BSAA Salt Spray Failure Troubleshooting

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The purpose of the salt spray test is to validate the "health" of an anodize process line. This test requires two weeks, which makes effective corrective action decisions paramount to avoiding long periods of downtime. By assimilation of many decades of Boeing documentation, external literature and consultation, an *Anodize Troubleshooting Guide* (ATG) has been developed. The ATG is a simple checklist and is mostly categorized by process solution but also includes sections on other non tankline processes, equipment, and salt spray test conditions. Although this guide is specific to Boric Acid - Sulfuric Acid Anodizing many references can be applied to a broader application that can help guide process engineers to a quick and effective remedy.

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The BSAA process is covered by U.S. Patent No. 4,894,127 (method for Anodizing Aluminum), U.S. Patent No. 4,504,325 (Methods for Sealing on Aluminum Oxide film) and U.S. Patent No. 6,149,795 (Fungus Resistant Boric Acid - Sulfuric Acid Anodizing). Patent licenses are available. For information, contact Patent Counsel, Boeing Commercial Airplane Group, P.O. Box 3707, Seattle, Washington, 98124-2207, U.S.A.

Introduction

The basic salt spray test is relatively simple and dates back to 1914. Shortly after the Aluminum smelting process made aluminum a viable commercial metal[1], the salt spray test was standardized by the US National Bureau of Standards (NBS, now known as NIST. The neutral salt spray procedure was formalized as an ASTM B117 specification in 1939[2] with the currently used 5% salt solution becoming the industry standard in 1954[46]. Ever since the salt spray test first existed; failing results have needed to be analyzed. What makes this an insidious problem is that the causes of salt spray failure on anodized aluminum structure are very numerous and in many instances, not well understood. The subject of this paper to describe a systematic means of determining a relatively quick root cause identification and to describe the Anodize Troubleshooting Guide that can be used as a process analysis checklist.

At Boeing, salt spray (SS) failure of anodized aluminum structure is a Quality Assurance (QA) test that determines the "health" of the process line chemical solutions. Repeated SS failures will cause the anodize process solution to be "tagged". QA then renders the process to be unavailable for further processing, until corrective action and passing SS results have been obtained. The test method ASTM B117 dictates that the test panels shall be kept in a salt fog chamber (Figure 1) for 336 hours (2 weeks).

Figure 1. Salt Fog Chamber

This inherently long test time makes effective corrective action decisions paramount to avoiding long periods of downtime. By assimilation of many decades of Boeing documentation, external literature and consultation, the *Anodize Troubleshooting Guide* (ATG) was developed. The ATG is a simple checklist and is mostly categorized by process solution but also includes sections on other non tankline processes, equipment, and SS test conditions. Although this guide is specific to Boric Acid - Sulfuric Acid Anodizing many references are generic and can be applied to a broader application that can also help guide process engineers to a quick and effective remedies for other anodize processes.

Process Solution Chemistry

A typical BSAA process involves emulsion degrease, alkaline etch, desmut, anodize and then dilute Cr Seal that are interspersed by rinsing (typically DCCR). Each process has a set of chemistry and parameter controls. Review of Quality Assurance log books rarely reveal an unnoticed out of specification condition. However, a drift to one side of a range can result in a set of conditions that is may lead to a SS failure even when all QA numbers are "good". For instance, two studies[3,42] reveal that the high end of the sulfuric acid concentration does result in better SS results. In any case, review of the QA log books is an easy first step.

Additionally, non-specification controlled chemistries may also be important. An example would be the ratio of Cr^{+6} to Cr^{+3} in a chromated deoxidizer solution. When a deoxidizer is relatively new this ratio should be about 3:1 and a well used Cr deoxidizer solution would have a ratio of 1:1.

Silicated degreaser chemistry is known to result in hard scale on auxiliary equipment and have been discouraged from use when also using a dilute chrome Seal process[12]. However, Boeing currently uses silicated cleaners and has been able to minimize scale formation and excessive silicates in solution by maintaining the Degreaser pH[26,27].

Temperature

Anodize temperatures are tightly controlled (80+/-4°F). Higher anodize solution temperatures yield higher coating weights[3,44] and is reported[45] to even provide a significant reduction in pits caused by outdoor exposure. However, if the BSAA solution is upwards of 95° F a significantly higher current density[42] can result. It is also interesting to note that temperature and chloride tolerance have a negative correlation[3] for salt spray performance. Given this tight range, typically the middle is the best place for a set-point for the BSAA solution.

A chromated hot de-ionized water seal temperature is also tightly controlled and studies[4,5,21] have recommended that the upper end of the BAC 5632 specification (195-200°F) be used to improve overall SS pitting performance but at the cost of potential paint adhesion loss[20].

The temperatures of other process solutions are controlled for reasons of etch rate (TEA etch) or cleaning performance (aqueous degrease) that are not directly related to SS performance. However, dryers that are used after the Seal process should not be too hot or purportedly[8] the hydration amount can be affected by unintended Seal solution weeping.

Immersion Time

Deoxidizer immersion time needs to be long enough to remove alloying metal oxides (smut) but studies[4] have determined that 6 minutes should not be exceeded. This leads to understanding that etch rates should be kept at the low end of the specification range[16,22] to reduce the potential for preferential etching of alloyed aluminum.

Anodize immersion times are crucial enough that this parameter is often automated or at least has a timer affixed with an alarm to signal the operator when the load must come out. Additionally, the load must be removed promptly when the rectifier has been shut off. This is crucial since the acid solution is removing anodize structure with every moment that the parts are being exposed to non-electrified anodize acid. If this parameter can be manipulated to be slightly longer, that would certainly produce higher coating weight[5,42,44] and thereby should provide better SS resistance to a weakened process but studies[44] have shown that anodize time only weakly contributes to corrosion protection. Additionally, longer anodize immersion times may be counterproductive to paint adhesion characteristics[17]. The following Anodize rinse should be relatively short to avoid potential lower hydration values[4] for parts that are subsequently Sealed.

Seal immersion time is specified (23-28 minutes) but being at the highest end of the allowed time would provide a higher hydration level and thus better SS resistance[4]. However, longer Seal immersion times again may be counterproductive to paint adhesion results[36].

Congruent to understanding immersion times is the load transfer time. Part movement should be quick enough so that they remain wet while in between tanks[8,9,10,16,37]. This illustrates the need for a troubleshooter to spend time on the shop floor observing the process, taking notes, talking to operators and not getting totally engulfed in data analysis and acquisition.

Contamination

This section is where the ATG has the most information. Certain metal and inorganic ionic species contamination is expected as a process solution ages. Some of these chemical species are important enough to have required monitoring and thus are listed in applicable process specifications. For example, BAC 5632, requires monitoring of Al, Cl, Cr, and Cu. These species are known to be interactive. For instance, it is well known that higher amounts of Al, in BSAA, decreases oxide formation efficiency and can contribute to poorer salt spray performance as a BSAA solution ages[42,44]. However higher amounts of Al in BSAA, will also result in a greater tolerance for Cl and thereby help remediate chloride pitting[3]. Chloride contamination build-up is lessened by charging the anodize tank with de-ionized water[12,18,19,44]. A very early study[34] determined that much lower chloride contamination (50 ppm), in anodize solutions, can contribute to attack on the tank walls. The resulting iron contamination can be significant and may then lead to lower coating weights.

In a Seal tank, the most important contaminant to monitor, is the amount of silicates and is required to be below 10 ppm. However, some documentation[22,23,41,43] have recommended even lower silicate values. In the ATG, many of the other values listed for the Seal solution are from an AESF course[6]. Also in the ATG, the value for Mg has a range since studies have indicated that traces of Mg can help increase the corrosion resistance of sealed anodic film[6]. Also, very small amounts of phosphates, in Seal tanks, reportedly help reduce smut formation and thereby help initiate "sealing" of hot DI water. Given the large number of documented ionic contaminants that can affect a Seal tank a frequent dump schedule is recommended[24] especially if production rates are high.

Another item worth noting is that Boeing studies[7,28] have revealed that excessive drag-out of "TEA etch" (contains sodium sulfide) will render the deoxidizer to be less effective by causing lower coating weights and subsequent paint adhesion and SS failures.

Table 1. Contamination criteria extract from Anodizing Troubleshooting Guide

Check	**Seal**	**BSAA**	**Deoxidizer**	**TEA etch**
Al		5.5 g/L max.	17.2 g/L max.	2.5 – 10.0 oz/gal
Cl	50 ppm max.	0.1 g/L max.		
Cr		500 ppm max.		
Cr^{+6}	45 ppm max.		4.5 – 13.5 g/L	
Cu	15 ppm max.	237 ppm max.	0.2 g/L max.	
Fe	15 ppm max.	50 ppm max.		
Fl	5 ppm max.			
Mg	100 – 150 ppm			
Na	200 ppm max.			
NO_3		100 ppm max.		
pH	3.1 – 3.8			
phosphates	3 - 15 ppm			
silicates	10 ppm max.			
SO_4	100 ppm max.	50 ppm max.		
sulfide			minimize	
Zn	15 ppm max.			

The values in bold type (Table 1) are those required by Boeing process specifications[8,9,10]. Incoming water quality should also be monitored and be commensurate[8] with drinking water standards established by the World Health Organization*. Of specific note is that Incoming Rinsewater Chloride and Fluoride levels not exceed 25 ppm and 1.7 ppm respectively.

Equipment

There are several equipment checks that can be performed when investigating a SS failure. Anodize Racks and Bus bars (Figure 2) should be kept clean and relatively free of heavy oxides[4,8], since poor contacts can cause low anodize coating weights[4,11,12,38].

* International Water Standards for Drinking Water, 3rd Edition WHO, Geneva, 1971

Figure 2. Anodize Bus Bars and Racks

Additionally, any notice of red gelatinous film, on the anodize tank walls, may be attributable to copper impurities and may be removed by plating out onto 1100 series aluminum. Anodize power requirements must be adhered to strictly[8]. Specifically, the voltage ramp up must be 1.5 V/minute minimum and the processing voltage is to be maintained at 15+/-1 V. Too quick of a voltage ramp-up may result in arc mark burning, localize coating dissolution, or powdery coatings[31]. If the operating voltage is too low, the resulting lower current density might contribute to SS failure again due to low resulting coating weights[44].

The BSAA process requires slightly more amperage per square foot than does the CAA process[19]. The higher the current density, the more important becomes the quality of the output current (ripple)[25]. Rectifier ripple can be defined[32] as the percentage of AC current that is passed through a rectifier on the way to the process. Ripple can be found directly on an oscilloscope as a peak-to-peak voltage measurement of the output signal. Excessive ripple can cause a loss in coating weight and also may affect the integrity of the anodize structure. Although there is no ripple requirement, for BSAA processing, monitoring should be periodically performed by an oscilloscope. The ripple should be maintained relatively low[31,35] (5-7%) by use of a ripple filter. The ripple filter is either an inductor, series of capacitors or both and is commonly referred[33] to as a "choke".

To prevent "spotting", corrective action would be to attach a Zinc anode to the racks, prior to Sealing. Sparge air agitation, of an anodize solution, provides uniform solution chemistry and helps to avoid hot spots (burning). However, according to one industry consultant too much air agitation can contribute to SS failure. Also, slow cranes might allow parts to dry in-between processes that would then contribute to low coating weights.

If converting to a BSAA process Seal tanks should avoid the use of Fiberglass construction[22] and Anodize tanks should have the steam pipes constructed of Carpenter 20 instead of 316L stainless steel[29].

Testing

An understatement is that the SS test is not celebrated for being infallible[15,30,39,40]. A thorough investigator should determine, visually, whether the test panels are in good condition and avoid the use of panels that have been in storage for an excessive period. Of course, the storage conditions will establish more exact storage times. To lengthen storage life, the SS panels can be kept in a cabinet and ideally be wrapped in Mylar. Salt spray failure investigations have been previously traced to the condition of the test panels where under magnification, defects have been visible on the panel surface[13].

Figure 3. Salt Spray Test Panels (Mylar On and Off)

Additionally, incomplete removal of roll code ink markings, from SS test panels, has been attributed[41] to premature salt spray failures. The anodized test panels[8] should be a light gray color, have no burn marks, be free of cracks and pits, and have no powder residue before placing in the SS chamber. There are many parameters that can be audited in relation to the proper operation of a salt fog chamber[46,47]. Of particular importance are: the position of panels to avoid splatter and drips onto test surfaces[40,47]; nozzle air pressure[48]; and most recently, at Boeing, even the type of supply water[49]. Additionally, the investigator should inspect the interior of a SS chamber for areas of rust that might then be contributing to failures[15].

When measured, the BSAA coating weight should be a minimum of 200 mg/ft2 for 2024-T3 aluminum and 700 mg/ft2 maximum for 7000 series aluminum. After seal the hydration level should be 8-14% as determined by Boeing test specification BSS 7325[14].

Summary

Anodize Salt Spray (SS) failures are infrequent due to the robust BSAA (Boric Acid Sulfuric Acid Anodizing) process. However, when failures do occur the problem is rather frustrating due to the numerous possible causes. The Anodize Troubleshooting Guide (ATG) is useful as a checklist to systematically isolate areas for further investigation. Boeing has used this technique on several occasions and the result has been quicker decisions of what immediate action is needed and successful resolution to the anodize Salt Spray failure problem at hand.

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