

additives, temperature, voltage, and amperage. Several conventional anodizing processes and their resulting properties are shown in Table 1. As indicated in the table, depending on the process chosen, an anodizer can impart to the surface of the aluminum item specific properties as desired, depending on the end use. Some reasons for anodizing are outlined below:

- **Increase corrosion resistance:** Sealed anodic coatings of aluminum oxide are corrosion resistant and highly resistant to atmospheric and salt-water attack. The anodic coating protects the underlying metal by serving as a barrier to would-be corrosive agents. In order to achieve the optimum corrosion resistance, the amorphous aluminum oxide produced by anodizing is sealed by treating in slightly acidified hot water, boiling deionized water, a hot dichromate solution, or a nickel acetate solution. Sealing is discussed in a subsequent section of this article.
- **Improve decorative appearance:** All anodic coatings are lustrous and have relatively good abrasion resistance. Therefore, these coatings are used as the final finishing treatment when the natural appearance of the aluminum is desired or when a mechanically induced pattern is to be preserved. The degree of luster of anodic coatings depends on the condition of the base metal before anodizing. Dull etching decreases luster; bright etching, chemical or electrolytic brightening, and buffing increase luster, either diffuse or specular. Most of the aluminum used in architectural applications is anodized.
- **Increase abrasion resistance:** The hard anodizing processes produce coatings from 25 μm (1 mil) to more than 100 μm (4 mils) thick. These coatings, with the inherent hardness of aluminum oxide, are thick enough for use in

applications involving rotating parts where abrasion resistance is required. Although all anodic films are harder than the substrate material, the coatings produced by chromic acid and some sulfuric acid baths are too thin or too soft to meet the requirements for abrasion resistance.

- **Increase paint adhesion:** The tightly adhering anodic coating offers a chemically active surface for most paint systems. Anodic films produced in sulfuric acid baths are colorless and offer a base for subsequent clear finishing systems. Aluminum-base materials that are painted for service in severe corrosive environments are anodized before being painted. A fully sealed anodize may result in interior adhesion.
- **Improve adhesive bonding:** A thin phosphoric acid or chromic acid anodize improves bond strength and durability. Such coatings are widely employed in the airframe structure of most modern aircraft.
- **Improve lubricity:** A combination of hand polishing and/or honing the hard anodizing to a smoother surface before applying a polytetrafluoroethylene coating is a perfect combination with the hard anodizing.
- **Provide unique, decorative colors:** Colored anodic coatings are produced by different methods. Organic dyes can be absorbed in the pores of the coatings to provide a whole spectrum of colored finishes. Certain mineral pigments can be precipitated within the pores to yield a limited range of stable colors. Integral color anodizing, depending on the alloy composition, is used to provide a range of stable earth-tone colors suitable for architectural applications. Electrolytic coloring is a two-step process involving conventional anodizing followed by electrodeposition of metallic pigments in the pores of the coating to achieve a

range of stable colors useful in architecture. Coloring is discussed in a subsequent section of this article.

- **Provide electrical insulation:** Aluminum oxide is a dielectric. The breakdown voltage of the anodic film varies from a few volts to several thousand volts, depending on the alloy and on the nature and thickness of the film. The degree of seal also affects insulation properties.
- **Permit subsequent plating:** The inherent porosity of certain anodic films enhances electroplating. Usually, a phosphoric acid bath is used for anodizing prior to plating.
- **Detection of surface flaws:** A chromic acid anodizing solution can be used as an inspection medium for the detection of fine surface cracks. When a part containing a surface flaw is removed from the anodizing bath, then washed and dried quickly, chromic acid entrapped in the flaw seeps out and stains the anodized coating in the area adjacent to the flaw.
- **Increase emissivity:** Anodic films more than 0.8 μm (0.032 mil) thick increase the emissivity of the aluminum. When dyed black, the film has excellent heat absorption up to 230 °C (450 °F).
- **Permit application of photographic and lithographic emulsions:** The porosity of the anodic film offers a mechanical means of holding the emulsion.

Anodizing Processes

The three principal types of anodizing processes are chromic processes, in which the electrolyte is chromic acid; sulfuric processes, in which the electrolyte is sulfuric acid; and hard anodic processes that use sulfuric acid alone or with additives. Other processes, used less frequently

Table 2 Typical products for which anodizing is used in final finishing

Product	Size		Alloy	Finishing before anodizing	Anodizing process	Post-treatment	Service requirements or environments
	mm	in.					
Auto head lamp	215 mm diam, 30	8½ in. diam, 1¼	5557-1125	Buff, chemical brighten	Sulfuric acid(a)	Seal	Atmospheric exposure
Canopy track	760 mm T-extrusion	30-in. T-extrusion	7075	Machine	Hard	None	Resist wear, sea air
Gelatin molds	150-205 mm overall	6-8 overall	1100-O	Chemical brighten as-drawn	Sulfuric acid	Dye, seal	Food
Landing gear	205 mm diam by 1.4 m	8 in. diam by 4½ ft	7079-T6	(b)	Chromic acid	Paint	Corrosion resistance
Mullion	3.7 m by 180 mm by 100 mm(c)	12 ft by 7 by 4	6063-T6	(d)	Sulfuric acid(e)	Seal, lacquer(f)	Urban atmosphere
Name plates	Various sizes	Various sizes	3003-1114	(g)	Sulfuric acid	Dye, seal	Atmospheric exposure
Percolator shell	125 mm diam by 150	5 in. diam by 6	...	Buff, chemical brighten	Sulfuric acid	Seal	Coffee
Seaplane-hull skin	2850 by 1020	112 by 40	Clad 2014-T6	(g)	Chromic acid	None	Erosion; corrosion(h)
Seat-stanchion tube	50 mm diam by 610	2 in. diam by 24	7075-T6	Machine	Hard	None	Wear resistance
Signal-cartridge container	190 by 140 by 165	7½ by 5½ by 6½	3003-O	As drawn	Chromic acid	Prime, paint	Marine atmosphere
Tray, household	430 mm diam	17 in. diam	...	Butler	Sulfuric acid	Seal, buff	Food
Utensil covers	Up to 0.20 m ² total area	Up to 2 ft ² total area	1100	Buff, chemical brighten	Sulfuric acid(j)	Dye, seal	Steam, cooked foods(k)
Voice transmitter	50 mm diam	2 in. diam	5052-O	Burnish, alkaline etch	Sulfuric acid	Dye, seal(m)	Gas mask
Wheel pistons	Up to 5200 mm ² area	Up to 8 in. ² area	6151	Machine	Sulfuric acid(n)	Seal	Wear and corrosion(p)
Computer chip hat	160 by 160	6.2 by 6.2	6063-T6	Non-etch clean	Sulfuric acid	Deionized water seal	High dielectric, thermally conductive
Ice cream scoop	400 by 50	8 by 2	6061-T6	Light etch	Hard	Polytetrafluoroethylene seal	Food; good release

(a) Anodic coating 8 μm (0.3 mil) thick. (b) Partially machine, clean with nonetching cleaner, and remove surface oxide. (c) 5 mm (0.2 in.) thick. (d) Lined finish (180-mesh grit) on 100-mm (4-in.) face; other surfaces alkaline etched. (e) Anodized for 80 min; minimum coating thickness, 30 μm (1.2 mils). (f) Sealed for 20 to 30 min. Methacrylate lacquer, 8 μm (0.3 mil) minimum. (g) Clean with nonetching cleaner, remove surface oxide. (h) Maximum resistance required. (j) Anodic coating 5 μm (0.2 mil) thick. (k) Must not discolor during service. (m) Sealed in dichromate solution. (n) Anodized in sulfuric acid solution (30% H₂SO₄) at 21 °C (70 °F) for 70 min at 2.5 A/dm² (25 A/ft²). (p) In presence of hydraulic brake fluids

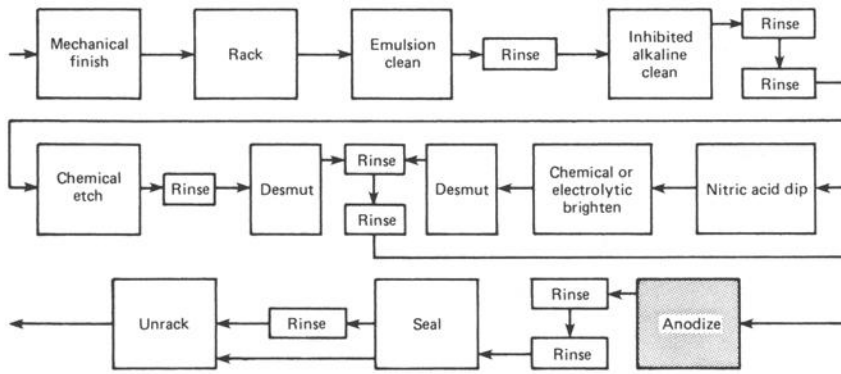


Fig. 1 Typical process sequence for anodizing operations

Table 3 Sequence of operations for chromic acid anodizing

Operation	Solution	Solution temperature		Treatment time, min
		°C	°F	
Vapor degrease	Suitable solvent
Alkaline clean	Alkaline cleaner	(a)	(a)	(a)
Rinse(b)	Water	Ambient	Ambient	1
Desmut(c)	HNO ₃ , 10-25 vol%	Ambient	Ambient	As required
Rinse(b)	Water	Ambient	Ambient	1
Anodize	CrO ₃ , 46 g/L (5¼ oz/gal)(d)	32-35	90-95	30(e)
Rinse(b)	Water	Ambient	Ambient	1
Seal(f)	Water(g)	90-100	190-210	10-15
Air dry	...	105 max(h)	225 max(h)	As required

(a) According to individual specifications. (b) Running water or spray. (c) Generally used in conjunction with alkaline-etch type of cleaning. (d) pH 0.5. (e) Approximate; time may be increased to produce maximum coating weight desired. (f) Dependent on application. (g) Water may be slightly acidulated with chromic acid, to a pH of 4 to 6. (h) Drying at elevated temperature is optional.

or for special purposes, use sulfuric acid with oxalic acid, phosphoric acid, oxalic acid, boric acid, sulfosalicylic acid, sulfophthalic acid, or tartaric acid. Except for thicker coatings produced by hard anodizing processes, most anodic coatings range in thickness from 5 to 18 µm (0.2 to 0.7 mil). Table 2 describes a few applications in which anodizing is used as a step in final finishing. The sequence of operations typically employed in anodizing from surface preparation through sealing is illustrated in Fig. 1.

Surface Preparation. A chemically clean surface (free of all grease and oil, corrosion products, and the naturally occurring aluminum oxide found

on even the cleanest-appearing aluminum) is a basic requirement for successful anodizing. The cleaning method is selected on the basis of the type of soils or contaminants that must be removed and the dimensional tolerance. Traditionally the first step employed was vapor degreasing; however, due to restrictions on ozone-depleting compounds, many of these degreasing solvents, such as trichloroethylene, are no longer in wide use. Alternatives to vapor degreasing, such as solvent wiping or alkaline soak cleaning, are now predominantly used for removing the major organic contaminants. The main function of this cleaning stage is to provide a chemically clean aluminum surface so that sub-

sequent acid pickles or caustic etches can react uniformly over the entire surface.

After cleaning, the work is etched, pickled, or otherwise deoxidized to remove surface oxides. When specular surfaces are required, the work is treated in a brightening solution. After etching or brightening, desmutting usually is required for the removal of heavy metal deposits resulting from the preceding operations.

In order to treat precision-machined aluminum components, anodize pretreatment procedures that require neither etching nor pickling have been developed and are now widely employed.

Chromic Acid Process. The sequence of operations used in this process depends on the type of part, the alloy to be anodized, and the principal objective for anodizing. Due to the corrosive nature of sulfuric acid, chromic acid anodizing is the preferred process on components such as riveted or welded assemblies where it is difficult or impossible to remove all of the anodizing solution. This process yields a yellow to dark-olive finish, depending on the anodic film thickness. Color is gray on high-copper alloys. Table 3 gives a typical sequence of operations that meets the requirements of military specification MIL-A-8625.

Chromic acid anodizing solutions contain from 3 to 10 wt% CrO₃. A solution is made up by filling the tank about half full of water, dissolving the acid in water, and then adding water to adjust to the desired operating level.

A chromic acid anodizing solution should not be used unless:

- pH is between 0.5 and 1.0.
- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The concentration of sulfates (as sulfuric acid) is less than 0.05%.
- The total chromic acid content, as determined by pH and Baumé readings, is less than 10%. When this percentage is exceeded, part of the bath is withdrawn and is replaced with fresh solution.

Figure 2 shows the amount of chromic acid that is required for reducing the pH from the observed value to an operating value of 0.5.

When anodizing is started, the voltage is controlled so that it will increase from 0 to 40 V

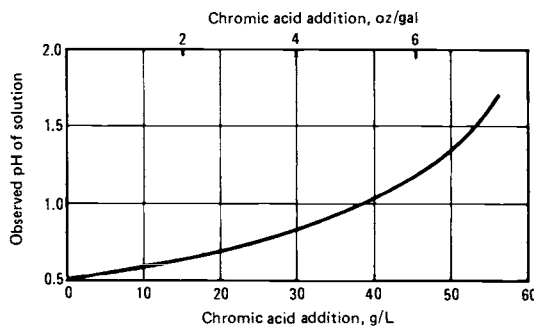


Fig. 2 Control of pH of chromic acid anodizing solutions. The graph shows the amount of chromic acid required to reduce pH to 0.5 from observed pH.

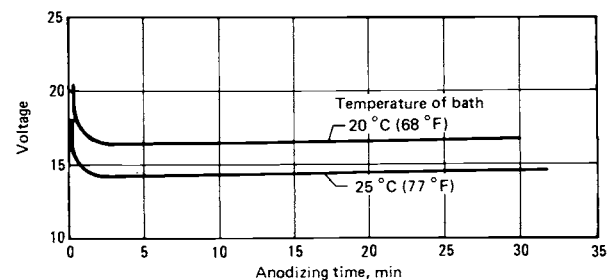


Fig. 3 Voltages required during sulfuric acid anodizing. To maintain a current density of 1.2 A/dm² (12 A/ft²), a bath temperature of between 20 and 25 °C (68 and 77 °F) must be maintained.

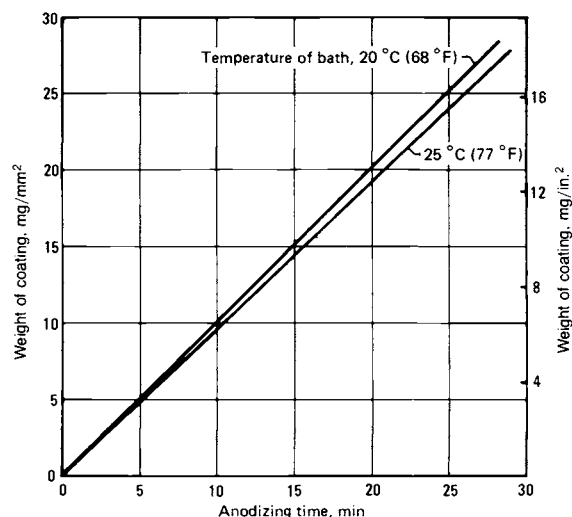


Fig. 4 Effect of anodizing time on weight of anodic coating. Data were derived from aluminum-alloy automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F) and at 1.2 A/dm² (12 A/ft²).

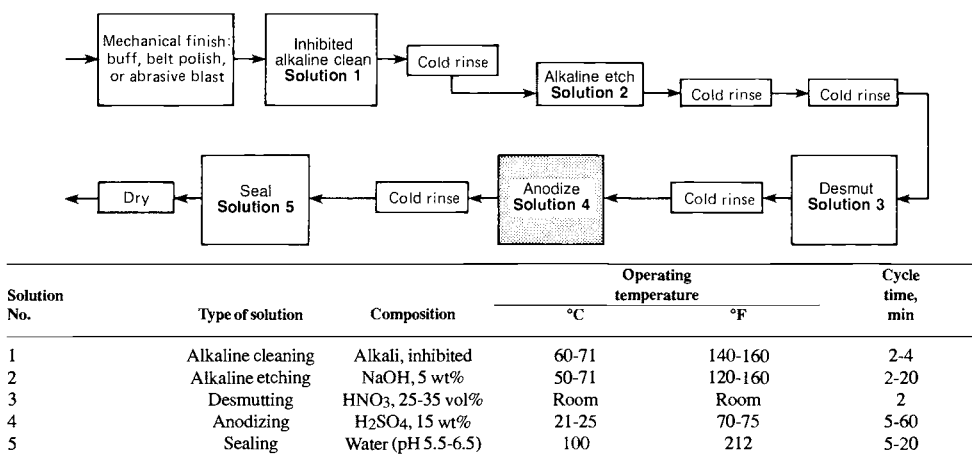


Fig. 5 Operations sequence in sulfuric acid anodizing of architectural parts

within 5 to 8 min. The voltage is regulated to produce a current density of not less than 0.1 A/dm² (1.0 A/ft²), and anodizing is continued for the required time, generally 30 to 40 min. Certain alloys, typically those in the 7xxx series, such as 7075, fail to develop a coating at 40 V, but running the process at 22 V produces acceptable results. Casting alloys should also be processed at 22 ± 2 V, as specified in military specification MIL-A-8625, type 18. Because of the porous structure of the casting alloys, processing them at higher voltages can cause excessive current densities that can be extremely damaging to the components. When the 22 V process is employed, times should be lengthened to 40 to 60 min. At the end of the cycle the current is gradually reduced to zero, and the parts are removed from the bath within 15 s, rinsed, and sealed.

According to MIL-A-8625, revision F, the coating weight should be checked prior to sealing, and depending on the type of alloy, the minimum coating weight should be 200 mg/ft². Measuring coating weight prior to sealing will allow

the parts to be put back in the chromic anodizing tank so that anodizing can continue, if needed, and subsequent stripping can be avoided.

Sulfuric Acid Process. The basic operations for the sulfuric acid process are the same as for the chromic acid process. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodized in the sulfuric acid bath. The concentration of sulfuric acid (1.84 sp gr) in the anodizing solution is 12 to 20 wt%. A solution containing 36 L (9.5 gal) of H₂SO₄ per 380 L (100 gal) of solution is capable of producing an anodic coating that when sealed meets the requirements of MIL-A-8625.

A sulfuric acid anodizing solution should not be used unless:

- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The aluminum concentration is less than 20 g/L (2.7 oz/gal), or less than 15 g/L (2 oz/gal) for dyed work.

- The sulfuric acid content is between 165 and 200 g/L (22 to 27 oz/gal).

At the start of the anodizing operation, the voltage is adjusted to produce a current density of 0.9 to 1.5 A/dm² (9 to 15 A/ft²). Figure 3 shows the voltage required to anodize at two different temperatures with current density of 1.2 A/dm² (12 A/ft²). The voltage will increase slightly as the aluminum content of the bath increases. The approximate voltages required for anodizing various wrought and cast aluminum alloys in a sulfuric acid bath at 1.2 A/dm² (12 A/ft²) are:

Alloy	Volts
Wrought alloys	
1100	15.0
2011	20.0
2014	21.0
2017	21.0
2024	21.0
2117	16.5
3003	16.0
3004	15.0
5005	15.0
5050	15.0
5052	14.5
5056	16.0
5357	15.0
6053	15.5
6061	15.0
6063	15.0
6151	15.0
7075	16.0
Casting alloys	
413.0	26.0
443.0	18.0
242.0	13.0
295.0	21.0
514.0(a)	10.0
518.0(a)	10.0
319.0	23.0
355.0	17.0
356.0	19.0
380.0	23.0

(a) Current density, 0.9 A/dm² (9 A/ft²)

When a current density of 1.2 A/dm² (12 A/ft²) is attained, the anodizing process is continued until the specified weight of coating is produced, after which the flow of current is stopped and the parts are withdrawn immediately from the solution and rinsed. Figure 4 shows the effect of time on the weight of the coating developed on automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F), operated at a current density of 1.2 A/dm² (12 A/ft²).

A flow chart and a table of operating conditions for operations typically used in anodizing architectural parts by the sulfuric acid process are presented in Fig. 5; similar information, for the anodizing of automotive bright trim, is given in Fig. 6.

Hard Anodizing. The primary differences between the sulfuric acid and hard anodizing processes are the operating temperature, the use of addition agents, and the voltage and current density at which anodizing is accomplished. Hard anodizing, also referred to as hardcoat or type III anodiz-

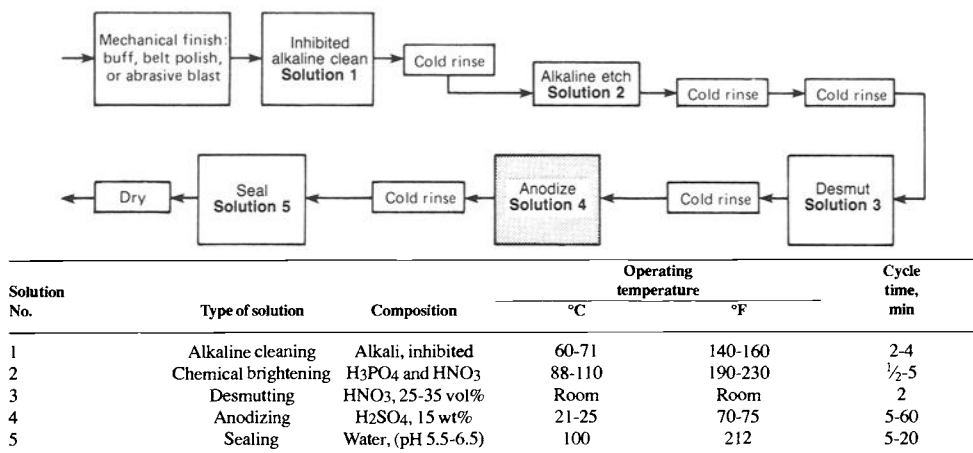


Fig. 6 Operations sequence in sulfuric acid anodizing of automotive bright trim

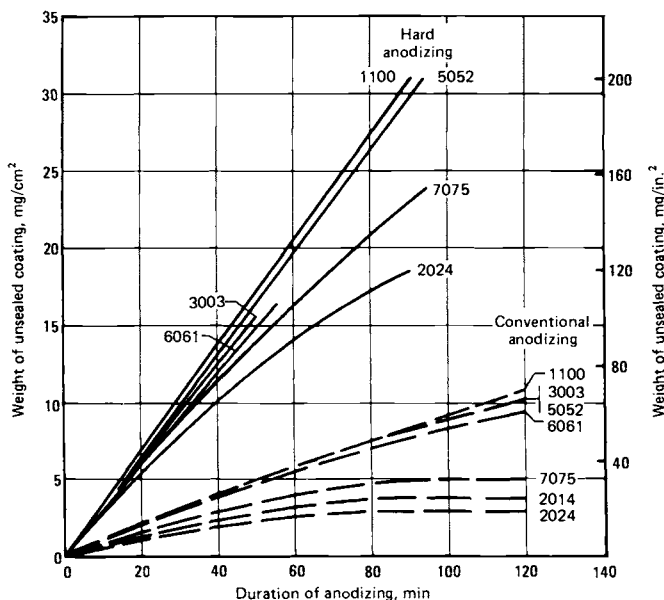


Fig. 7 Effect of anodizing time on weight of hard and conventional anodic coatings. The hard anodizing solution contained (by weight) 12% H₂SO₄ and 1% H₂C₂O₄ and was operated at 10 °C (50 °F) and 3.6 A/dm² (36 A/ft²). The conventional anodizing solution contained 1% (by weight) H₂SO₄ and was operated at 20 °C (70 °F) and 1.2 A/dm² (12 A/ft²).

ing, produces a considerably heavier coating than conventional sulfuric acid anodizing in a given length of time. Coating weights obtained as a function of time are compared for the two processes in Fig. 7.

The hard anodizing process uses a sulfuric acid bath containing 10 to 20 wt% acid, with or without additives. Typical operating temperatures of the bath range from 0 to 10 °C (32 to 50 °F), and current density ranges between 2 and 3.6 A/dm² (20 and 36 A/ft²). With the use of particular additives and modified power, hard anodizing processes can operate at temperatures in excess of room temperature. However, some hard anodizing processes operated at high temperature may result in the formation of soft and more porous outer layers of the anodic coating. This change in coating characteristics reduces wear resistance significantly and tends to limit coating thickness. Without use of specific additives and/or modified power, such as superimposed alternating current over direct current or pulsed current, excessive operating temperatures result in dissolution of coating and can burn and damage the work.

Proprietary processes are commonly used. One of the more common of these processes uses a solution containing 120 to 160 g (16 to 21 oz) of sulfuric acid and 12 to 20 g (1.6 to 2.8 oz) of oxalic acid (H₂C₂O₄) per 3.8 L (1 gal) of water. This solution is operated at 10 ± 1 °C (50 ± 2 °F) and a current density of 2.5 to 3.6 A/dm² (25 to 36 A/ft²) (voltage is increased gradually from zero to between 40 and 60 V); treatment time is 25 min/25 μm (1 mil) of coating thickness. Additional proprietary processes for hard anodizing are listed in Table 4.

A recent development in hard anodizing uses an intermittent pulse current that reduces tank time and makes it possible to use a 20 vol% sulfuric acid solution as the electrolyte.

Special Anodizing Processes. Table 5 gives the operating conditions for anodizing baths that are used to produce an anodic coating with a hardness and porosity suitable for electroplating, or to produce anodic coatings of hardness or thickness intermediate to those obtainable from chromic acid, sulfuric acid, and hard anodizing baths.

Table 4 Process and conditions for hard anodizing

Process	Bath	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance	Remarks
		°C	°F			A/dm ²	A/ft ²	μm	mils		
Martin Hard Coat (MHC)	15 wt% sulfuric acid, 85 wt% water	-4 to 0	25-32	45(b)	20-75	2.7	29	50	2	Light to dark gray or bronze	Very hard, wear resistant
Alumilite 225 and 226	12 wt% sulfuric acid, 1 wt% oxalic acid, water	10	50	20, 40	10-75	2.8(b)	30(b)	25, 50	1, 2	Light to dark gray or bronze	Very hard, wear resistant, allows a higher operating temperature over MHC
Alcanodox	Oxalic acid in water	2-20	36-68	(a)	(a)	(a)	(a)	20-35	0.8-1.4	Golden to bronze	...
Hardas	6 wt% oxalic water, 94 wt% water	4	39	(a)	60 dc plus ac override	2.0	22	Light yellow to brown	...
Sanford	Sulfuric acid with organic additive	0-15	32-58	(a)	15-150 dc	1.2-1.5	13-16	Light to dark gray or bronze	...
Kalcolor	7-15 wt% sulfosalicylic acid, 0.3-4 wt% sulfuric acid, water	18-24	64-75	1.5-4	16-43	15-35	0.6-1.4	Light yellow to brown to black	A self-coloring process, colors are dependent on alloy chosen, the colors produced are light fast
Lasser	0.75 wt% oxalic acid, 99.25 wt% water	1-7	35-44	to 20	From 50-500 rising ramp	Voltage controlled	Voltage controlled	700	28	Colorless	Hard, thick coatings produced with special cooling processes

(a) Proprietary information available to licensees only. Also, the entire Toro process is proprietary information available to licensees only. (b) Changes from 9th edition, *Metals Handbook*

Table 5 Compositions and operating conditions of solutions for special anodizing processes

Type of solution	Composition	Current density		Temperature		Treatment time, min	Use of solution
		A/dm ²	A/ft ²	°C	°F		
Sulfuric-oxalic	15-20 wt% H ₂ SO ₄ and 5 wt% H ₂ C ₂ O ₄	1.2	12	29-35	85-95	30	Thicker coating(a)
Phosphoric	20-60 vol% H ₃ PO ₄	0.3-1.2(b)	3-12(b)	27-35	80-95	5-15	Preparation for plating
Phosphoric, Boeing process	10-12 wt%	0.5-0.8(c)	5-8(c)	21-24	70-75	20-25	Adhesive bonding preparation
Oxalic	3 wt% H ₂ C ₂ O ₄	1.2	12	22-30	72-86	15-60(d)	Harder coating(e)

(a) Coating is intermediate in thickness between the coating produced by sulfuric acid anodizing and the coating produced by hard anodizing. (b) Potential, 5 to 30 V. (c) Potential, 10 to 15 V. (d) Depends on coating thickness desired. (e) Hardness greater than by other processes except hard anodizing

Process Limitations

Composition of the aluminum alloy, surface finish, prior processing, temper or heat treatment, and the use of inserts influence the quality of anodic coatings. The limitations imposed by each of these variables on the various anodizing processes are described below.

Alloy Composition. The chromic acid process should not be used to anodize aluminum casting alloys containing more than 5% Cu or more than 7.5% total alloying elements, because excessive pitting, commonly referred to as burning, may result. The sulfuric acid process can be used for any of the commercially available alloys, whereas the hard anodizing process is usually limited to alloys containing less than 5% Cu and 7% Si. Choice of alloys is important when maximum corrosion and/or abrasion resistance is required. Alloys such as 6061 are superior to the copper and copper-magnesium alloys in their ability to produce a hard, corrosion-resistant coating.

A recent development permitting hard anodizing of any aluminum alloy, including such newly released alloys as aluminum-lithium alloys, is ion vapor deposition of a thin layer of pure aluminum over the difficult alloy followed by subsequent anodizing. The newly deposited aluminum is entirely incorporated into the anodic layer without interference of troublesome alloying elements. This method is also useful in repairing expensive aluminum components undersized as a result of overcleaning or overetching.

Two or more different alloys can be anodizing at the same time in the same bath if the anodizing voltage requirements are identical. However, simultaneous anodizing of two different alloys is not normally recommended. This condition is more difficult for the sulfuric acid process than for the chromic acid process.

Surface Finish. Anodic films accentuate any irregularities present in the original surface. However, surface irregularities are emphasized more by the chromic acid bath than by the sulfuric acid bath. Additionally, the sulfuric acid anodizing process should be used instead of the chromic acid process where optimum corrosion- and/or abrasion-resistant surfaces are required. Clad sheet should be handled with care to prevent mechanical abrasion or exposure of the core material. Anodizing magnifies scratches, and if the core material is

exposed, it will anodize with a color different from that of the cladding.

Anodizing grade must be specified for extruded products so that mill operations are controlled to minimize longitudinal die marks and other surface blemishes. Surface irregularities must be removed from forgings, and the surfaces of the forgings must be cleaned by a process that removes trapped and burned-in die lubricants. Special attention is required when polishing the flash line if this area is to appear similar to other areas of the forging after anodizing.

Castings can be anodized provided their composition is within the process limits described under alloy composition. From the standpoint of uniform appearance, however, anodizing usually is undesirable for castings because of their nonuniform surface composition and their porosity.

The cosmetic concerns surrounding anodizing of castings, especially dyed anodic processes, can be overcome by vacuum impregnation of the casting. Using this process, exposed casting porosity is filled with an impregnant such as a thermosetting epoxy polyester. In sealing this porosity, the corrosion resistance of the anodized casting is also improved. Improved results may also be obtained by soaking castings in boiling water after cleaning and before anodizing. This treatment, however, merely attempts to fill surface voids with water, so that voids do not entrap anodizing solution.

Usually, permanent mold castings have the best appearance after anodizing, then die castings, and finally sand castings. Permanent mold castings should be specified if an anodic coating of uniform appearance is required. Anodizing usually reveals the metal flow lines inherent in the die-casting process, and this condition is objectionable if uniform appearance is desired. In general, solution heat treatment prior to anodizing is beneficial for producing the most uniform and bright anodized finish obtainable on castings.

To facilitate better cleaning of a casting prior to anodizing, aggressive cleaning with fluorides (in the case of castings high in silicon) can be accomplished prior to final machining. Following aggressive cleaning, the part is returned to the customer for final machining and returned to the finisher for anodizing. However, if close machining tolerances are involved, removal of metal with aggressive cleaning may not be permissible.

Regardless of the product form, rough finishing should be avoided when maximum corrosion resistance or uniformity of appearance of the anodic coating is desired. Rough surfaces, such as those produced by sawing, sand blasting, and shearing, are difficult to anodize and should be strongly etched prior to anodizing to ensure even minimal results. The machined areas of castings or forgings may have an appearance different from that of the unmachined surfaces.

Prior Processing. Because of their effect on surface finish, welding, brazing, and soldering affect the appearance of the anodic coating, for the reasons discussed above. In addition, the compositions of solders usually are not suited to anodizing. Spot, ultrasonic pressure, or other types of welding processes where there is no introduction of foreign metal, fluxes, or other contaminants do not affect the appearance of the anodic coating. However, the sulfuric acid anodizing process should not be used for coating spot-welded assemblies or other parts that cannot be rinsed to remove the electrolyte from lap joints.

Temper or Heat Treatment. Identification of not only the alloy that is being used but also the temper to which the alloy has been heat treated is extremely important. For alloy 2024, for example, the voltage required to produce a given film thickness can vary by 25%, depending on whether the T-3 treatment or T-4 treatment was used. Failure to recognize the difference in heat treatment can be catastrophic, most notably in hard anodizing.

Differences in temper of non-heat-treatable alloys have no marked effect on the uniform appearance of the anodic coating. The microstructural location of the alloying elements in heat-treatable alloys affects the appearance of anodic coatings. Alloying elements in solution have little effect, but the effect is greater when the elements are precipitated from solid solution. The annealed condition should be avoided when maximum clarity of the anodic film is desired.

Inserts or attachments made of metals other than aluminum must be masked off, both electrically and chemically, to prevent burning and corrosion in surrounding areas. The masking must completely seal the faying surface between the insert and parent metal, to prevent adsorption of solution, which may result in corrosion and staining. Therefore, it is desirable to install inserts after anodizing.

Anodizing Equipment and Process Control

Chromic Acid Anodizing. Low-carbon steel tanks are satisfactory for chromic acid baths. It is common practice to line up to half of the tank with an insulating material, such as glass, to limit the cathode area with respect to the expected anode area (a 1-to-1 ratio is normal). The cathode area need only be 5% of the maximum anode area. In nonconducting tanks, suitable cathode area is provided by the immersion of individual lead cathodes; however, these require the installation of additional busbars to the tanks for suspension of individual

cathodes. Provision must be made for heating the anodizing solution to 32 to 35 °C (90 to 95 °F); electric or steam immersion heaters are satisfactory for this purpose. Electric heaters are preferred, because they are easy to operate and do not contaminate the bath.

The anodizing process generates heat; therefore, agitation is required to prevent overheating of the bath and especially of the electrolyte immediately adjacent to the aluminum parts being anodized. Exhaust facilities must be adequate to trap the effluent fumes of chromic acid and steam.

Sulfuric Acid Anodizing. Tanks for sulfuric acid anodizing may be made of low-carbon steel lined throughout with plasticized polyvinyl chloride and coated on the outside with corrosion-resistant synthetic-rubber paint. Other suitable materials for tank linings are lead, rubber, and acid-proof brick. Tanks made of special sulfuric acid-resistant stainless steel containing copper and molybdenum, or made entirely of an organic material, may be used. As with chromic acid anodizing, individual lead cathodes or lead-lined tanks may be used for sulfuric acid anodizing. Alternatively, aluminum cathodes have been used, resulting in energy savings because they have higher conductivity than lead. The fact that lead effluent results from lead cathodes is another reason to prefer aluminum cathodes.

The tank should have controls for maintaining temperatures at between 20 to 30 °C (68 to 85 °F). Requirements for agitation and ventilation are the same as for chromic acid solutions. The surface of the floor under the tank should be acid resistant. The bottom of the tank should be about 150 mm (6 in.) above the floor on acid-resistant and moisture-repellent supports.

A separate heat exchanger and acid make-up tank should be provided for sulfuric acid anodizing installations. Tanks have been made of lead-lined steel. Lead may be preferred over plastic for the lining because lead withstands the heat generated when sulfuric acid is added. Polyvinyl chloride pipes are recommended for air agitation of the solution and for the acid-return lines between the two tanks. Cooling coils have also been made of chemical lead or antimonial lead pipe.

Hard Anodizing. Most of the hard anodizing formulations are variations of the sulfuric acid bath. The requirements for hard anodizing tanks are substantially the same as those for sulfuric acid anodizing tanks, except that cooling, rather than heating, maintains the operating temperature at 0 to 10 °C (32 to 50 °F).

Temperature-control equipment for all anodizing processes must regulate the overall operating temperature of the bath and maintain the proper temperature of the interface of the work surface and electrolyte. The operating temperature for most anodizing baths is controlled within ± 1 °C (± 2 °F). This degree of control makes it necessary for the temperature-sensing mechanism and heat lag of the heating units to be balanced.

When electric immersion heaters are used, it is common practice to have high and low heat selection so that the bath can be heated rapidly to the operating temperature and then controlled more

accurately on the low heat setting. Standard thermostat thermostats are used for sensing the temperature within the bath and activating the heating elements.

In steam-heated systems, it is advantageous to have a throttling valve to prevent overheating. An intermediate heat exchanger is used in some installations to prevent contamination of the electrolyte and the steam system by a broken steam line within the anodizing bath.

Agitation may be accomplished by stirring with electrically driven impellers, by recirculation through externally located pumps, or by air. In some installations, the anode busbars are oscillated horizontally, thus imparting a stirring action to the work.

The two primary requirements of an agitation system are that it is adequate and that it does not introduce foreign materials into the solution. With air agitation, filters must be used in the line to keep oil and dirt out of the solution. In the case of hard anodizing, attention to proper agitation is critical to correct processing. Agitation that is not uniform or not adequate will be instrumental in burning.

Power requirements for the principal anodiz-

Process	Voltage	Current density	
		A/dm ²	A/ft ²
Chromic	42	0.1-0.3	1-3
Sulfuric	24	0.6-2.4	6-24
Hard	100	2.5-3.6(a)	25-36(a)

(a) Alloys prone to burning (i.e., high-copper alloys) may demand lower current density (down to 2 A/dm², or 20 A/ft²) rather than the lower limit of 2.5 A/dm² (25 A/ft²).

ing processes are as follows:

Direct current is required for all processes. Some hard anodizing procedures also require a superimposed alternating current or a pulsed current. At present, most power sources for anodizing use selenium or silicon rectifiers. Compared to motor generators, the selenium rectifiers have greater reliability, are lower in initial cost and maintenance cost, and have satisfactory service life.

Voltage drop between the rectifier and the work must be held to a minimum. This is accomplished by using adequate busbars or power-transmission cables. Automatic equipment to program the current during the entire cycle is preferred. Manual controls can be used, but they necessitate frequent adjustments of voltage. The presence of a recording voltmeter in the circuit ensures that the time-voltage program specified for the particular installation is being adhered to by operating personnel. Current-recording devices also are advantageous.

Masking. When selective anodizing is required, masking is necessary for areas to be kept free of the anodic coating. Masking during anodizing may also be required for postanodizing operations such as welding, for making an electrical connection to the base metal, or for producing multicolor effects with dye coloring techniques.

Masking materials are usually pressure-sensitive tapes, stop-off lacquers, or plastic or rubber

plugs. Various tape materials, including polyvinyl chloride, Mylar, or Kapton, may be used. One type of tape may adhere better or be easier to remove after anodizing than another. For instance, while more expensive than other tapes, tapes with silicone adhesive hold up best during chromic acid anodizing, generally considered by anodizers to be the toughest anodize process to mask for. Metallic aluminum foil tape may also be used.

Stop-off lacquers provide satisfactory masking, but they are labor-intensive to apply and thus costly. Secondly, they are difficult to remove, often requiring the use of organic thinners or solvents. Rubber plugs, such as tapered laboratory stoppers, are effective for masking holes. They are widely available in various configurations and are known to anodizers by such names as "pull plugs," "dunce caps," and "mouse tails." In addition, where volumes and lead times are warranted, customized plugs may be molded from plastisol (unplasticized polyvinyl chloride) or another acid-resistant material.

Lastly, anodize itself may be used as a maskant. For example, on a precision-machined aluminum aerospace component requiring one small area to be abrasion resistant, the part might be chromic acid anodized all over, then machined in the area required to be abrasion resistant and subsequently hard anodized. The key to such an approach is to seal the initially applied chromic anodize. In such cases, nickel acetate sealing is highly preferable. Care must also be exercised by the machinist not to damage the chromic anodize layer in areas where hard anodize is undesirable.

Racks for Anodizing

Anodizing racks or fixtures should be designed for efficiency in loading and unloading of workpieces. Important features that must be included in every properly designed rack are:

- **Current-carrying capacity:** The rack must be large enough to carry the correct amount of current to each part attached to the rack. If the spline of the rack is too slender for the number of parts that are attached to the rack, the anodic coating will be of inadequate thickness, or it will be burned or soft as the result of overheating.
- **Positioning of parts:** The rack should enable proper positioning of the parts to permit good drainage, minimum gassing effects and air entrapment, and good current distribution.
- **Service life:** The rack must have adequate strength, and sufficient resistance to corrosion and heat, to withstand the environment of each phase of the anodizing cycle.

The use of bolt and screw contacts, rather than spring or tension contacts, is a feature of racks designed for anodizing with the integral color processes. These processes require high current densities and accurate positioning of workpieces in the tank. Bolted contacts are used also on racks for conventional hard anodizing. However, bolt-

ing requires more loading and unloading time than tension contacts.

Materials for Racks. Aluminum and commercially pure titanium are the materials most commonly used for anodizing racks. Aluminum alloys used for racks should contain not more than 5% Cu and 7% Si. Alloys such as 3003, 2024, and 6061 are satisfactory. Contacts must be of aluminum or titanium. Racks made of aluminum have the disadvantage of being anodized with the parts. The anodic coating must be removed from the rack, or at least from contacts, before the rack can be reused. A 5% solution of sodium hydroxide at 38 to 65 °C (100 to 150 °F), or an aqueous solution of chromic and phosphoric acids (40 g or 5 $\frac{1}{3}$ oz CrO₃ and 40 mL or 5 $\frac{1}{3}$ fluid oz of H₃PO₄ per liter or per gallon of water) at 77 to 88 °C (170 to 190 °F) can be used to strip the film from the rack. The chromic-phosphoric acid solution does not continue to attack the aluminum rack after the anodic film is removed.

Caustic etching prior to anodizing attacks aluminum spring or tension contacts, causing a gradual decrease in their strength for holding the parts securely. This condition, coupled with vibration in the anodizing tank, especially from agitation, results in movement and burning of workpieces.

On many racks, aluminum is used for splines, crosspieces, and other large members, and titanium is used for the contact tips. The tips may be replaceable or nonreplaceable. Although replaceable titanium tips offer versatility in racking, the aluminum portions of the rack must be protected with an insulating coating. However, if the anodizing electrolyte penetrates the coating, the aluminum portion of the rack may become anodized and thus become electrically insulated from the replaceable titanium contact. A more satisfactory rack design uses nonreplaceable titanium contacts on aluminum splines that are coated with a protective coating. Titanium contacts that are welded to replaceable titanium crossbars offer a solution to many racking problems created by the variety of parts to be anodized. These crossbar members can be rapidly connected to the spline.

Titanium should not be used in solutions containing hydrofluoric acid or any solution bearing any fluoride species. Titanium has the disadvantage that it has less than half the current-carrying capacity of aluminum, which can handle 650 A per square inch of cross-sectional area. However, recent rack designs employing cores of titanium-clad copper have offset this disadvantage.

Plastisol is used as a protective coating for anodizing racks. This material has good resistance to chemical attack by the solutions in the normal anodizing cycle; however, it should not be used continuously in a vapor degreasing operation or in chemical bright dip solutions. Furthermore, if the coating becomes loose and entraps processing solution, the solution may bleed out and drip on the workpieces, causing staining or spotting. Entrapment of bright dip solution containing phosphates can be a "silent killer" of sealing solutions. Phosphates in very small quantities that are subsequently released in the seal bath will prevent sealing from occurring.

Bulk Processing. Small parts that are difficult to rack are bulk anodized in perforated cylindrical containers made of fiber, plastic, or titanium. Each container has a stationary bottom, a threaded spindle centrally traversing its entire length, and a removable top that fits on the spindle to hold the parts in firm contact with each other. While bulk processing is more economical in that parts do not have to be individually racked, the drawbacks are that it results in random unanodized contact marks on the exterior of the part, and that it is usable only on parts without flat sections or blind holes. It is usually used on relatively small parts.

Anodizing Problems

Causes and the means adopted for correction of several specific problems in anodizing aluminum are detailed in the following examples.

Example 1. Anodic coatings were dark and blotchy on 80 to 85% of a production run of construction workers' helmets made of alloy 2024. After drawing, these helmets had been heat treated in stacks, water quenched, artificially aged, alkaline etched with sodium hydroxide solution, anodized in sulfuric acid solution, sealed, and dried. The dark areas centered at the crowns of the helmets and radiated outward in an irregular pattern. Examination disclosed the presence of precipitated constituents and lower hardness in the dark areas. The condition proved to be the result of restricted circulation of the quench water when the helmets were stacked, which permitted precipitation of constituents because of a slower cooling rate in the affected areas. The problem was solved by separating the helmets with at least 75 mm (3 in.) of space during heating and quenching.

Example 2. Pieces of interior trim made from alloy 5005 sheet varied in color from light to dark gray after anodizing. Rejection was excessive, because color matching was required. Investigation proved that the anodizing process itself was not at fault; the color variation occurred because the workpieces had been made of cutoffs from sheet stock obtained from two different sources. To prevent further difficulty, two recommendations were made:

- All sheet metal of a given alloy should be purchased from one primary producer, or each job should be made of material from one source. In the latter instance, all cutoffs should be kept segregated.
- More rigid specifications should be established for the desired quality of finish. Most producers can supply a clad material on certain alloys that gives better uniformity in finishing.

Example 3. The problem was to improve the appearance of bright anodized automotive parts made of alloy 5357-H32. Deburring was the only treatment preceding anodizing. An acceptable finish was obtained by changing to an H25 temper. The H25 had a better grain structure for maintaining a mirror-bright finish during anodizing.

Example 4. After alkaline etching, web-shape extrusions made of alloy 6063-T6 exhibited black spots that persisted through the anodizing cycle.

These extrusions were 3 m (11 ft) long and had cross-sectional dimensions of 100 by 190 mm (4 by 7 $\frac{1}{2}$ in.) and a web thickness of 5 mm ($\frac{3}{16}$ in.). Cleaning had consisted of treatment for 1 to 4 min in 15% sulfuric acid at 85 °C (185 °F) and etching for 8 min in a sodium hydroxide solution (40 g/L or 5 oz/gal) at 60 °C (140 °F). The spots occurred only on the outer faces of the web. Affected areas showed subnormal hardness and electrical conductivity. Metallographic examination revealed precipitation of magnesium silicide there.

The defects were found to have occurred in areas where cooling from the extrusion temperature was retarded by the presence of insulating air pockets created by poor joints between the carbon blocks that lined the runout table. The extrusion had only to remain stationary on the runout table (end of extrusion cycle, flipped on side for sawing) for as little as 1 min for MgSi₂ to precipitate at locations where cooling was retarded. This type of defect is not limited to a particular shape; it can result from a critical combination of size and shape of the extrusion, or from extrusion conditions and cooling rate.

The solution to the problem was to provide uniform cooling of the extrusion on the runout table; this was accomplished by modifying the table and employing forced-air cooling.

Sealing of Anodic Coatings

When properly done, sealing in boiling deionized water for 15 to 30 min partially converts the as-anodized alumina of an anodic coating to an aluminum monohydroxide known as Boehmite. It is also common practice to seal in hot aqueous solution containing nickel acetate. Precipitation of nickel hydroxide helps in plugging the pores.

The corrosion resistance of anodized aluminum depends largely on the effectiveness of the sealing operation. Sealing will be ineffective, however, unless the anodic coating is continuous, smooth, adherent, uniform in appearance, and free of surface blemishes and powdery areas. After sealing, the stain resistance of the anodic coating also is improved. For this reason, it is desirable to seal parts subject to staining during service.

Tanks made of stainless steel or lined low-carbon steel and incorporating adequate agitation and suitable temperature controls are used for sealing solutions.

Chromic acid anodized parts are sealed in slightly acidified hot water. One specific sealing solution contains 1 g of chromic acid in 100 L of solution (0.1 oz in 100 gal). The sealing procedure consists of immersing the freshly anodized and rinsed part in the sealing solution at 79 ± 1 °C (175 ± 2 °F) for 5 min. The pH of this solution is maintained within a range of 4 to 6. The solution is discarded when there is a buildup of sediment in the tank or when contaminants float freely on the surface.

Sulfuric acid anodized parts may also be sealed in slightly acidified water (pH 5.5 to 6.5), at about 93 to 100 °C (200 to 212 °F). At temperatures

Table 6 Sealing processes for anodic coatings

Process	Bath	Temperature		Duration, min	Appearance, properties	Remarks
		°C	°F			
Nickel-cobalt	0.5 kg (1.1 lb) nickel acetate, 0.1 kg (0.2 lb) cobalt acetate, 0.8 kg (1.8 lb) boric acid, 100 L (380 gal) water	98-100	208-212	15-30	Colorless	Provides good corrosion resistance for a colorless seal after anodizing bath buffered to pH of 5.5 to 6.5 with small amounts of acetic acid sodium acetate
Dichromate	5 wt% sodium dichromate, 95 wt% water	98-100	208-212	30	Yellow color	Cannot be used for decorative and colored coatings where the yellow color is objectionable
Glauber salt Lacquer seal	20 wt% sodium sulfate, 80 wt% water Lacquer and varnishes for interior and exterior exposure	98-100 ...	208-212 ...	30 ...	Colorless Colorless to yellow or brown	... Can provide good corrosion resistance provided that the correct formulation is selected. Formulations for exterior exposure use acrylic, epoxy, silicone-alkyds resins and for interior exposure the previously mentioned resins plus urethanes, vinyls and alkyds.

below 88 °C (190 °F), the change in the crystalline form of the coating is not satisfactorily accomplished within a reasonable time.

Dual sealing treatments are often used, particularly for clear anodized trim parts. A typical process involves a short-time immersion in hot nickel acetate 0.5 g/L (0.06 oz/gal) solution followed by rinsing and immersion in a hot, dilute dichromate solution. Advantages of dual sealing are less sealing smudge formed, greater tolerance for contaminants in the baths, and improved corrosion resistance of the sealed parts in accelerated tests (e.g., the CASS test, ASTM B 368).

One specific sealing solution contains 5 to 10 wt% potassium dichromate and sufficient sodium hydroxide to maintain the pH at 5.0 to 6.0. This solution is prepared by adding potassium dichromate to the partly filled operating tank and stirring until the dichromate is completely dissolved. The tank is then filled with water to the operating level and heated to the operating temperature, after which the pH is adjusted by adding sodium hydroxide (which gives a yellow color to the bath).

For sealing, the freshly anodized and rinsed part is immersed in the solution at 100 ± 1 °C (210 ± 2 °F) for 10 to 15 min. After sealing, the part is air dried at a temperature no higher than 105 °C (225 °F). The dichromate seal imparts a yellow coloration to the anodic coating.

Control of this solution consists of maintaining the correct pH and operating temperature. The solution is discarded when excessive sediment builds up in the tank or when the surface is contaminated with foreign material. Sealing is not done on parts that have received any of the hard anodized coatings unless properties other than abrasion resistance are required. If the parts are to be used in a corrosive environment, sealing would be a requirement after hard anodizing. Another application where sealing would be a requirement would be to increase electrical resistance. Sealing will reduce abrasion resistance by 30%. Some other sealing processes are given in Table 6.

Water for sealing solutions can significantly affect the quality of the results obtained from the sealing treatment, as evidenced in the following example.

Strips for automotive exterior trim that were press formed from 5457-H25 sheet were found to have poor corrosion resistance after anodizing, even though appearance was acceptable. The

strips had been finished in a continuous automatic anodizing line incorporating the usual steps of cleaning, chemical brightening, desmutting, and anodizing in a 15% sulfuric acid electrolyte to a coating thickness of 8 µm (0.3 mil). They had been sealed in deionized water at a pH of 6.0 and then warm air dried. Rinses after each step had been adequate, and all processing conditions had appeared normal.

Investigation eliminated metallurgical factors as a possible cause but directed suspicion to the sealing operation, because test strips sealed in distilled water showed satisfactory corrosion resistance. Although the deionized water used in processing had better-than-average electrical resistance (1,000,000 Ω · cm or 10,000 Ω · m), analysis of the water showed that it contained a high concentration of oxidizable organic material. This was traced to residues resulting from the leaching of ion-exchange resins from the deionization column. The difficulty was remedied by the use of more stable resins in the deionization column.

When the resin is approaching full absorption rate, the silicons (silicates) are one of the first elements to come across as regeneration is imminent. Silicates above 5 mg/L will subsequently stop the sealing process in a water seal environment.

Color Anodizing

Dyeing consists of impregnating the pores of the anodic coating, before sealing, with an organic or inorganic (e.g., ferric ammonium oxalate) coloring material. The depth of dye adsorption depends on the thickness and porosity of the anodic coating. The dyed coating is transparent, and its appearance is affected by the basic reflectivity characteristics of the aluminum. For this reason, the colors of dyed aluminum articles should not be expected to match paints, enamel, printed fabrics, or other opaque colors.

Shade matching of color anodized work is difficult to obtain. Single-source colors usually are more uniform than colors made by mixing two or more dye materials together. Maximum uniformity of dyeing is obtained by reducing all variables of the anodizing process to a minimum and then maintaining stringent control of the dye bath.

Mineral pigmentation involves precipitation of a pigment in the pores of the anodic coating

before sealing. An example is precipitation of iron oxide from an aqueous solution of ferric ammonium oxalate to produce gold-colored coatings.

Integral color anodizing is a single-step process in which the color is produced during anodizing. Pigmentation is caused by the occlusion of microparticles in the coating, resulting from the anodic reaction of the electrolyte with the microconstituents and matrix of the aluminum alloy. Thus, alloy composition and temper strongly affect the color produced. For example, aluminum alloys containing copper and chromium will color to a yellow or green when anodized in sulfuric or oxalic acid baths, whereas manganese and silicon alloys will have a gray to black appearance. Anodizing conditions such as electrolyte composition, voltage, and temperature are important and must be controlled to obtain shade matching. One electrolyte frequently used consists of 90 g/L (10 oz/gal) sulfophthalic acid plus 5 g/L (0.6 oz/gal) sulfuric acid.

Another method for coloring anodic coatings is the two-step (electrolytic) coloring process. After conventional anodizing in sulfuric acid electrolyte, the parts are rinsed and transferred to an acidic electrolyte containing a dissolved metal salt. Using alternating current, a metallic pigment is electrodeposited in the pores of the anodic coating. There are various proprietary electrolytic coloring processes. Usually tin, nickel, or cobalt is deposited, and the colors are bronzes and black. The stable colors produced are useful in architectural applications.

Evaluation of Anodic Coatings

Coating Thickness. In the metallographic method, the evaluator measures coating thickness perpendicular to the surface of a perpendicular cross section of the anodized specimen, using a microscope with a calibrated eyepiece. This is the most accurate method for determining the thickness of coatings of at least 2.5 µm (0.1 mil). This method is used to calibrate standards for other methods and is the reference method in cases of dispute. Because of variations in the coating thickness, multiple measurements must be made and the results averaged.

In the micrometer method, the evaluator determines coating thickness of 2.5 µm (0.1 mil) or more by micrometrically measuring the thickness of a coated specimen, stripping the coating using

Table 7 ASTM and ISO test methods for anodic coatings

Method	ASTM	ISO
Coating thickness		
Eddy current	B 244	2360
Metallographic	B 487	...
Light section microscope	B 681	2128
Coating weight	B 137	2106
Sealing		
Dye stain	B 136(a)	2143
Acid dissolution	B 680	3210
Impedance/admittance	B 457	2931
Voltage breakdown	B 110	2376
Corrosion resistance		
Salt spray	B 117	...
Cooper-accelerated, acetic acid salt-spray	B 368	...

(a) ASTM B 136 shows extremely poor sealing and is not considered a true sealing test. It is better classified as a test for staining by dyes.

the solution described in ASTM B 137, microscopically measuring the thickness of the stripped specimen, and subtracting the second measurement from the first.

Effectiveness of Sealing. The sulfur dioxide method comprises exposure of the anodic coating for 24 h to attack by moist air (95 to 100% relative humidity) containing 0.5 to 2 vol% sulfur dioxide, in a special test cabinet. The method is very discriminative. Coatings that are incompletely or poorly sealed develop a white bloom.

Abrasion Resistance. In the Taber abrasion method, the evaluator determines abrasion resistance by an instrument that, by means of weighted abrasive wheels, abrades test specimens mounted on a revolving turntable. Abrasion resistance is measured in terms of either weight loss of the test specimen for a definite number of cycles or the number of cycles required for penetration of the coating. These procedures are covered by Method 6192 in Federal Test Method Standard 141. Weight (thickness) loss (see Method 6192-4.1.3 in Federal Test Methods Standard 141) is measured using eddy current as a check, because milligram weight loss in checking abrasion resistance is difficult to duplicate. Penetration testing can take more than 30 h. Although described in Method 6192, it is rarely used for hard anodizing.

Lightfastness. The fade-O-meter method is a modification of the artificial-weathering method, in that the cycle is conducted without the use of water. Staining and corrosion products thus cannot interfere with interpretation of results. A further modification entails the use of a high-intensity ultra-violet mercury-arc lamp and the reduction of exposure to a period of 24 to 48 h. Table 7 lists the various ASTM and ISO methods that can be used to evaluate the quality of anodic coatings.

Effects of Anodic Coatings on Surface and Mechanical Properties

As the thickness of an anodic coating increases, light reflectance, both total and specular, de-

Table 8 Effect of anodizing on reflectance values of electrobrightened aluminum

Thickness of anodic coating μm	mil	Specular reflectance, %			Total reflectance after anodizing, %
		Electro-brightened	Electro-brightened and anodized	After removal of anodic coating(a)	
Aluminum, 99.99%					
2	0.08	90	87	88	90
5	0.2	90	87	88	90
10	0.4	90	86	88	89
15	0.6	90	85	88	88
20	0.8	90	84	88	88
Aluminum, 99.8%					
2	0.08	88	68	83	89
5	0.2	88	63	85	88
10	0.4	88	58	85	87
15	0.6	88	53	85	86
20	0.8	88	57	85	84
Aluminum, 99.5%					
2	0.08	75	50	70	86
5	0.2	75	36	64	84
10	0.4	75	26	61	81
15	0.6	75	21	57	77
20	0.8	75	15	53	73

(a) Anodic coating removed in chromic-phosphoric acid. Source: Aluminum Development Council

creases. This decrease is only slight for pure aluminum surfaces, but it becomes more pronounced as the content of alloying elements other than magnesium, which has little effect, increases. The decrease in reflectance values is not strictly linear with increasing thickness of anodic coating; the decrease in total reflectance levels off when the thickness of the coating on super-purity and high-purity aluminum is greater than about $2.5 \mu\text{m}$ (0.1 mil).

Data comparing the reflectance values of chemically brightened and anodized aluminum materials with those of other decorative materials are given in "Anodic Oxidation of Aluminium and Its Alloys," Bulletin 14 of the Aluminium Development Association (now the Aluminium Federation), London, England, 1949.

Table 8 shows the effect of anodized coatings 2 to $20 \mu\text{m}$ (0.08 to 0.8 mil) thick on the reflectance values of electrobrightened aluminum of three

degrees of purity. This table also includes specular reflectance values for surfaces after removal of the anodic coating. These data show that the degree of roughening by the anodizing treatment increases as the purity of the aluminum decreases. The reflectance values of the anodized surfaces are influenced by the inclusion of foreign constituents or their oxides in the anodic coating.

Metallurgical factors have a significant influence on the effect of anodizing on reflectance. For minimum reduction in reflectance, the conversion of metal to oxide must be uniform in depth and composition. Particles of different composition do not react uniformly. They produce a nonuniform anodic coating and roughen the interface between the metal and the oxide coating.

Anodizing Conditions. The composition and operating conditions of the anodizing electrolyte also influence the light reflectance and other prop-

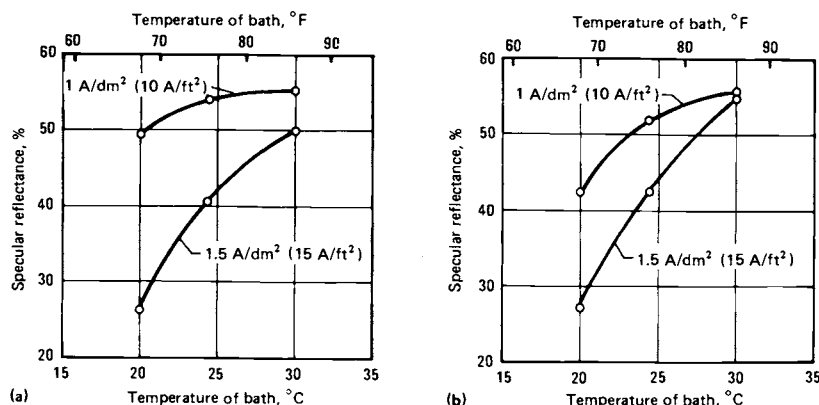


Fig. 8 Effect of anodizing conditions on specular reflectance of chemically brightened aluminum. Data are for a $5 \mu\text{m}$ (0.2 mil) anodic coating on 5457 alloy. (a) 17 wt% H_2SO_4 . (b) 8.8 wt% H_2SO_4

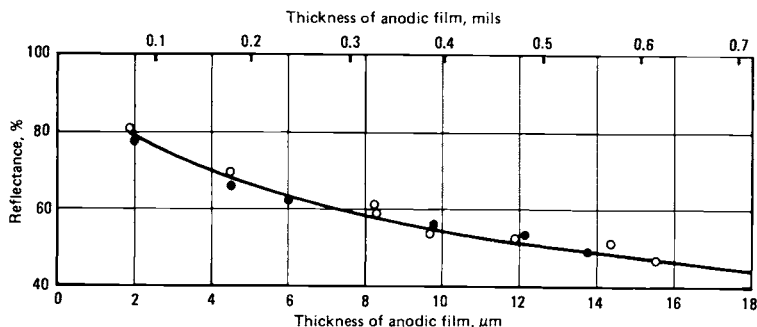


Fig. 9 Effect of anodic coating thickness on reflectance of infrared radiation. Temperature of infrared radiation source, 900 °C (1650 °F). ○: 99.99% Al. ●: 99.50% Al. Courtesy of Aluminum Development Council

Table 9 Effect of anodizing on fatigue strength of aluminum alloys

Alloy	Fatigue strength at 1,000,000 cycles			
	Not anodized		Anodized	
	MPa	ksi	MPa	ksi
Wrought alloys				
2024 (bare)	130	19	105	15
2024 (clad)	75	11	50	7.5
6061 (bare)	105	15	40	6
7075 (bare)	150	22	60	9
7075 (clad)	85	12	70	10
Casting alloys				
220	50	7.5	52	7.5
356	55	8	55	8

Note: Values are for sulfuric acid hard coatings 50 to 100 μm (2 to 4 mils) thick applied using 15% sulfuric acid solution at -4 to 0 °C (25 to 32 °F) and 10 to 75 V dc. Source: F.J. Gillig, WADC Technical Report 53-151, P.B. 111320, 1953

erties of the polished surface. Figure 8 shows the effect of sulfuric acid concentration, temperature of bath, and current density on the specular reflectance of chemically brightened aluminum alloy 5457. These data show that a particular level of specular reflectance can be produced by varying operating conditions.

Thermal Radiation. The reflectance of aluminum for infrared radiation also decreases with increasing thickness of the anodic coating, as shown in Fig. 9. These data indicate that the difference in purity of the aluminum is of minor significance. Figure 10 compares anodized aluminum surfaces and polished aluminum surfaces at 21 °C (70 °F) with respect to absorptance when exposed to blackbody radiation from sources of different temperatures. Although anodized aluminum is a better absorber of low-temperature radiation, as-polished aluminum is a more effective absorber of blackbody radiation from sources at temperatures exceeding 3300 °R (1850 K).

Fatigue Strength. Anodic coatings are hard and brittle, and they will crack readily under mechanical deformation. This is true for thin as well as thick coatings, even though cracks in thin coatings may be less easily visible. Cracks that develop in the coating act as stress raisers and are potential sources of fatigue failure of the substrate metal. Typical fatigue-strength values for aluminum alloys before and after application of a hard anodic coating 50 to 100 μm (2 to 4 mils) thick are given in Table 9.

Anodizing Non-Aluminum Substrates

Magnesium Anodizing. Three methods of anodizing magnesium are widely employed by industry. One uses only internal voltage generated as a result of a galvanic couple, and two use an external power source. The first method, often referred to as galvanic anodize or the Dow 9 process, uses a steel cathode electrically coupled to the magnesium component to be anodized. Dow 9 coatings have no appreciable thickness and impart little added corrosion resistance. However, the resulting coating is dark brown to black, which makes it useful for optical components and for heat sinks in electronic applications. This coating also serves as an excellent paint base.

The other anodizing processes, known as the HAE and Dow 17 processes, use an external power source. Both processes deposit an anodic layer about 50 μm (2 mils) thick, but they differ in that the solution used for Dow 17 coatings is acidic, a combination of ammonium bifluoride, sodium dichromate, and phosphoric acid, whereas the HAE process employs an alkaline bath. Details for both processes may be found by consulting military specification MIL-M-45202.

Titanium Anodizing. While extremely corrosion resistant in itself, titanium and its alloys are often anodized to impart properties other than corrosion resistance. For instance, in wear situations,

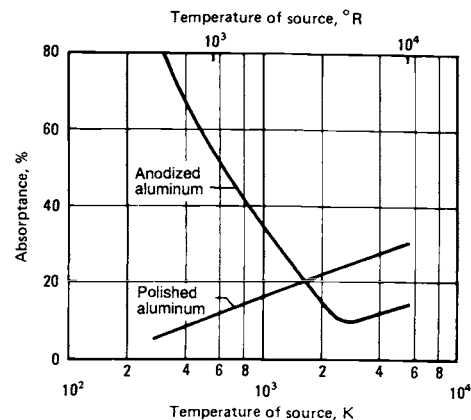


Fig. 10 Comparison of absorptance of blackbody radiation by anodized aluminum and polished aluminum. Temperature of aluminum surface, 530 °R (21 °C, or 70 °F)

titanium components are very prone to galling. In order to overcome its tendency to gall, titanium is often anodized in a caustic electrolyte. This application is detailed in the SAE specification AMS 2488.

Decorative colored coatings on titanium can be achieved by anodizing in slightly acidified solutions of phosphoric or sulfuric acid. By controlling the terminal voltage, vivid colors from magenta to cobalt blue can be obtained. Such decorative uses have been widely utilized by the jewelry industry for years, and these coatings are now finding functional use for medical implants and dental instruments.

Zinc Anodizing. Zinc can be anodically treated in a wide range of electrolytes using either alternating or direct current to form decorative, yet protective, coatings. Anodic coatings on zinc and zinc alloys are covered in military specification MIL-A-81801. The zinc to be anodized may be wrought or die cast zinc parts or zinc coatings obtained by electroplating, mechanical deposition, thermal spraying, or galvanizing.

Electrolytes are formulated from such materials as phosphates, silicates, or aluminates to which are added chromates, vanadates, molybdates, and/or tungstates. Solutions are typically heated to 65 °C (150 °F), and anodize times vary from 5 to 10 min. The resulting coatings are 30 to 40 μm (1.2 to 1.6 mils) thick and are either green, gray, or brown, depending on the electrolyte used. For optimum corrosion resistance, anodic zinc coatings should be sealed using a material such as sodium silicate or an organic lacquer or enamel.

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