dilute chromate	5	4	5	5	5	5	5	5	4	5	5	5
H2O 25 min.	5	4	5	3	5	5	5	5	3	4	5	4
TCP 20 min.	3	4	5	5	5	3	5	5	3	5	5	5
TCP 20 min. & H2O 25 min.	5	4	5	5	5	4	5	5	3	4	5	5
None	5	2	2	0	5	5	5	5	5	5	5	5

BSAA

Primer	85582c1				85582n2				23377c1			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
Dilute chromate	5	2	5	4	5	4	1	5	5	5	5	4
H2O 25 min.	5	4	5	5	5	4	5	4	4	4	5	4
TCP 20 min.	2	2	5	5	3	4	5	4	3	4	5	4
TCP 20 min. & H2O 25 min.	4	4	4	5	3	3	4	5	3	4	5	5
None	5	1	0	0	5	3	5	2	5	5	5	5

Key

adhesion rating	0	1	2	3	4	5
blister rating	dense	med dense	med	few	none	

Note: discounted blisters when along panel edge only

Figure 9: Paint Adhesion Performance of TFSAA Aluminum with Varied TCP Immersion Times

alloy 2024

Primer	85582c				85582nc			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
TCP 2 min.	5	5	5	5	5	5	5	5
TCP 5 min.	5	5	5	5	5	5	5	5
TCP 10 min.	5	5	5	5	5	5	5	5
TCP 20 min.	4	4	5	5	3	3	5	5
TCP 2 min./Hot H2O 25 min.	4	0	3	3	5	5	4	4
TCP 5 min./Hot H2O 25 min.	5	5	5	5	5	5	5	5
TCP 10 min./Hot H2O 25 min.	5	4	5	5	5	5	5	5
TCP 20 min./Hot H2O 25 min.	5	5	5	5	5	5	5	5
Dilute chromate 25 min.	5	4	5	5	5	5	5	5

alloy 7075

Primer	85582c				85582nc			
Postreatment	dry	1-day wet	4-day wet	7-day wet	dry	1-day wet	4-day wet	7-day wet
TCP 2 min.	5	5	5	5	5	5	5	5
TCP 5 min.	5	5	5	5	5	5	5	5
TCP 10 min.	5	5	5	5	5	5	5	5
TCP 20 min.	5	5	5	5	5	5	5	5
TCP 2 min./Hot H2O 25 min.	5	0	3	3	5	5	5	5
TCP 5 min./Hot H2O 25 min.	5	5	5	5	5	5	5	5
TCP 10 min./Hot H2O 25 min.	5	5	5	5	5	5	5	5
TCP 20 min./Hot H2O 25 min.	5	5	5	5	5	5	4	5
Dilute chromate 25 min.	5	5	5	5	5	5	5	5

Key

adhesion rating	0	1	2	3	4	5
blister rating	**dense**	**med dense**	**med**	**few**	**none**	

Note: discounted blisters when along panel edge only

Abrasion Resistance

The data generated during abrasion resistance testing in Investigation #1 are presented in Figure 10. The results verified that unsealed anodic coatings are more resistant to abrasion than sealed anodic coatings. In general, the dichromate sealer degraded abrasion resistance the least, and both TCP sealers provided better abrasion resistance than the hot water sealer. TFSAA was slightly more abrasion resistant than BSAA. Abrasion testing was not performed as part of Investigation #2.

Acid Dissolution

Figure 11 shows the acid dissolution test data generated during Investigation #1. The results validated that dichromate sealers do not provide resistance to chemical acid attack. The 20-minute TCP immersion with subsequent 25-minute hot water immersion provided significantly better acid resistance than any other sealer. 20-minute TCP immersion provided better acid resistance than the hot water sealer. TFSAA offered as good as or better acid resistance as BSAA.

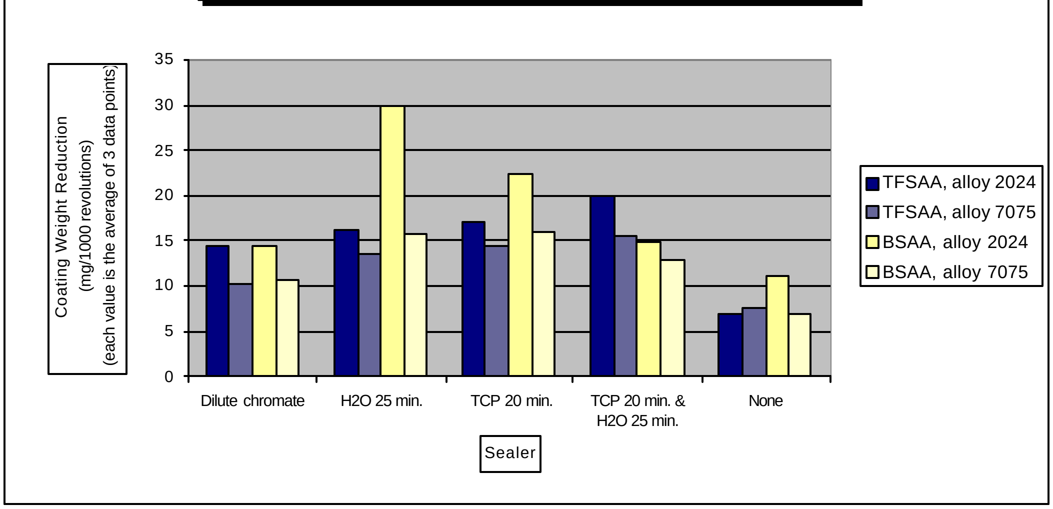


Figure 10: Abrasion Resistance of Anodized Aluminum with Various Sealers, ASTM D4060

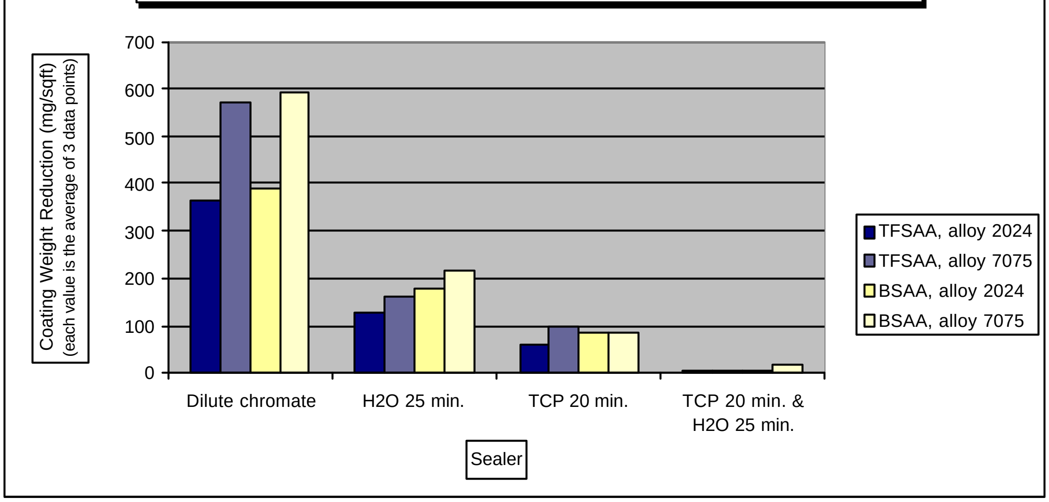
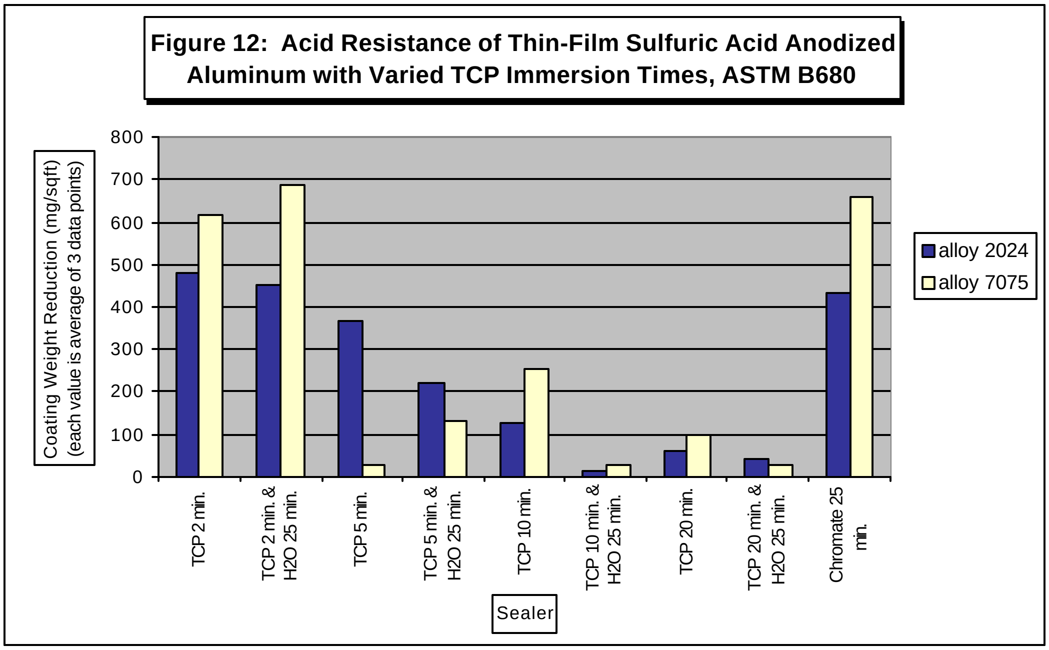


Figure 11: Acid Resistance of Anodized Aluminum with Various Sealers, ASTM B680

Figure 12 shows the acid dissolution test data generated during Investigation #2. The results generally show that acid resistance increases with TCP immersion time, and that addition of a hot water seal after TCP immersion provides additional acid resistance. Due to processing problems the data for 20-minute TCP immersion in this test is replaced with the acid resistance data generated in Investigation #1 for 20-minute TCP immersion.



Adhesive Bonding

Previous work presented at the 2002 Triservice Corrosion Conference proved that the corrosion resistance of PAA coatings is substantially improved without significantly affecting adhesive bond performance when specimens are sealed with TCP for 20 minutes at ambient conditions. In Investigation #3 a variety of TCP immersion times and temperatures were tested to optimize the adhesive bonding and corrosion performance of PAA coatings.

The results presented in Figure 13 show that moderate sealing conditions provided the best bonding surfaces in this study based on wedge crack growth rates and observed failures in the crack growth regions of the split specimens. The panels sealed with 10-minute TCP immersion at 85°F exhibited the lowest crack growth rates, followed closely by PAA surfaces sealed with 10-minute TCP immersion at 100°F and 40-minute immersion at ambient conditions (68°F to 70°F). PAA specimens sealed with 20-minute TCP immersion at 85°F also exhibited low crack growth rates, but the cohesive failure was higher than the 10-minute/100°F and 40-minute/ambient specimens. Longer immersion times at higher temperatures gave higher crack growth rates and poor bonding adhesion. Sealing for 40 minutes at both 85°F and 100°F resulted in unacceptable bonding surfaces. A photograph of all test specimens split completely open after completion of the test is shown in Figure 14.

As stated in the previous study there are no universal standards for pass or fail in terms of initial crack opening and crack growth. One recent proposal set a maximum 1.400-inch initial crack and a maximum 0.300-inch growth during the exposure test period when bonding with AF-163 film adhesive. In this study the initial crack openings were slightly more that 1.400 inches, but the crack growth lengths were less than 0.300 for the top three sets of wedge crack test specimens. Making an allowance for the initial crack openings of slightly more than 1.400 inches, the sets passed that were exposed to sealing treatments of 10 minutes at 85°F, 10 minutes at 100°F and 40 minutes at ambient temperature.

Comparison of Figures 6 and 13 show that both adhesive bonding and corrosion performance are optimized for 10-minute TCP immersion at 100°F and 40-minute TCP immersion at ambient conditions (68°F to 70°F).

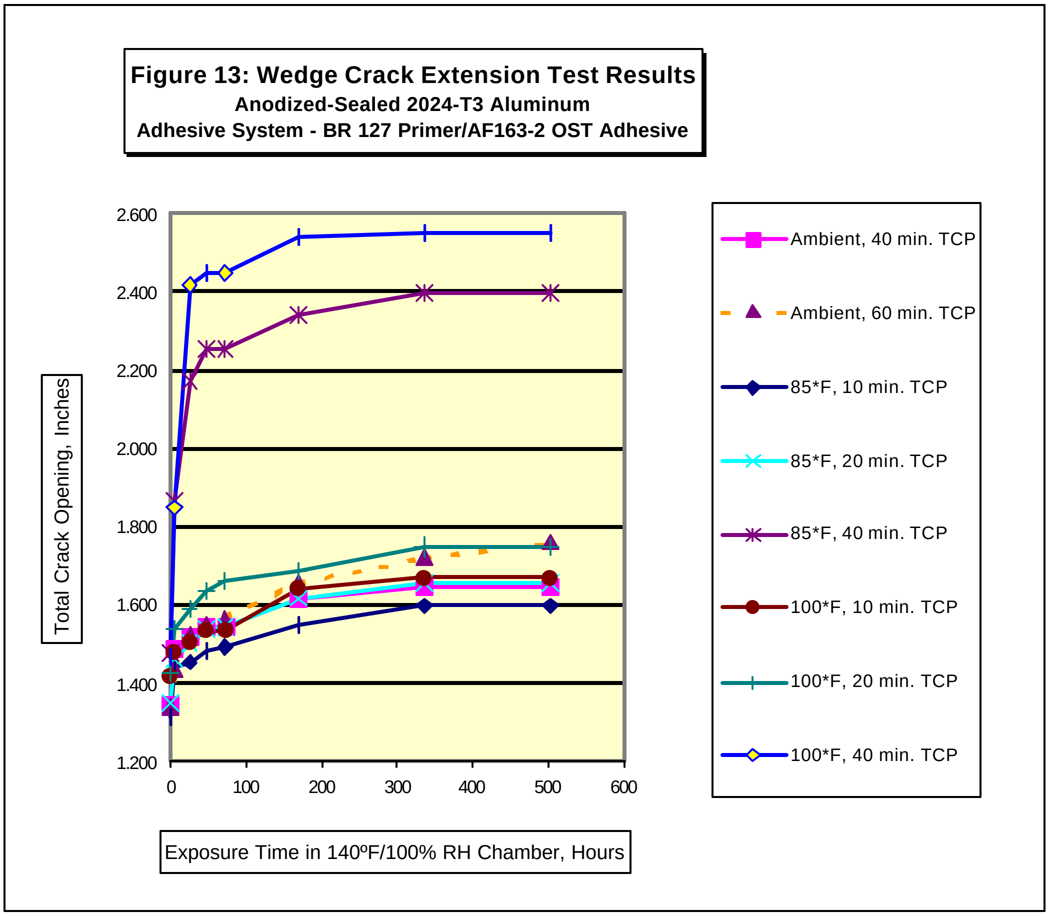
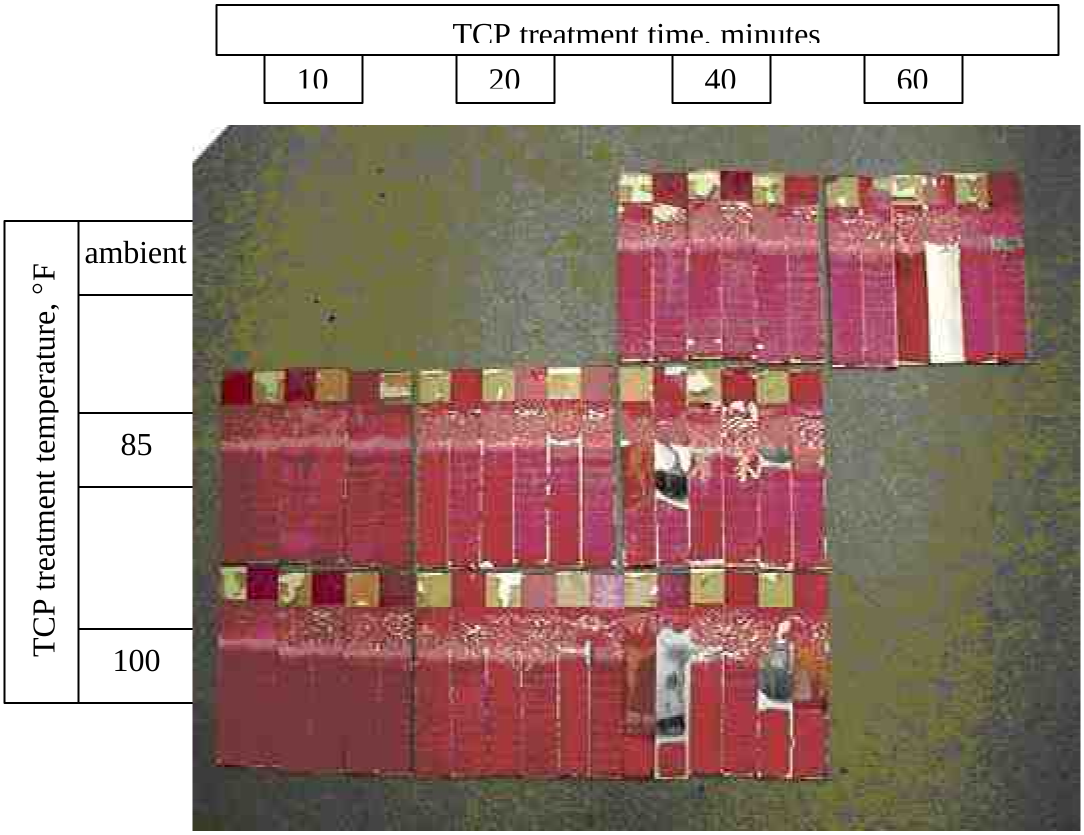


Figure 13: Wedge Crack Extension Test Results
Anodized-Sealed 2024-T3 Aluminum
Adhesive System - BR 127 Primer/AF163-2 OST Adhesive

Figure 14: Wedge Crack Extension Test performed on TCP sealed PAA on 2024-T3 aluminum



Conclusion

The purpose of this study is three-fold: first, determine the potential for TFSAA as an alternative to BSAA for tank applications; second, determine the potential for TFSAA as an alternative to PAA for structural adhesive bonding applications; and third, determine the potential for TCP as an alternative to dichromate anodic coating sealer. Follow-on testing will determine the potential for TFSAA as an alternative to CAA for bare and painted brush applications.

The data generated in the study show that TFSAA is a strong competitor to BSAA. The corrosion and paint adhesion performance of TFSAA was similar to BSAA, and met the performance requirements of MIL-A-8625F for the coating weights achieved using the TFSAA process specification. TFSAA provided better abrasion resistance than BSAA, and offered as good as or better resistance to acid attack.

TFSAA showed good potential as an alternative to PAA and CAA for structural adhesive bonding applications. Unsealed TFSAA performed similar to the unsealed PAA control in the wedge crack extension test, and "passed" based on recently developed proposed criteria.

The data show that TCP is a strong potential alternative to dichromate anodic coating sealers. All TCP immersion times evaluated on TFSAA and BSAA provided similar corrosion protection to dichromate-sealed test specimens, and met MIL-A-8625F corrosion performance requirements. Shorter TCP immersion times tend to produce less powdery coatings, and paint adhesion testing verified that less powdery coatings result in better paint adhesion performance. Optimization of both corrosion protection and paint adhesion is achieved with 10-minute TCP immersion at ambient conditions.

Finally, the data validate that TCP-sealed PAA is a strong potential alternative to CAA for structural adhesive bonding applications where corrosion protection is required. The corrosion performance of PAA sealed with TCP at moderate time and temperature conditions is dramatically improved without significantly compromising adhesive bond strength.

The data generated in this study substantiates follow-up testing to validate the corrosion and paint adhesion laboratory results. During follow-up testing coating systems are applied in production facilities with production-scale equipment. In addition, follow-up testing is planned to determine the corrosion resistance and paint adhesion performance of TFSAA relative to CAA for brush applications. Additional adhesive bonding tests are planned to validate wedge crack extension laboratory results. Follow-up adhesive bonding tests are planned to evaluate unsealed and TCP- sealed PAA, unsealed TFSAA, CAA, and FPL Etch with single lap shear, floating roller peel, wedge crack extension, climbing drum peel, and salt spray lap shear tests. Finally, fatigue testing is planned to evaluate the fatigue debit imposed by TFSAA, BSAA, SAA, and CAA for a variety of aluminum alloys.

Acknowledgments
This work was sponsored by the NAVAIR Aviation Pollution Prevention Program.

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