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ALUMINUM ANODIZING

ALUMINUM ANODIZING is an electrochemical method of converting aluminum into aluminum oxide (Al_2O_3) at the surface of the item being coated. It is accomplished by making the work piece the anode while suspended in a suitable electrolytic cell. Although several metals can be anodized, including aluminum, titanium, and magnesium, only aluminum anodizing has found widespread use in industry.

Because a wide variety of coating properties can be produced through variations in the process, anodizing is used in almost every industry in which aluminum can be used. The broadest classification of types of anodize is according to the acid electrolyte used. Various acids have been used to produce anodic coatings, but the most common ones in current use are sulfuric (H_2SO_4) and chromic (CrO_3) acids. Although CrO_3 anodizing is standardized, there are two main types of H_2SO_4 anodizing. The first is a room-temperature H_2SO_4 process termed conventional anodizing. In addition to CrO_3 conventional, and hardcoat anodizing, a process known as sealing can be used to enhance certain characteristics. A number of standard tests are used in the industry to test the quality and characteristics of anodic coatings.

The three common types of anodize described above are usually controlled and described through the use of military specification MIL-A-8625 (Table 1). It has become standard in the industry to describe anodic coatings with the type and class nomenclature outlined in this specification.

The articles "Corrosion of Magnesium and Magnesium Alloys" and "Corrosion of Aluminum and Aluminum Alloys" in this Volume contain information on the corrosion resistance of anodized magnesium alloys and aluminum alloys. More information on the anodizing process for aluminum is available in the article "Cleaning and Finishing of Aluminum and Aluminum Alloys" in Volume 5 of the 9th Edition of *Metals Handbook*.

CHROMIC ANODIZE

Chromic anodize (type I; see Table 1) is formed by immersing the workpiece in an aqueous solution of CrO_3. Current is then applied, with the workpiece being positively charged. Typical operating parameters for the CrO_3 anodizing process are:

- *Electrolyte concentration: 50 to 100 g/L CrO3*
- *Temperature: 37 + 5 0C (100 + 9 0F)*
- *Time in bath: 40 to 60 min*
- *Voltage: Increase from 0 to 40 V in 10 Min; hold at 40 V for balance of time*
- *Current density: 0.15 to 0.30 A/dm2 (1.4 to 4.3 A/ft2)*

Chromic Anodized Coatings. The CrO_3 anodizing process produces a coating that is nominally 2 µm (0.08 mils) thick. It is relatively soft and susceptible to damage through abrasion or handling. The color of the class 1 coating ranges from clear to gray, depending on whether the coating is sealed and on the alloy coated. The coating can be dyed to produce a class 2 coating; however, this is not generally done, because the coating is thin and does not retain the dye color well. About two-thirds of the coating thickness penetrates the base metal; one-third of the coating builds above the original base metal dimension. Thus, for a coating thickness of 2 µm (0.08 mils) per side, the dimensional change of the workpiece would be 0.7 µm (0.028 mils) per side.

Although the industry has adopted the penetration/buildup terminology, the terms are somewhat misleading. Actually, when the aluminum is converted to Al_2O_3 it takes up more space- approximately 133% of the space previously occupied by the aluminum converted. The penetration/buildup terms are used only as a convenience in predicting dimensional change in a coated article. The corrosion resistance of this coating is very good. The coating will pass in excess of 336 h in 5% salt (NaCl) spray per ASTM B 117.

Advantages. Although CrO_3 anodizing is the least used of the three types of anodize, it has several advantages that make its use desirable. First, because CrO_3 is much less aggressive toward aluminum than H_2SO_4, it should be used whenever part design is such that rinsing is difficult. Difficult rinsing designs would include welded assemblies,

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TABLE 1 CLASSIFICATION OF ANODIZE ACCORDING TO MIL-A-8625

Type	Class	Description	Dye	Seal	Thickness µm	Thickness mils
I	1	CrO3anodize	No	Yes	1.3-2.5	0.05-0.1
I	2	CrO3anodize,dyed	Yes	Yes	1.3-2.5	0.05-0.1
II	1	H2SO4 anodize	No	Yes	7.5-15	0.3-0.6
II	2	H2SO4 anodize, dyed	Yes	Yes	7.5-15	0.3-0.6
III	1	Hardcoat anodize	No	No	46-56	1.8-2.2
III	2	Hardcoat anodize, dyed	Yes	Yes	46-56	1.8-2.2

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riveted assemblies, and porous castings. Second, a typical CrO_3 anodize buildup is 0.7 µm (0.028 mils) per side with good repeatability. Therefore, it is very good coating to use when it is necessary to coat a precise dimension to size. Third, because CrO_3 anodize produces the least reduction in fatigue strength of the three coatings, it should be used where fatigue strength is a critical factor. Fourth, the color of CrO_3 anodize will change with different alloy compositions and heat-treat conditions; this makes it useful as a test of the homogeneity of structural components. Lastly, when properly applied, CrO_3 anodize can be used as a mask for subsequent hardcoat anodize operations.

Suitable Alloys. Most alloys can be successfully coated by the CrO_3 process. Exceptions are high-silicon die-cast alloys and high-copper alloys. The rule for suitability is that any alloy containing more than 5% Cu, 7% Si, or total alloying elements of 7.5% should not be coated by this process.

Relative Costs. Chromic anodize costs more than H_2SO_4 but less than hardcoat anodize.

SULFURIC ANODIZE

Sulfuric anodize, or type II anodize, is formed by immersing the item in an aqueous solution of H_2SO_4. Current is then applied, and the workpiece is positively charged. Typical operating parameters for the H_2SO_4 anodizing process are:

- *Electrolyte concentration: 15% H2SO4*
- *Temperature: 21+ 1 oC (70 + 2 oF)*
- *Time in bath: 30 to 60 min*
- *Voltage: 15 to 22 V, depending on the alloy*
- *Current density: 1 to 2 A/dm2 (9.3 to 18.6 A/ft2)*

Sulfuric Anodized Coatings. This process produces a coating that is normally 8 µm (0.31 mils) in minimum thickness. Although harder than type I coatings, H_2SO_4 anodize may still be damaged by moderate handling or abrasion. The color of the class I coating is yellow-green because of the preferred sealing method of immersion in sodium dichromate ($Na_2Cr_2O_7$). Clear coatings can also be produced by sealing in hot water. Clear coatings should be specified by the notation "class I, clear." This coating can also be dyed to produce a class 2 coating. This type of anodize produces the most pleasing colors of the three anodizing methods. Dyed H_2SO_4 anodize coatings have deep colors with good repeatability. Like CrO_3 anodize, H_2SO_4 anodize coatings penetrate the base metal for two-thirds of their thickness and build above the original base metal dimension for one-third the total thickness. As with all types of anodize, the corrosion resistance of H_2SO_4 anodize is very good; it has an ASTM B 117 salt spray resistance of at least 336 h.

Advantages. Sulfuric anodize is the most widely used type of anodize and has many desirable benefits. First, because it has a fairly hard surface, it can be used in situations that require light-to-moderate wear resistance. Applications include lubricated sliding assemblies and items subject to handling wear, such as front panels. Second, because it is the most aesthetically pleasing type of anodize, it should be used where final appearance is important. It can be dyed almost any color and produces deep, rich shades that make the item appear to be made of a material bearing a color throughout, rather than an applied coating. Lastly, because corrosion resistance is needed and the specialized benefits of the other two anodize types are not required.

Suitable Alloys. With the exception of high-silicon die-cast alloys, all alloys can be successfully coated with H_2SO_4 anodize. Clarity and depth of color of the anodize increase with the purity of the alloy. Therefore, alloys should be chosen for maximum purity consistent with the physical requirements needed in the item.

Relative Cost. Sulfuric anodize is the least costly and most widely available type of anodize.

HARDCOAT ANODIZE

Hardcoat anodize, or type III anodize, is formed by immersing the item in an aqueous solution of H_2SO_4. Current is then applied, with the workpiece being the anode. The operation parameters for a generic hardcoat anodize process are:

- *Electrolyte concentration: 22 to 24% H2SO4*
- *Temperature: 0 + 1 oC (32 + 2 oF)*
- *Time in Bath: 20 to 120 min*
- *Voltage: constantly increased to maintain current density at 2.5 to 4.0 A/dm2 (23.2 to 27 A/ft2)*

Hardcoat Anodize Coatings. This process produces a coating that is normally 50 µm (2 mils) thick, although other thicknesses can be specified. The coating is extremely hard. It is described as file hard (equal to about 60 to 70 HRC). The color of the class I coating ranges from gray to bronze to almost black, depending on the alloy coated, the coating thickness, and the electrolyte temperature. The coating can be dyed to produce a class 2 coating. Because thick coatings are naturally very dark, only colors darker than natural are possible. Generally, this limits the dying of hardcoat to black in common processes. If a more extensive color choice is required, there are several proprietary hardcoat processes available to accomplish this.

Hardcoat penetrates the base metal for one-half of its thickness and builds above the original base metal dimension for one-half of its thickness. Thus, for a thickness of 50 µm (2 mils) per side, the dimensional change of the workpiece would be 25 µm (1mil) per side. Commercially available coating thickness tolerances are the greater of ± 5 µm or ± 10% of the total targeted thickness. The corrosion resistance of the unsealed class I coating is very good and comparable to the other types of anodize. When the hardcoat anodize is sealed, as in a class 2 coating, it becomes the most corrosion-resistant type of anodize.

Advantages. Hardcoat anodize, because its variety of desirable properties, has found widespread use in manufactured products. First, because of its extreme hardness, it is used in situations in which wear resistance is required. Applications include valve/piston assemblies, drive belt pulleys, tool holders and fixtures, and many other items requiring wear resistance.

Second, because of its excellent resistance to corrosion, hardcoat is used on aluminum components in harsh environments. Third, because hardcoat is an excellent electrical resistor, it can be used to insulate heat sinks for direct mounting of electrical or electronic equipment. Also, it is used in welding fixtures where some areas may need to be insulated from work.

Fourth, because hardcoat is a naturally porous substance, it is used in many areas in which the bonding or impregnation of other materials to aluminum is needed. This coating bonds very well with paints and adhesives. Also, it can be impregnated with Teflon (polytetrafluoroethylene or PTFE) and many dry film lubricants to impart lubricating properties to the coating.

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Lastly, because of its desirable properties and also because it produces a buildup of coating, it is widely accepted as a salvage coating to restore worn or improperly machined parts to usable dimensions. Coating thicknesses in excess of 250μm (10 mils) per side are possible on some alloys with certain proprietary hardcoat processes.

Suitable Alloys. Although almost all alloys can be coated, the 6000-series aluminum alloys produce the best hardcoat properties. As with the other anodize types, high-silicon die castings produce the lowest-quality coatings. Also, because the hardcoat process is sensitive to copper, alloys in the 2000-series should be avoided if possible. Alloys containing copper can be hardcoated, but only a relatively few commercial sources have the ability to coat these alloys with reliability.

Relative Costs. Hardcoat anodize is the most expensive type of anodize. It is generally twice the cost of H_2SO_4 anodize and 50% more than CrO_3 anodize.

SEALING OF ANODIZED COATINGS

Because all of the anodic processes produce porous Al_2O_3 coatings, it is often desirable to seal the coating to close these pores and to eliminate the path between the aluminum and the environment. Sealing involves immersing the coating in hot water: this hydrates the Al_2O_3 and causes the coating to swell in order to close the pores. Conventional sealing is generally done at a minimum temperature of 95 ^oC (200 ^oF) for not less than 15 min. There are also several proprietary nickel-base sealing agents available that are said to produce sealing at low temperature through catalytic action. Chromic and sulfuric anodizes are almost always sealed. However, because sealing softens the coating somewhat, hardcoat anodize is usually not sealed unless criteria other than hardness have the maximum importance in the finished coating.

TESTING OF ANODIZED COATINGS

There are six commonly used tests to determine the quality of anodized coatings. These are visual, corrosion resistance, wear resistance, adhesion, thickness, and coating weight. Only a brief overview will be given here; extensive instructions are available in specification MIL-A-8625.

Visual inspection often indicates the overall quality of a coating. The anodic film should be uniform in appearance and free from breaks, scratches, and powdery areas.

Corrosion resistance is most often tested by salt spray. A coated panel is suspended in a salt fog for a period of time (typically 336 h) and then examined for pits and corrosion.

Wear resistance is tested through an abrasive cycle. A test is weighed, abraded for a number of cycles, and weighed again to determine the coating weight lost through the abrasion.

Adhesion is tested by bending a coated panel around a mandrel and checking for delamination.

Thickness is commonly checked by using one of three methods. The first is by metallographic microscope. Second, thickness can be determined by measuring a dimension of the coated part, stripping the coating, and measuring again to determine dimensional change. Third, coatings can be measured using eddy-current instruments.

Coating weight is an indication of the density of the coating in relation to its thickness. Coating weight is determined by weighing a coated panel of known area, stripping the coating, reweighing the panel, and dividing the weight loss by the panel area for the indication of weight loss per unit area.

Table 2 lists standard test methods for anodize. More information on the testing of anodize is available.

STRIPPING OF ANODIZED COATINGS

Stripping a part that has been anodized always results in some loss of dimensions as compared to the original sizes of the part. This is because the aluminum that was consumed to form the coating is removed since it has now become part of the coating. Thus, while a type II coating 7.5 μm (0.3 mils) thick would result in a 2.5-μm (0.1 mil_ increase from original dimensions, stripping would decrease this by at least 7.5 μm (0.3 mils), depending on the precision of the operation.

There are three main methods of stripping, with varying degrees of controllability. Controllability is defined as the ability to remove only the anodize and not damage the aluminum base metal. The least controllable method is by immersion in warm sodium hydroxide (NaOH). This is known as caustic etching. In addition to removing anodize, this process also dissolves aluminum at a fast rate. A more controllable method is by immersion in a H_2SO_4-CrO_3, solution. These solutions are generally classified as deoxidizers. This process will also dissolve aluminum, but at a much slower rate than etching. The most controllable method is by immersing the part to be stripped in a CrO_3-H_2PO_4, solution at a minimum temperature of 95 ^oC (200 ^oF). This solution will dissolve only the coating and will not harm the aluminum.

TABLE 2
ASTM STANDARD TEST METHODS FOR ANODIZED COATINGS

Method	Standard
Coating Thickness	
Eddy Current	B 244
Metallographic	B 487
Light section microscope	B 681
Coating Weight	B 137
Sealing	
Dye stain	B 136
Acid dissolution	B 680
Impedance/admittance	B 457
Voltage breakdown	B 110
Corrosion resistance	
Salt spray	B 117
Copper-accelerated, acetic acid salt spray	B 368
Ford anodized aluminum corrosion test	B 538

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