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Cadmium Plating Replacements

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Abstract

The Boeing Company has been searching for replacements to cadmium plate. Two alloy plating systems seem close to meeting the needs of a cadmium replacement. The two alloys, zinc-nickel and tin-zinc are from alloy plating baths; both baths are neutral pH. The alloys meet the requirements for salt fog corrosion resistance, and both alloys excel as a paint base. Currently, tests are being performed on standard fasteners to compare zinc-nickel and tin-zinc on threaded hardware where cadmium is heavily used. The Hydrogen embrittlement propensity of the zinc-nickel bath has been tested, and just beginning for the tin-zinc bath. Another area of interest is the electrical properties on aluminum for tin-zinc and will be discussed. The zinc-nickel alloy plating bath is in production in Boeing Commercial Airplane Group for non-critical low strength steels. The outlook is promising that these two coatings will help The Boeing Company significantly reduce its dependence on cadmium plating.

Introduction

Boeing has been studying cadmium replacements for over 10 years. The original impetus came when Japan strictly limited and then outlawed the use of cadmium after elevated levels of cadmium were found in marine life. Cadmium accumulates in the liver and kidneys; therefore, long term exposure is harmful to humans. Cadmium is most frequently plated from a cyanide bath, and the acute toxic affects of cyanide are well-known[1]. In 1990 Environmental Protection Agency's (EPA) "33/50" Plan for reduction of 17 chemicals including cadmium and cyanide became a goal for Boeing to reduce its hazardous chemical usage. Heretofore, Boeing has been looking for a replacement to cadmium.

Cadmium has some unique properties. One of its most useful properties is its lubricity. Cadmium plate smears and lubricates as it is pushed or torqued against itself or other metals, hence its usefulness on fasteners and gears. The sacrificial corrosion tendency is also a valuable asset of cadmium; cadmium is used on steel fasteners, gears, and various steel parts which need protection from corrosion. The ease of application and sacrificial corrosion properties of cadmium have made it the material of choice for dissimilar metal stackups.

Two alloy plating systems are the promising candidates for replacing cadmium at Boeing. Zinc-nickel alloy (90-10%) plated from a neutral chloride bath has been in production for a year in the Boeing Commercial Airplane Group. The typical parts plated in the zinc-nickel bath are clips and brackets, mostly flat, low alloy steel parts. The second alloy plating being pursued is tin-zinc alloy (80-20%) from a neutral, tin^{+2}, bath. This system is still being tested on a laboratory scale. This paper will discuss the properties such as: corrosion resistance, adhesion, paint adhesion, torque tension, hydrogen embrittlement, and electrical resistance of these alloy plates.

Technical Accomplishments:

Corrosion Resistance.

One of the most important aspects of cadmium plate is its corrosion resistance. Any replacement must meet or exceed its performance. Boeing uses the requirement of no corrosion products after 96 hours of salt fog testing per ASTM B117[2] as the determination of corrosion protection, the same criteria as cadmium, QQ-P-416, type II. Unofficially, 500 hours and no red rust is also a criteria to beat. Zinc-nickel and tin-zinc alloys (with a chromate conversion coating) have been shown to pass the 96 hours of salt spray, and also to pass 500 hours typically with no red rust. Zinc-nickel routinely lasts 1100 to 2000 hours before red rust occurs[3]. Tin-zinc has lasted up to 1000 hours before red rust occurred.

One concern with the tin-zinc alloy is the variability of the alloy composition and its effect on salt spray. Figure 1 shows salt spray data for various alloy compositions; the best salt spray results for tin-zinc are seen at a composition of 8 to 18% zinc with red rust appearance averaging 850 hours of salt spray. Panels with very low zinc concentrations (1% or less) exhibit the properties of a pure tin coating, i.e., the coating is no longer a sacrificial coating, but a barrier type coating, and the thin (8 to 13 μm) coating does not protect against corrosion.

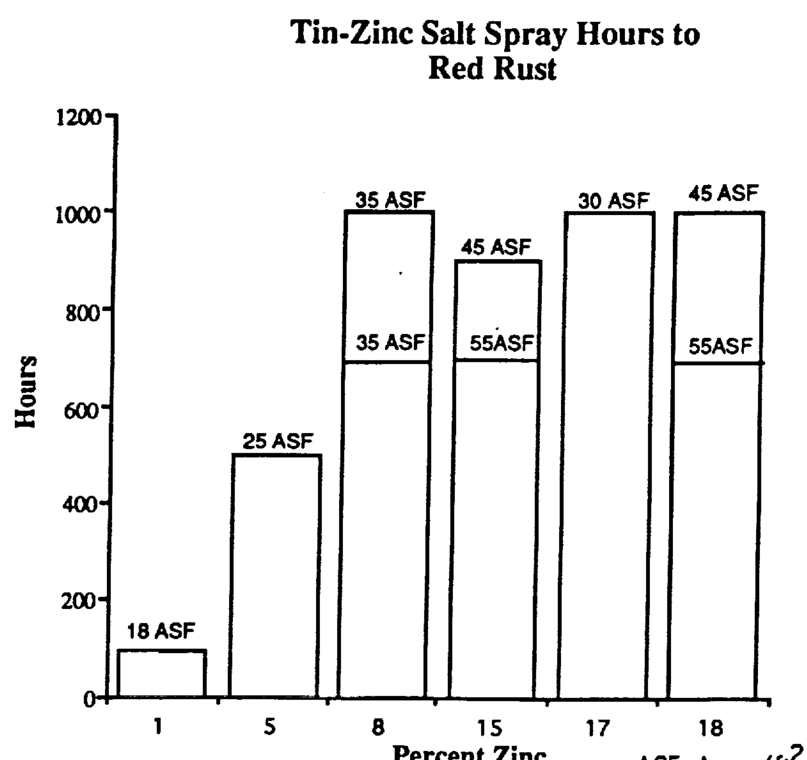

Figure 1. Tin-Zinc Salt Spray Data Based on Percent Zinc

Boeing has spent a great deal of time researching the properties and control of the alloy compositions from the alloy baths, since alloy composition can impact performance.

Boeing's zinc-nickel alloy does not have this problem of alloy dependant corrosion protection. The alloy composition remains stable when the bath is controlled within the ranges given in the process specification[4]. An experiment (full factorial with 3 replicates) varying the current density, pH, and temperature resulted in a stable alloy of 80 to 94% zinc, 20 to 6% nickel with a 3% variation per panel[3,4]. Although composition was in the given range, high pH values at ambient temperatures did result in salt spray failures. Another experiment (half-fractional factorial) with four factors was run on zinc-nickel specifically to identify alloy composition variations. The four factors were zinc and nickel concentrations, pH, and current density. Results showed a steady alloy composition of 81 to 89% zinc. An incompatibility of high zinc concentration and higher than pH 7.0 caused a precipitate to form during two runs, and the baths were not used in the experiment. If an all zinc panel were to be plated, it would still protect sacrificially, and thereby ensuring corrosion protection. A pure zinc coating is not optimum since excessive white corrosion products can form.

Tin-zinc is much more difficult to control for alloy composition. An experiment was run using a half-fractional factorial with five factors (resolution III). The five factors were: tin+2, zinc, pH, agitation, and temperature. This experiment was run in a Multi-cell (similar to a Hull cell), so that the current density was also a variable measured. Current density has been shown to influence the alloy composition, low current density plates out lower zinc concentrations (Figure 1). This experiment was completed in June, and thorough analysis of all the data has not been completed. However, the initial trend is that the most significant factor is the current density; temperature also appears to be significant. The zinc concentration and pH do not appear to effect alloy composition. Confirmation runs need to be completed to double check these results. The next step is to determine the practical ways to control the factors to yield optimum alloy composition for corrosion resistance with every run.

Adhesion/Paint Adhesion

There have been few problems with either alloy plate acheiving adhesion on various substrates. The most common use is on low alloy steels. Substrate preparation involves: degreasing, descale/derust, alkaline clean and activation, dilute acid dip and plate. A strike in the zinc-nickel bath (60 to 90 ASF for 60 seconds initially) increases adhesion. Plating on stainless steel has also been accomplished using a nickel strike prior to plating. Both alloys have been plated onto aluminum, for experimental purposes only, following a Boeing Process Specification[5] for activation of the aluminum, and with adequate adhesion following plating.

Adhesion testing on steel[6] involves bending substrates around a mandrel equal to the thickness of the panel (essentially 180°) until fracture, then identifying any peeling or flaking as adhesion failure of the coating. Adhesion testing for aluminum is not as severe, with a 225°F bake for one hour and then noting any blistering as failures.

Both zinc-nickel and tin-zinc were also tested for adhesion of primers and topcoats to the plated surface. Electroplated panels were primed with an epoxy primer, and then tested. There was no loss of adhesion, for both chromated and non-chromated panels.

Fasteners

An important use of cadmium is on threaded hardware where its lubricating qualities allow easy installation and removal of fasteners. Although Boeing is not involved in fastener manufacturing or finishing, a great number are used in the manufacturing of airplanes, and other hardware. A replacement for cadmium on fasteners would be beneficial to the fastener manufacturers also in reducing their use of an EPA targeted material.

Zinc-nickel and tin-zinc alloys were plated onto standard nuts and bolts which had been stripped of their original cadmium finish. Next the nuts were dry lubed, this is the standard finish for cadmium plated nuts. The nut and bolt combinations were tested for: run-on torque, breakaway torque, and tension. A cadmium-cadmium combination was the control. Tests were run with the alloy-plated bolts mated with cadmium nuts, and alloy-plated bolts and nuts. All conditions except one produced desirable results as compared to cadmium in the as-plated condition. The only condition which failed was zinc-nickel on corrosion resistant steel with cadmium plated nuts (Figure 3). The run on torques and tensions were similar to cadmium for tin-zinc and zinc-nickel plated fasteners (Figures 2 and 3). Breakaway torque was also similar in the initial condition (Figures 4 through 7). Run-on torque, measured during the time the nut was screwed onto the bolt, was not to exceed 30 in-lbs, or excessive galling would occur. Breakaway torque is the torque needed to initially loosen a nut from a bolt, this should also be below 30 in-lbs. The tension is measured when the nut and bolt are mated. Ideal tension (lbs) is 60% of the ultimate tensile strength (UTS) for a particular bolt; in this case it is a 160ksi bolt = 6470 lb UTS yields 3882 lb ideal tension. If the tension is too low, the nut will not stay screwed in place, too high and it cannot be removed.

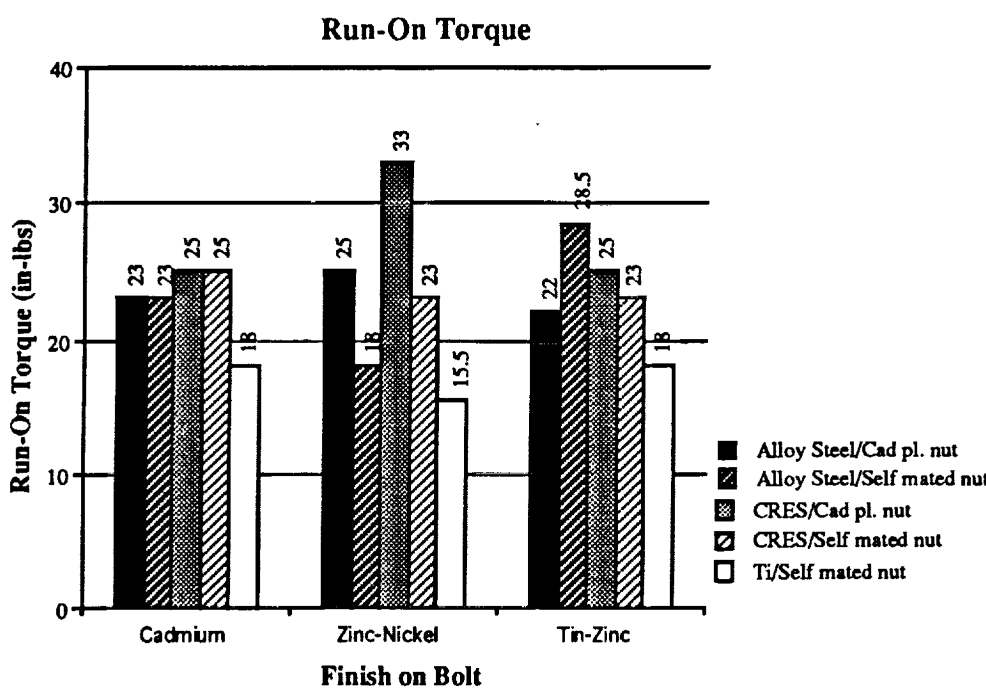

Figure 2. Run-on Torque

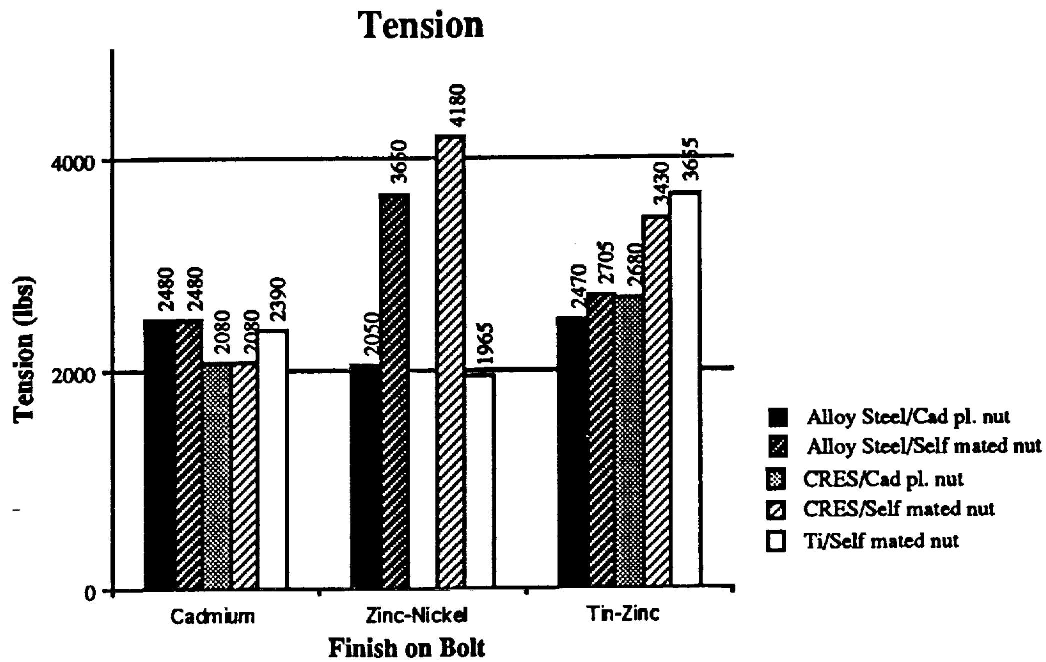

Figure 3. Tension

The nut and bolt combinations were then placed into the salt spray chamber for 500 and 1000 hours. There was not a standard test procedure for salt spray testing of fasteners, so the cadmium breakaway torque specimen was considered the control, and any large deviations from its value would be considered unacceptable. The data from 500 hours indicated tin-zinc and zinc-nickel breakaway torques were much higher than cadmium, and would probably be unacceptable for removal and reinstallation. Breakaway torque values at 1000 hours of salt spray were improved for tin-zinc, the values were similar to cadmium in every combination except alloy steel nuts and bolts (Figures 4 through 7). The alloy steel combination is the most important in terms of usage; however, since this is a small sample size further testing is necessary to confirm. Zinc-nickel nuts and bolts had high breakaway torques after 1000 hours on all combinations.

Concurrently nuts and bolts were installed on a block of bare 7075 Aluminum, then primed and painted with an epoxy primer and enamel, to see the corrosion potential in such a coupling. The cadmium and titanium controls performed the best after 1000 hours of salt spray with very little corrosion. Next, tin-zinc looked better than the zinc-nickel except for one set of CRES with tin-zinc. Zinc-nickel is not being pursued as a coating for fasteners, but more testing is being planned to determine the viability of tin-zinc on fasteners.

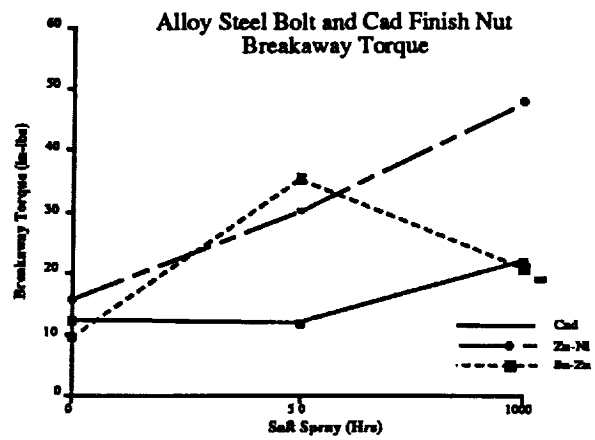

Figure 4. Breakaway Torque for Alloy Steel Bolts with Cad Plated Nuts

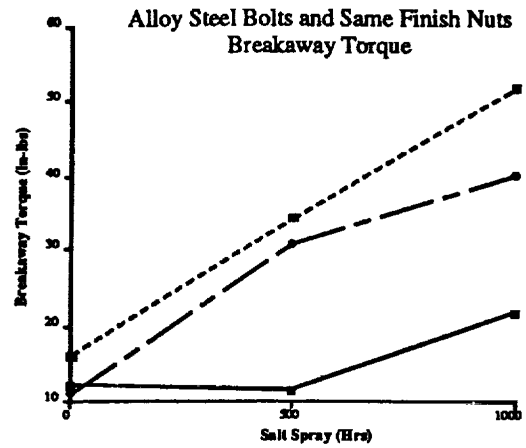

Figure 5. Breakaway Torque for Alloy Steel Bolts with Same Finish Nuts

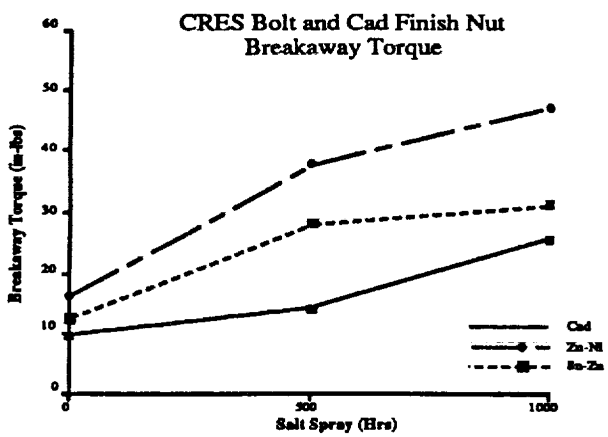

Figure 6. Breakaway Torque for Corrosion Resistant Steel Bolts with Cadmium Finish Nuts

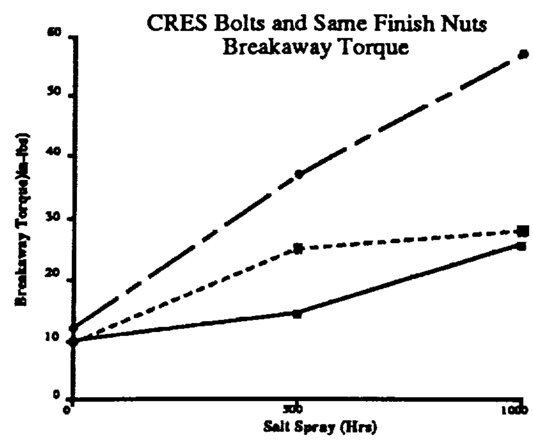

Figure 7. Breakaway Torque for Corrosion Resistant Steel Bolts with Same Finish Nuts

Hydrogen Embrittlement

Hydrogen embrittlement is a critical concern on high strength steel parts due to the possibility of catastrophic failures. Boeing currently uses a cadmium-titanium alloy plating[7] for high strength steel parts needing corrosion protection. During the development of the zinc-nickel plating process, the propensity to low hydrogen embrittlement was considered a critical criteria. Over 150 notched tensile specimens were tested per ASTM F519[8,9]. Specimens passed when they were baked for hydrogen removal[9]. A Boeing-developed system for measuring hydrogen pick-up[10] in cadmium-titanium alloy is used to reduce the time to qualify the bath from 200 hours for ASTM F519[8] testing to less than one day. This system does not work for the zinc-nickel system. The lack of a quick method for measuring hydrogen in zinc-nickel plating has hindered the implementation of zinc-nickel for high strengths steels.

Preliminary testing on tin-zinc (six notched tensile specimens) has yielded one failure. The use of this bath as a low hydrogen embrittlement alloy is possible, but many more tests are needed.

Electrical Properties

Electrical conductivity across the overlapping joints is required of "black boxes" to prevent electromagnetic interference (EMI) problems. The conducting joints are not allowed to pass high frequency currents either into or out of the electrical boxes. These boxes are often made of aluminum which is nickel plated because of nickel's good radio frequency (RF) response. Nickel is; however, not compatible with aluminum so it is typically overplated with cadmium. Tin-zinc was tested as a replacement for cadmium in this situation.

Aluminum panels (2024-T3) were tested for electrical contact resistance. The following surface preparations were used prior to tin-zinc plating: 1) anodize with electroless nickel, 2) zincate no nickel plate, 3) zincate with nickel strike and plate, 4) zincate with iron strike and nickel plate. Low electrical resistance for tin-zinc plating, in the range of 0.5 to 2.5 milliohms was measured (Figure 9). The panels were then placed in salt spray for 96 hours. There was no change in the resistivity measurements. Corrosion resistance was worst using a nickel plate and nickel strike in method 3. The best corrosion results were using the zincate/copper strike and tin-zinc plate as in method 2. Although some corrosion products formed during the salt spray, it was not considered a result of galvanic incompatibility.

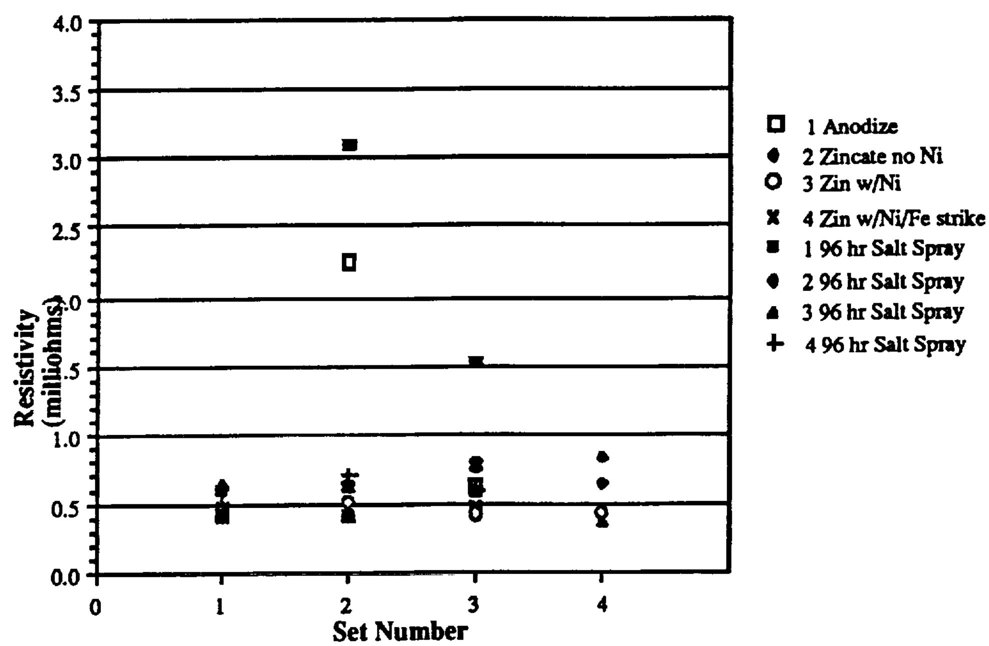

Figure 9. Resistivity Measurements

Conclusions

Zinc-nickel alloy is already in use at Boeing reducing our reliance on cadmium plate. As more production time is garnered, evidence of its superior corrosion resistance will be noted, and the question of its usefulness for high strength steels will be resolved. Tin-zinc is still in the developmental stages, but appears to be a superior coating for more lubricity type uses such as gears and possibly fasteners. Process control of the alloy composition still needs to be optimized, but the properties such as corrosion resistance, adhesion, resistivity and galvanic couplings are positive benefits of tin-zinc plating as a replacement for cadmium plating.

References

[1] National Bureau of Standards Conference, September, 1977, Washington D.C.

[2] ASTM B117 Salt Spray (Fog) Testing

[3] Tran, L.M., Phosphate Conversion Coating for Zinc-Nickel Alloy Plating, Boeing Defense & Space Group, OTDR 9-04001, March 1993, p. 7.

[4] BAC 5637, Zinc-Nickel Alloy Plating, Boeing Commercial Airplane Group.

[5] BAC 5714, Electroplating of Aluminum Alloys, Boeing Defense & Space Group.

[6] BSS7235, Adhesion Test Method, Plating,

[7] BAC 5804, Low Hydrogen Embrittlement Cadmium-Titanium Alloy Plating, Boeing Commercial Airplane Group.

[8] ASTM F519, Standard Method for Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals.

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[10] BSS 7321, Hydrogen Detection Instrument Test Method, Boeing Commercial Airplane Group.