Selection & Application of Inorganic Finishes: Anodic Coatings for Aluminum—Part II

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This space continues to review the 25-year-old "AES Update" series begun and coordinated by the late Dr. Donald Swalheim, and carried on by many others. This review is offered with the goal of going back and seeing what has gone on before. Much of it remains relevant today. Perhaps those new to the field might gain new insight, and the many veterans in the field might pick up something inadvertently forgotten. As usual, my comments and updates are shown in [].

Fred Pearlstein contributed several articles to the "AES Update" series on the selection and application of inorganic finishes. These included material on conversion, barrier, anodic and metal coatings, among others. Last month, we looked at the first part of the article on anodic coatings for aluminum, which dealt with the basics of sulfuric acid electrolytes. Here, the second part of the article is presented, emphasizing hard anodizing and electrolytes other than the sulfuric acid type. Again, the abstract reads:

"Metals are made anodic in electrolytes in which they react with oxygen ions to form an intimately bonded metal-oxide conversion coating. [This segment] explores the various anodic coatings for that most frequently anodized metal - aluminum.

Hard Anodic Coatings

"If the conventional 15-percent sulfuric anodizing electrolyte is reduced in temperature to about $-3^{\circ}C$ (27°F) and saturated with carbon dioxide, an anodic current density of about 28 A/dm² (2.8 A/ft²) (the Martin process) will form a relatively dense anodic coating considerably more abrasionand wear-resistant than conventional coatings. The proprietary Sanford process is similar but the solution contains additives claimed to be advantageous. Another proprietary process involves use of 12-percent sulfuric acid plus 1-percent oxalic acid at 10° C (50° F) and an anodic current density of about 4.0 A/dm² (37 A/ft²).

"Hard anodic coatings are usually applied at a thickness of 15 to 100 μ m (0.6 to 40 mil); 50 μ m (2 mil) is usually recommended. Typical applications include gears and pinions, valves, hinge mechanisms, cams, swivel joints, impeller blades, pistons, orthopedic braces, weapons components and rocket nozzles where advantage can be taken of the light weight of aluminum. Wear or abrasion resistance may be superior to that of hard chromium plate or case-hardened steel.¹

"Major components of the M-16 rifle are made from 7075-T6 forgings that are hard anodized. Though the coating proved to be effective in providing wear resistance under combat conditions and provided excellent corrosion resistance during atmospheric exposure, highly penetrating exfoliation corrosion resulted at regions of the rifle subjected to prolonged contact with the perspiring hands of the user. Laboratory tests showed that chromates in the hard anodic coating, from dichromate sealing, had a profound effect on preventing exfoliation corrosion, whereas water or nickel acetate sealing had little effect in retarding this catastrophic corrosion. Also, abrasive (Al₂O₃) blasting of aluminum prior to hard coating had no adverse effect on the abrasion resistance, yet markedly increased the ability for the coating to absorb chromate during 10 min of dichromate sealing at 90°C (194°F). Though dichromate sealing decreased abrasion resistance somewhat, the effect was superficial and

could be further reduced by decreasing the sealing time.

"The hard anodic coatings formed by different processes vary in their ability to absorb dyes or inhibitors but are usually much less absorptive than conventional coatings. When deep dyeing of a hard anodic coating is required, porosity can be induced by immersion in a 50-percent (vol) nitric acid at 25 to 35° C (77 to 95° F) or in other solutions that attack the anodic coating.²

"Since anodic coatings are very brittle, deformation should be avoided because cracks can form that act as stress risers to cause fracture of a normally ductile substrate. Anodic coatings also reduce the fatigue strength of wrought aluminum alloys subjected to cyclic stresses. However, such adverse effects are usually insignificant when anodic coatings of about 6 µm (0.2 mil) or less are applied. When using common thicknesses of hard anodic coatings, the potential adverse effects must be seriously considered and proper allowances made before selecting any application.

'Shot-peening of aluminum parts prior to anodizing can minimize reduction of fatigue life and susceptibility to stress corrosion cracking. Sharp edges and corners must be avoided as defective anodic coatings are likely to form there; a radius of about 8 mm is recommended for a 25-µm (1-mil) anodic coating. When close tolerances are required, it is important to take into consideration the increase in dimensions resulting from the application of a hard anodic coating. A cylinder to which a 50-µm (2-mil) hard coating is applied will increase in diameter by approximately 50 µm.

Specifications

Specifications for coating processes discussed in this article include:

- Anodic coatings on aluminum: MIL-A-8625C (Type II) "Anodic Coatings for Aluminum and Aluminum Alloys" and ASTM B-580, "Anodic Oxide Coatings on Aluminum."
- Hard anodic coatings on aluminum: MIL-A-8625C (Type III), "Anodic Coatings for Aluminum and Aluminum Alloys."
- Shot-peening of aluminum prior to anodizing: MIL-S-5002C, "Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapons Systems."
- Abrasion resistance of anodized aluminum: Federal Test Standard No. 141, Method 6192, "Abrasion Resistance (Tabor Abrader)."

Integral Color Coatings

"Proprietary electrolytes comprised of organic acids such as sulfophthalic or sulfosalicylic acid (plus some sulfuric acid) produce "integral color" anodic coatings, known by the commercial names of "Duranodic," "Kalcolor," "Reynocolor" and others.

"The lightfast colors that form during anodizing are gray, tan, gold, bronze, brown or black, depending on alloy, temper and coating thickness. These coatings are considered "hard anodic coatings," based upon abrasion-resistance measurements, yet are formed at temperatures used for normal anodizing [21°C (70°F)]; an anodic current density of about 2.8 A/dm^2 (26 A/ft²) is usually employed. The durable and decorative integral-colored coatings have been used extensively for exterior and interior architectural applications. One such example is the common bronze-brown color of store fronts. The coatings have also been used for decorative shelving, ornamental grillwork and protective screening. A coating thickness of 2.5 to 10 µm (0.1 to 0.4 mil) is commonly used for interior applications, and 10 to 25 µm (0.4 to 1.0 mil) for exterior applications. A relatively new development is the Multipurpose Anodizing Electrolyte,³ which is used at 21°C (70°F) to produce conventional decorative coatings, architectural coatings or anodic hard coatings simply by varying the applied current density and anodizing time.

Chromic Acid Electrolyte

"Chromic acid anodizing is of significant commercial interest, though not as widely used as sulfuric acid processes. [Today, however, this is one of many hexavalent chromium-based processes under environmental and health scrutiny.] The anodic coating is generally formed in 3- to 10-percent chromic acid solutions at 35°C (95°F) by raising the voltage at the rate of 5 V per minute until 40 V is reached, and then holding it at this voltage for about 30 min to form deposits of about 1.5 μ m (0.06 mil) thickness. Deposits are usually gray in color.

"The chromic acid process is highly desirable for items that have crevices, recesses or blind holes that could trap electrolyte. While entrapment of residual sulfuric acid could have deleterious or even disastrous effects on an item, chromic acid solution is harmless [in terms of etching]. Chromic acid anodizing is commonly applied to spot-welded or riveted aircraft assemblies for this reason, but also because the coating is an excellent base for paint or adhesive bonding and provides excellent corrosion resistance despite its thinness. In fact, the thinness is an advantage because there is no adverse effect on fatigue strength. and allowances need normally not be made for dimensional change. Exterior aluminum components of military aircraft subject to wear or severely corrosive conditions are anodized by the chromic or sulfuric acid processes.

"Corrosion resistance is improved and good adhesive bonding properties obtained by sealing up to 10 min in deionized water containing 10 mg/L (10 ppm) CrO_3 at about 95°C (203°F) and pH 6. For maximum corrosion resistance, a seal in 50 g/L sodium dichromate solution is used.

"Chromic acid anodizing has been used to detect cracks in critical items such as aircraft propeller blades. Any cracks in the metal will be revealed as brown lines. If no cracks are found, the coating is imply sealed and used for its protective properties. An additional specialized application for chromic acid anodic coatings, sealed in nickel acetate solution, is to act as a resist at specific areas of parts where all other areas are to be hard anodized.

Chromic acid anodizing is generally not suitable for alloys that contain more than 5-percent copper or 7-percent silicon. Another disadvantage of the process is the necessity of effectively treating waste rinse solutions for removal of toxic hexavalent chromium to meet water pollution regulations.

Other Electrolytes

"Oxalic acid electrolytes produce anodic coatings with light yellow to bronze color which are more dense and abrasion resistant than conventional anodic coatings formed at the same temperature. The process has found some application for lithographic plates, but its use has been very limited in the U.S.

"Phosphoric acid anodizing has been used as a pretreatment for obtaining adherent electrodeposits on aluminum but has been largely supplanted for this purpose by immersion deposition processes such as the zincate process. Phosphoric acid anodizing finds some current application for promoting adhesive bonding to aluminum. PerSF

References

- 1. C.F. Burrows, *The Iron Age*, **8**, 24 (1950).
- 2. A. Gallaccio & R. Wick, U.S. patent #3,140,245 (1964).
- 3. K.H. Dale, *Plating*, **59**, 84 (September 1972).

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