Shop Talk: Practical Information for Finishers

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

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As has been the case over the last several months, this space continues to review the 25-year-old “AES Update” series begun and coordinated by the late Dr. Donald Swalheim, and continued by others. The intent of revisiting these articles has been to bring to light the valuable material that may have been forgotten over the years. Perhaps those new to the field might gain new insight and the many veterans in the field might pick up something inadvertently forgotten.

In 1979, Fred Pearlstein made an enormous contribution to the “AES Update” series with seven articles on the selection and application of inorganic finishes. These included material on conversion coatings, barrier coatings, anodic coatings and metal coatings. I intend to resurrect several of these in the coming months. Read on as Mr. Pearlstein gives us a comprehensive look at the selection and application of anodic coatings for aluminum. Though many advances have been in anodizing since these words were crafted, much of it remains very valid indeed. The abstract begins:

“*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.*

“An anodic coating is characteristically a corrosion- and wear-resistant barrier between the metal substrate and the environment. The coatings may be relatively pore-free but are usually formed with a multitude of micropores. Though this porosity may seem to be a drawback, it actually provides the option of adding inhibitors, dyes, resins, polymers, waxes, oils and other materials to modify the coating for engineering or decorative purposes.

“Anodic coatings applied to aluminum alloys are of greatest commercial significance. Extremely thin, uniform and nonporous anodic coatings can be formed on aluminum and utilized for electronics applications. Such deposits have even been formed on vacuum-deposited aluminum on glass to achieve certain optical properties and some wear resistance. These so-called “barrier layers” are formed in borate or tartrate electrolytes in which the oxide is essentially insoluble. A limiting thickness is produced at a given voltage. Barrier-layer anodic coatings on tantalum have found considerable use in forming electrolytic capacitors for industry.

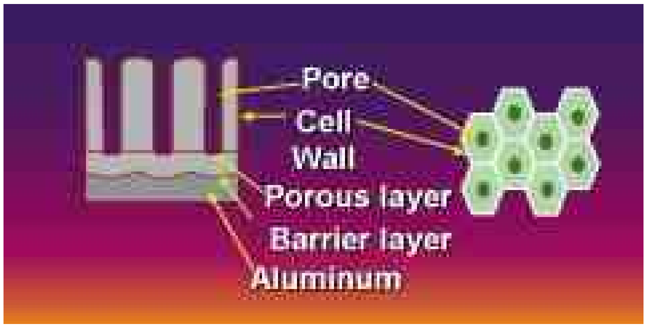

Fig. 1—Diagrammatic structure of typical unsealed anodic coating. Barrier layer thickness—less than 0.03 µm (1.2 µin.); Pore diameter—0.002 µm (0.08 µin.); Pores per cm^2 —5 x 10^{10} (in.^{2} - 3.2 x 10^{11}); Porosity —15 per cent.

“In anodizing electrolytes in which the metal oxide is appreciably soluble, oxide development does not cease with formation of a thin barrier layer; growth continues with a more or less porous structure and coating thicknesses of 20µm (0.8 mil). The porous-type coatings account for most of the commercial applications.

Sulfuric Acid Electrolytes

“Solutions comprised of 12 to 22 percent (wt) sulfuric acid are most commonly used for applying anodic coatings to aluminum; 15 percent (wt) is usually favored. Alternating current can be used, but superior anodic coating characteristics are produced using direct current at an anode current density of 1.0 to 1.8 A/dm^2 (9 to 17 A/ft^2). An electrolyte temperature of 20 to 22°C (68 to 72°F) is usually recommended, but a higher or lower temperature may be used when more porous or less porous deposits are desired.

“The anodic coating produced, diagrammatically represented by Fig. 1, consists of a nonporous barrier layer that forms initially, and a porous outer coating. It is important to recognize that the porous oxide forms from the barrier layer so that the visible exterior surface is the first formed and is longest in contact with the electrolyte. Depending upon the degree of solvent action exerted by the electrolyte on the oxide, the outer surface is increased in porosity and decreased in wear resistance; in extreme cases, a powdery outer layer may be formed.

“Anodic coatings are formed at a rate of about 0.3 µm (0.01 mil) per min in 15 percent (wt) H_2SO_4 at 21°C (70°F) at 1.3 A/dm^2 (12 A/ft^2). Workpiece dimensions are increased by about two-thirds the coating thickness; thus a metal section with a 15 µm (0.6 mil) thick anodic coating on each side increases in section thickness by about 10 µm (0.4 mil). Anodic coatings have the ability to “throw” into crevices and recesses. Cartridge cases (5.56-mm mouth diameter x 48-mm long) with a 12.5 µm (0.5 mil) thick anodic coating on the outside have an 8-µm (0.3 mil) thick coating in the interior. Considering the primer hole is only 2 mm in diameter and that racking inside the mouth partially shields current flow, the throwing power achieved is remarkable.

Bright Anodizing

“Anodic coatings can be formed with a glass-like transparency on certain alloys. Polished aluminum of alloys such as 1188, 5252, 5457, 5657 and 6463 can be provided with a protective anodic coating without adversely affecting the bright metallic appearance of the substrate. This “bright anodizing” has been applied decoratively to automotive parts, appliances, holloware, ballpen parts, drapery hardware and light reflectors. The coatings are sealed by immersion in boiling or near-boiling water of high purity (*i.e.*, very low in solids, phosphates, fluorides, silicates and chlorides) at pH 6 for approximately 15 min. It is often advantageous to add 10 to 50 mg/L (10 to 50 ppm) CrO_3 to the sealing water to counteract adverse effects of certain contaminants. Contacting the anodic coating (Al_2O_3) with hot water results in hydration ($Al_2O_3.H_2O$), accompanied by a swelling action which closes the pores to increase corrosion resistance and prevent the tendency for permanent staining from contact with colored substances. Live steam can also be used to seal anodic coatings.

Dyed Anodic Coatings

"Anodic coatings can be readily dyed to provide a great variety of attractive, decorative finishes which are both corrosion and abrasion resistant. An even greater variety of visual effects can be obtained by performing mechanical or chemical surface treatments (*e.g.*, scratch brushing, abrasive blasting or tumbling, etching) on the aluminum prior to anodizing. Beautiful multicolored effects, limited only by imagination and artistry, can be produced on a single item to form *objets d'art*, instrument panels, appliance trims, plaques, etc. The degree to which dyes can be absorbed into anodic coatings depends on the coating thickness and porosity. Coatings of 2.5 µm (0.09 mil) can be dyed with light colors, but 5 µm (0.2 mil) or more is needed for dark colors. When deep black is required, bath temperature may be increased to 27°C (81°F), anodizing time to 45 min, and thickness to 15 µm. (A new process [new in 1979] developed by Martin Marietta Aerospace is said to provide an anodic coating "as black or blacker than any substance known to man" and with potential in the solar energy field [Reference: H. E. Chandler and D. F. Baxter, Jr., *Metal Progress*, **114**, 28 (January 1978)].) In order to facilitate deep dye absorption, it is sometimes useful to immerse an anodized part in 50 percent (vol) HNO_3 at 25°C (77°F) for a minute or so before rinsing and dyeing. The same treatment can be used for decolorizing unsealed, dyed items when necessary.

Water-soluble organic dyestuffs are usually used at a concentration of one to several grams per liter at pH 5.5 to 7.0 and at about 65°C (149°F). The dyed anodic coatings have been used to produce innumerable products; the striking appearance and durability of dyed anodized aluminum tumblers, giftware, jewelry, cooking utensils, eyeglass frames, knitting needles, keys, doorknobs and plaques are familiar to everyone [and are selling at high prices on E-Bay].

Fig. 2—Dyed anodic coatings, after five years of exposure to sunlight (Kingston, Canada), illustrate lightfastness of selected dyes. Bottoms - continuously exposed; Tops - shielded from sunlight.

Most organic dyed coatings are not sufficiently lightfast for outdoor use, though some have changed little after years of exposure to sunlight (Fig. 2). Fade-resistance is improved with relatively thick (17.5 µm; 0.7 mil) anodic coatings and a proper seal. These factors should be considered if much exposure to sunlight is expected.

"Inorganic pigments provide excellent lightfastness. A process called "mineral pigmentation" has been developed for the formation and incorporation of white barium sulfate, yellow lead chromate, black cobalt sulfide, blue ferric ferrocyanide and other compounds into the anodic coating. However, the most commonly used inorganic pigment is produced by immersing the freshly anodized part in a 20 g/L (2.7 oz/gal) ferric ammonium oxalate solution at pH 5.0 and 50°C (122°F); this provides an attractive, metallic gold appearance on bright anodized aluminum. A variety of lightfast colors can also be obtained for decorative architectural applications by a proprietary process that follows anodizing and consists of electrolysis in a solution containing metal salts.

"Alloy constituents in aluminum can affect the color of anodic coatings. Aluminum-silicon alloys form sunlight-stable anodic coatings of a pleasing gray color which have found architectural applications. Alloys containing chromium form yellow-tinted anodic coatings, and those containing manganese form brownish coatings.

Sealing

"Dyed coatings are almost universally sealed by a 5- to 40-min immersion in a boiling, 5 g/L (0.7 oz/gal) nickel-acetate solution at pH 5.5 (using acetic acid) to prevent dye leaching. In some instances, a short (15 sec to 2 min) nickel acetate seal is followed by immersion in boiling water or in a 10 g/L (1.3 oz/gal) sodium dichromate solution at pH 5.5 and 90°C (194°F). The latter substantially improves corrosion resistance in marine environments; but not all dyes are compatible with dichromate, so care is advised when this process is applied.

"Anodized aluminum for military purposes in commonly sealed in 50 g/L (6.7 oz/gal) $Na_2Cr_2O_7.2H_2O$ solution at pH 5.5 near the boiling point to provide a high degree of corrosion resistance during exposure to the most adverse natural environments. A characteristic yellow-green color results from the incorporation of corrosion-inhibitive chromates into the anodic coating. Interestingly, heating dichromate-sealed anodic coatings at 200°C (392°F) does not adversely affect corrosion resistance - as is true of chromate coatings - though crazing of the anodic coating may occur.

"Anodized cartridge cases and fuze housings are often dyed for color identification, and many items are dyed black to provide a nonreflective surface. A 5-min nickel acetate seal followed by a 20-min dichromate seal provides long-term protection for highly corrodible 2024-T3 alloy during continuous marine exposure and is superior to the single dichromate seal.

"When some areas are devoid of anodic coating by design or because of a final machining operation, the bare areas are touched-up with solution to produce a chromate conversion coating.

"Anodic coatings are sometimes painted to provide optimum corrosion

Typical Applications for Anodic Coatings Of Varying Thicknesses (ASTM B 580)

Min. thickness µm	mil	**Description**	**Typical applications**
2.5	0.1	Interior - limited abrasion	Housewares, auto interior parts
5.0	0.2	Interior - moderate abrasion	Appliances, nameplates, lawn furniture
7.5	0.3	Automotive exterior	Exterior auto trim
10.0	0.4	Architectural Class II	Maintained exterior facades, windows
17.5	0.7	Architectural Class I	Unmaintained exterior facades

resistance and/or decorative effects. Good results have been obtained with relatively thin coatings, dichromate sealed, thoroughly rinsed with high-purity water, dried and promptly painted. There is some evidence that dyed coatings sealed first in nickel acetate solution and followed by a dichromate seal have superior paint base properties.

"Anodic coatings have a fairly high coefficient of friction but can be sealed to increase lubricity. Even nickel acetate sealing significantly reduces friction, but a high degree of lubricity can be obtained by sealing in oils, soap solutions, wax emulsions or Teflon dispersions. Wax sealing is also used for antistick properties on items such as ice cube trays.

Racking

"Firm, rigid contact on aluminum or titanium racks is important during anodizing. Endless-belt titanium racks have been used for economically and effectively anodizing aluminum cartridge cases for small weapons. Small items such as rivets and threaded fasteners can be anodized in bulk by tightly packing parts in a perforated titanium basket. Circulation of liquid through the parts during anodizing is essential and can be accomplished by rotating an annulus-shaped basket. Bulk anodizing is usually followed by transfer to open perforated baskets for dyeing and sealing. The use of titanium is advantageous in anodizing because it is not necessary to strip anodic coatings after each use, as with aluminum. However, titanium racks in contact with anodized aluminum parts can set up a galvanic couple that may result in pitting of aluminum at defects in the anodic coating during rinsing, dyeing or sealing in contaminated solutions. The electrical conductivity of titanium is substantially lower than that of aluminum, and this property must be taken into account. No more than about 8 A should be expected to flow through each titanium rack-tip contact, whereas 20 A can safely flow through each aluminum rack tip.

"Table 1 shows some typical applications for anodic coatings of various thicknesses." *P&SF*

Author's note: *This first installment discusses the basics of sulfuric acid electrolytes. Next month, the second part of this article will continue with hard anodizing and electrolytes other than the sulfuric acid type.*