

COLORING ANODIZED ALUMINUM

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ORGANIC DYES

Colored, anodized aluminum is used in a wide variety of applications ranging from giftware and novelties through automotive and application trim, and even in such demanding situations as exterior architecture. Imitations of precious and semi-precious metals such as gold, copper, brass, etc., as well as a wide variety of new and interesting colors have given this type of finish wide appeal. The utilization of electropolishing or bright dipping in conjunction with a thin anodic film produces a finish whose appeal cannot be duplicated by other means.

The actual process of dyeing the aluminum oxide film is very simple. A water solution of 0.025 to 1.0% of dyestuff at a temperature of 150°F composes the dyebath. The aluminum, previously anodized, is simply immersed in this bath for a short period of time, usually ten minutes. The work is then sealed and is resistant to further dyeing or staining.

The equipment required, in addition to that needed for the actual anodizing operation, consists of the following:

Rinse tanks with clean, flowing water.

A dye tank for each color desired.

A sealing bath preferably equipped with continuous filtration through activated carbon.

The dye tanks must be of stainless steel, plastic, fiberglass, or some other inert substance; never of copper or steel. They must be supplied with means of maintaining a constant 150° temperature and should be equipped with some form of agitation. Usual plant practice is to use air agitation. With air agitation the use of water and oil traps, plus a filter on the air supply, is necessary to prevent contamination of the dye solution. A few drops of oil spread on the surface of the dyebath is very often the cause of streaked and spotted work.

Rinsing after anodizing, followed by immediate dyeing, is of prime importance. Since some dyes will not dye aluminum in the presence of sulfate ion, poor rinsing can cause streaks and discolorations. Even in the case of dyes not affected by sulfates, any carry-over of acid causes a lowering of the pH of the dyebath which means shade variations in succeeding batches of work. In the design of parts to be color anodized, care must be taken to avoid the use of closed heads or seams which are impossible to rinse. In the case of parts containing recesses which are difficult to rinse, a neutralizing bath of sodium bicarbonate is of value. In working with coated racks, care must be taken that the rack coating does not separate, thereby forming pockets that can entrap sulfuric acid, later allowing it to seep out into the dyebath. Work must not be allowed to stand in the rinse tanks between anodizing and dyeing, but should be dyed immediately, following a thorough rinsing. For most effective rinsing three tanks should be used. In this way the final tank will remain relatively free of acid.

SEALING

The sealing process consists of immersing the anodized metal in a hot water bath wherein the aluminum oxide coating is converted from AlO to the monohydrate, Al₂O₃ · H₂O, with an accompanying increase in volume. Thus, the microscopic pores in the coating are closed and the coating becomes resistant to further staining. In the sealing of dyed coatings, the addition of 0.5% nickel acetate prevents leaching out of the dye in the hot solution before the pores are completely closed. When sealing with the

nickel acetate bath, a smutty deposit may form on the work. This can be minimized by the addition of 0.5% boric acid to the bath or by the use of acetic acid to lower the pH of the solution to 5.3-5.5. Too low a pH, however, causes leaching out of the dye. Use of 0.1% wetting agent in this bath also aids in preventing formation of the smut. A proprietary sealing material designed to completely eliminate this smut is now available.

The sealing tank should be of stainless steel or other inert material and must be maintained at 200°F. Use of the filter enables a number of colors to be sealed in the same bath without danger of contamination.

FACTORS INFLUENCING SHADE

In order to obtain reproducible results from batch to batch, a large number of variables must be kept under close control. First to be considered are those which affect the nature of the coating.

Alloy:

The type of aluminum alloy has a pronounced effect on shade, especially with certain dyes. The brightest and clearest anodic films are produced on the purest form of aluminum, the coatings becoming duller as the amount of alloying constituents are increased. Superpurity aluminum (99.996 Al) and its alloys with small amounts of magnesium produce an extremely bright film which does not become cloudy upon being anodized for extended periods. Alloys containing copper, such as 2017 and 2024, although forming a thinner and less durable coating than the purer forms, produce a heavier and duller shade. Magnesium in excess of 2% has a similar effect although not as pronounced. The presence of silicon imparts a gray color to the coating; alloys containing more than 5% silicon are not recommended for use with bright colors. The majority of casting alloys contain appreciable amounts of silicon, ranging as high as 13%, and present difficulty in anodizing. Use of a hydrofluoric acid dip prior to anodizing is of value when high-silicon alloys are encountered.

Since the various alloys produce different shades when anodized identically, the designer of an assembled part must use the same alloy throughout if the shades of the individual components are to match.

Anodizing Conditions:

Other variables affecting the nature of the coating, that is its thickness, hardness, and porosity are the concentration and temperature of the anodizing bath, the current density (or the applied voltage which actually controls the current density), and the time of anodizing. These factors must be rigidly controlled in order to achieve consistent results.

The *sulfuric acid* anodizing bath produces the best coatings for dyeing. The standard anodizing solution consists of 15 to 16% by weight sulfuric acid and is operated in the range between 70 and 75°F. As the temperature is increased the coating becomes more porous and improves in its ability to absorb the dye. However, it also loses its hardness and its luster. As the pore size increases, sealing becomes more difficult and a greater amount of dye is bled out in the sealing bath. The ideal temperature, except where a special effect is desired, is 70°F.

Coatings produced by anodizing in *chromic acid* solutions can also be dyed. The opaque nature of the oxide film produced in this manner has a dulling effect upon the appearance of the dyed work. Consequently, some dyes, notably the reds which produce pleasing shades on sulfuric acid anodized metal, are unsuitable for use with the chromic acid type coating. Lightfastness of this type of dyed film is extremely poor, possibly because the dye does not penetrate to a sufficient extent. The best chromic acid coatings for dyeing are produced with a 6% to 10% by weight solution operated at 120°F. A potential of 40 to 60 volts is used, depending upon alloy, copper, and silicon bearing materials requiring the lower voltage. The usual time is from 40 to 60 minutes.

DYEING CONDITIONS

The variables in the dyebath are time, temperature, concentration, and pH. Time

and temperature are readily controlled in plant practice; however, regulation of concentration presents some difficulties. Fortunately, in the case of most single component dyes, concentration control is not very critical, a variation of 100% causing little change in depth of shade.

The usual dye bath concentration for full shades is two grams per liter, except for black which requires from six to ten grams per liter. In the case of pastel shades, concentrations of considerably less than two grams per liter may be required in order that the shade does not become too deep.

Control of pH is important and a daily check should be made. The range between pH 6.0 and 7.0 gives the best results with the majority of dyes. However, a few are more effective at values close to 5.0. Initial adjustments should always be made since it is not practical for the manufacturer to standardize the dyes with respect to the pH of their solutions. These adjustments are made by addition of small amounts of acetic acid to lower the pH value and sodium hydroxide or acetate to raise it. Solutions may be buffered against possible carry-in of sulfuric acid by adding one gram per liter of sodium acetate and then adding sufficient acetic acid to reduce the pH to the desired value.

SURFACE PREPARATION

The type of mechanical preparation prior to anodizing gives the metal finisher a choice of effects. By combining techniques, such as scratch brushing or sandblasting with buffing and bright-dipping, interesting effects can be achieved.

A chemical or electro-brightening treatment is required where an extremely high luster is to be obtained. The electro-brightening or electro-polishing treatment is particularly applicable to the superpurity aluminum now used extensively in the jewelry and optical field. Proprietary chemicals for these treatments are available from a number of suppliers.

Mat finishes may be produced chemically by etching in 5% caustic soda or by treatment with a number of specially prepared etching compounds.

The beauty of dyed anodized aluminum is further enhanced by color buffing the work after it is sealed and dried, using a lime type composition, preferably containing some wax. In addition to actually polishing the coating, this step removes any traces of the sealing smut.

Irregular shaped parts, castings, etc. are best finished by brushing with a Tampico brush or by tumbling with sawdust.

COLORFASTNESS OF THE DYED COATING

Of the many dyes that color anodized aluminum, possibly several hundred, it should be understood that only a very few possess sufficient inherent resistance to fading to be considered for applications where exposure to direct sunlight is intended. Where items of long life expectancy are involved; for example, architectural components, even greater selectivity must be imposed, since all organic colorants now known will exhibit some fading when subjected to sunlight of sufficient intensity and duration. Also, the parameters of application as well as the colorant are involved in the resistance to premature loss or change of color. The following additional factors are considered by most authorities as affecting the lightfastness of the dyed coating:

1. Coating Thickness and Penetration of the Dye:

Accelerated exposure tests and practical experience both here and abroad verify that an anodic coating thickness is the order of 20 microns (0.8 mil) and its complete penetration by the colorant is required for optimum resistance to fading and weathering.

2. Intensity of Shade:

Generally speaking, the greater the amount of dye absorbed, the better its resistance to fading. Also, whatever fading may occur will be less apparent to the observer. Pastel shades may therefore be expected to exhibit inferior light and weather fastness as compared to full strength dyeing.

3. Type and Degree of Sealing:

Those dyes that are reactive with the nickel or cobalt salts present in the sealing bath usually require this treatment for optimum performance. It is reported that certain selected dyestuffs benefit from aftertreatment with other heavy metals; for example, lead, copper, zinc, or chromium. Generally, such treatments are not utilized because of the requirement of an individual sealing tank for each dye.

In the case of extremely porous anodic coatings, for example, those formed on alloys of high copper content, effective sealing is particularly important with certain dyes to prevent color loss from sublimation of the dye or by chemical reaction in oxidizing or reducing environments.

MULTICOLOR ANODIZING

The application of two or more colors for the production of nameplates, instrument panels, automotive and appliance trim, etc. has now achieved sufficient commercial importance that a number of large firms deal exclusively with such items. The following methods of multicolor anodizing are possible:

1. The multiple anodizing process, which entails a complete cycle of anodizing, dyeing, and sealing; application of a resist to selected areas; stripping of the entire anodic film from the remaining unprotected surfaces and repetition of this entire procedure for each color.
2. The single anodizing method, wherein an anodic coating of sufficient thickness and porosity to absorb the dye required for the darkest shade is first applied. This coating is then dyed and left unsealed, a resist applied, and the dye alone discharged or bleached out with a solution that leaves the anodic coating intact. The operation is then repeated for each successive shade. Finally, the resist is removed with a suitable solvent, and the entire surface sealed. In certain cases, where a dark shade is to be applied after a pastel shade, a modification of this technique omits the bleaching step with the supplementary dye being applied directly over the preceding color.
3. The use of a specialized combination ink-and-resist enables information or designs to be printed directly on the previously formed anodic coating in several colors. The background color may then be applied by conventional dyeing methods, while the ink serves as a stop-off for the printed areas.
4. Pre-anodized, photosensitized aluminum alloy material is available, wherein the image, in black, may be produced by photographic methods, and the background colored by the conventional dye immersion method.

INORGANIC COLORING METHODS

For exterior applications of architectural quality certain inorganic coloring methods offer the advantage of superior resistance to fading and weathering. The range of colors, however, is extremely limited and, in most instances, the processes require either or both special aluminum alloys or processing conditions. Listed below are the most useful inorganic coloring processes:

INTEGRAL COLOR ANODIZING

This terminology applies to those processes whereby the developed color is a function of the particular alloy and anodizing treatment in organic acid electrolytes such as sulfophthalic or sulfosalicylic acids. Proprietary commercial processes of this type are available from the aluminum companies. The range of color may vary from a golden bronze through deep bronze to black, depending upon the composition of the material and the operating parameters.

The natural coloration of anodic coatings by elemental silicon is utilized to produce a range of light and weather resistant gray shades on certain special alloys. Also, of lesser commercial importance, chromium bearing alloys may be "clear anodized" to a gold color.

Integral colored anodic coatings may be overdyed with conventional organic dyes to produce a great variety of interesting shades, a number of which are sufficiently stable to sunlight and weathering for use in exterior architectural applications.

ELECTROLYTIC COLORING

This method (also referred to as "The Two-Stage Electrolytic Process") consists of conventional anodizing, followed by an alternating current electrolytic treatment in an acidic solution of the salts of various metals such as tin, nickel, cobalt, copper, and others. Processes of this type have been used extensively in Japan and Europe and are now rapidly replacing the Integral Color method here, since they offer the advantage of relatively low energy consumption and the ability to obtain matching colors without the limitation of a specific alloy composition.

Although the most commonly produced colors are black and bronze, it is technically feasible to obtain dull shades of many other colors by varying the composition of the electrolyte with respect to the metals used. There are now in the order of two dozen proprietary electrolytic coloring processes in existence, most of which require a license from the patent holder.

As in the case of integral colored anodic coatings, a complete range of durable and architecturally attractive shades may be achieved by over dyeing the light to medium electrolytically produced bronze shades with selected fade-resistant organic dyes.

PIGMENTATION BY PRECIPITATION OF INSOLUBLE COMPOUNDS

Before the development of special organic dyes for coloring anodized aluminum, the precipitation of various insoluble metal compounds within the anodic coating was used commercially. The treatment consists of alternatively immersing the anodized surface in concentrated solutions of suitable metal salts until a sufficient amount of the pigment is precipitated to produce the desired color. Although seldom used in today's state of the art, a number of these reactions are listed below:

Lead nitrate or acetate with potassium dichromate	Yellow
Lead nitrate or acetate with potassium permanganate	Red
Copper sulfate with ammonium sulfide	Green
Ferric sulfate with potassium ferrocyanide	Blue
Cobalt acetate with ammonium sulfide	Black

Ferric oxalates, applied to conventional anodic coatings in the same manner as organic dyes are, under proper conditions, hydrolyzed to deposit ferric hydroxide within the coating pores, imparting a gold to orange color of outstanding resistance to fading. Special proprietary chemicals are available for this treatment. The deposit of ferric oxide produced in the above manner may, in addition, be converted to ferric sulfide, the resultant shade of which is black. Alternatively, a bronze shade may be formed by reduction of the ferric oxide with pyrogallol acid.

Cobalt acetate reduction, although commercially used in Europe, is not well known in the U.S.A. It consists of saturating a conventional anodic coating with the cobalt solution and then reacting this with potassium permanganate to produce a cobalt-manganese dioxide complex. The resultant bronze shade has excellent lightfastness and offers some potential for architectural applications.

"The Surface Treatment and Finishing of Aluminum and its Alloys"

by: S. Wernick, R. Pinner, and P. G. Sheasby . . . \$222.00

This is the classic work of reference on the subject and should meet the requirements of designers, engineers, anodizers and others concerned with the finishing of aluminum. The work is in two volumes and covers every conceivable aspect of aluminum treatment.

Include postage and handling; \$3.50 US, Canada & Mexico; \$6.00 foreign (in NJ add 6% Sales Tax) Price subject to change. Payment in US funds.

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CHROMATE CONVERSION COATINGS

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Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment with mixtures of hexavalent chromium and certain other compounds. These treatments convert the metal surface to a superficial layer containing a complex mixture of chromium compounds. The coatings are usually applied by immersion, although spraying, brushing, swabbing, or electrolytic methods are also used. A number of metals and their alloys can be treated: notably, aluminum, cadmium, copper, magnesium, silver and zinc.

The appearance of the chromate film can vary, depending on the formulation of the bath, basis metal and process parameters. The films can be modified from thin, clear-bright and blue-bright to the thicker, yellow iridescent, to the heaviest brown, olive drab and black films. A discussion of specific formulations is not included in this article because of the wide variety of solutions used to produce the numerous types of finishes. It is intended to present sufficient general information to permit proper selection and operation of chromating baths. Proprietary products which are designed for specific applications are available from suppliers.

PROPERTIES AND USES

Physical Characteristics:

Most chromate films are soft and gelatinous when freshly formed. Once dried, they slowly harden or "set" with age and become hydrophobic, less soluble, and more abrasion resistant. While heating below 150°F (66°C) is of benefit in hastening this aging process, prolonged heating above 150°F may produce excessive dehydration of the film, with consequent reduction of its protective value. Coating thickness rarely exceeds 0.00005", and often is on the order of several microinches. The amount of metal removed in forming the chromate film will vary with different processes.

Variogated colors are normally obtained on chromating, and are due mainly to interference colors of the thinner films and to the presence of chromium compounds in the film. Since the widest range of treatments available is for zinc, coatings for this metal afford an excellent example of how color varies with film thickness. In the case of electroplated zinc, clear-bright and blue-bright coatings are the thinnest. The blue-brights may show interference hues ranging from red, purple, blue, green to a trace of yellow, especially when viewed against a white background. Next, in order of increasing thickness, comes the iridescent yellows, browns, bronzes, olive drabs and blacks.

Physical variations in the metal surface, such as those produced by polishing, machining, etching, etc., also affect the apparent color of the coated surface. The color of the thinner coatings on zinc can also be affected indirectly by chemical polishing, making the finish appear whiter.

Corrosion Prevention:

Chromate conversion coatings can provide exceptionally good corrosion resistance, depending upon the basis metal, the treatment used and the film thickness. Protection is due both to the corrosion inhibiting effect of hexavalent chromium contained in the film and to the physical barrier presented by the film itself. Even scratched or abraded films retain a great deal of their protective value, since the hexavalent chromium content is slowly leachable in contact with moisture, providing a self-healing effect.