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[54] INTEGRAL HARD COAT ANODIZING SYSTEM
9 Claims, No Drawings

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ABSTRACT: Hard, integrally colored oxide coatings are formed on aluminum and aluminum alloys by anodizing the surface to produce thereon an oxide coating while simultaneously producing a desired coloring effect. There is used as an electrolyte an inorganic acid, such as sulfuric acid, together with an additional acid which is either an aliphatic alpha-hydroxy monocarboxylic or an aliphatic dicarboxylic acid, or sulfamic acid, and a metal salt of either of the aforementioned organic acids, such as a ferric salt. The process employs ordinary temperatures, and a current density between about 12 and 60 amperes per square foot.

INTEGRAL HARD COAT ANODIZING SYSTEM

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 649,095, filed June 17, 1967 now abandoned, which is in turn a continuation-in-part of application Ser. No. 403,352, filed Oct. 12, 1964 (now abandoned), which is in turn a continuation-in-part of application Ser. No. 353,591, filed Mar. 20, 1964 (now abandoned).

BACKGROUND OF THE INVENTION

The hard anodizing of aluminum and aluminum base alloys has conveniently been performed in aqueous electrolytes containing mineral acids, or organic acids, or mixtures of such acids. Where it was desired to obtain resistance to abrasion it has been considered necessary to operate at low temperatures, in the range of 0° to 32° F., involving the use of expensive refrigeration. The known processes for hard coat anodizing also have the drawback of providing only a limited range of colors in the anodized product, namely dark gray to black shades, which are not suitable for decorative architectural applications where a market exists for a wider range of colors.

Another shortcoming of conventionally produced hard coat films on aluminum and its alloys employing the aforementioned low temperatures is the occurrence of crazing or cracks in the film. These are apparently attributable to the difference in the thermal coefficient of expansion of the two materials constituting the anodized surface, namely, the aluminum substrate and the aluminum oxide film. The aluminum expands at approximately four times the rate of the aluminum oxide. Hence, when the anodized surface is removed from the electrolyte bath having a temperature substantially below ambient or room temperature, and is suddenly brought up to room temperature, the resulting thermal expansion produces tensile stresses in the anodic film, thereby introducing numerous cracks. These cracks may subsequently form sites for pitting type corrosion where the anodic surface is exposed to a corrosive atmosphere.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a novel method of anodizing the surface of aluminum or an aluminum base alloy to produce thereon an oxide coating while simultaneously producing a desired coloring effect, thereby providing on said surface a hard integrally colored oxide coating, which possesses numerous advantages over known processes.

By "hard coating" or "hard coat" as used in the anodizing art, there is meant an oxide coating which, on 1100 aluminum alloy (commercial purity aluminum), will have a Knoop hardness number, taken in the cross section of the coating, of 400 KHN or more; see also Wernick and Pinner, "The Surface Treatment and Finishing of Aluminum and its Alloys," Chapter 8 (1959).

The anodizing process of the invention provides a harder anodized surface which is less susceptible to crazing and which possesses greater corrosion resistance, and resistance to abrasion. Integral nonfading colors are imparted, ranging from light shades of gold, and deeper shades of brasses and bronzes, to charcoal grays and blacks. This color range is obtainable with a smaller number of different aluminum alloys than is the case with existing methods, and scrap and rerun rates are considerably lower. A particular advantage lies in drastically reduced anodizing times and in operation at ordinary or ambient temperatures.

The colored anodized products are applicable in such fields as architectural finishes and trim, coated cooking utensils, machine parts, automotive trim, or in any other areas where the decorative and special physical properties of hard coated aluminum are required.

The novel process of the invention is applicable to pure aluminum as well as to various aluminum base alloys. The colors obtained range from light gold in the case of high-purity al-

loys, and shades of bronze-brown in intermediate alloys, to dark brown and black for high constituent alloys.

In accordance with the invention, there is employed a novel anodizing bath which contains three components: (1) a conductor component, (2) a voltage component; and (3) a color control component.

The conductor component is a moderate concentration of an inorganic acid which will impart the necessary conductivity to the bath and which does not form undesirable byproducts during the electrolysis. Examples of suitable inorganic acids include sulfuric, sulfamic, hydrofluoric, and boric acids, or mixtures thereof. These acids are employed in amounts ranging from a lower limit below which the acid will not dissolve the oxide to an upper limit marked by excessive attack on the oxide or the coloring constituents of the aluminum.

Sulfuric acid is the preferred conductor component meeting these requirements, and is employed within the approximate concentration range of 0.05 percent to 4.5 percent by weight. The hydrofluoric acid range is from about 0.001 percent to 0.5 percent; boric acid, about 0.5 percent to 2 percent; and sulfamic, about 0.5 percent to 5 percent.

The voltage component of the bath is either sulfamic acid or an aliphatic organic acid which is soluble in the bath at the temperatures employed for anodizing and which possesses a dissociation constant facilitating the application of an increasing impressed voltage sufficient to maintain the necessary current density. The organic acid of the voltage component is selected so that any decomposition products which it forms on electrolysis will also behave as voltage components, and facilitate the electrolysis of the third, or color control component.

The color control (dissolution inhibiting) component is a metal salt of an organic acid, preferably the organic acid of the voltage component or a similar type of organic acid. The application of the increasing impressed voltage results in electrolysis of the metal salt, probably causing a complex metal oxide to form in the anodic film, and making the film harder. It is believed that the action is one of the metal salt inhibiting the dissolution attack of the acid components on the alloying constituents of the metal being anodized, and the oxide film. The inclusion of the undissolved or partially dissolved constituents in the oxide film produces light traps and colored particles which impart the principal coloring effect in the coating. Even anodizing high-purity aluminum (99.9 percent) has been found to produce only a light coloring of the metal itself and this is overcome by the coloration due to the constituents in the usual commercial alloys. This differs from the previously known approach of impregnating a previously formed oxide coating with dyes, pigments and coloring media, which are readily removed by chemical reagents, such as nitric acid.

The three component anodizing bath of the invention is operated at a current density advantageously in the range of about 12 to about 60 amperes per square foot, and preferably at about 48 amperes per square foot.

In order to maintain the foregoing current density, it is an important feature of the use of the novel anodizing bath of the invention that the anodizing step involves a program for the gradual increase of the impressed voltage, for example, from about 20 volts direct current initially, to as high as 250 volts for heavy films on some aluminum alloys. Generally, the impressed voltage will range from about 20 to 35 volts. The control of impressed voltage makes it possible to apply that voltage necessary to decompose the metal salt and to obtain the desired color in the anodic film.

The anodizing bath temperature may range from about 50° F. to about 80° F., depending upon the solubility limits of the organic acids or their metal salts. The preferred operating temperature is between about 68° F. and about 72° F., and this constitutes an advantage over known methods employing low operating temperatures.

The aliphatic organic acids which are employed as voltage components in the practice of the invention include saturated aliphatic alpha-hydroxy monocarboxylic acids, such as, for ex-

ample, glycolic acid (hydroxyacetic acid), lactic acid (alpha-hydroxypropionic acid), and malic acid (2-hydroxybutanedioic acid), as well as also saturated and unsaturated aliphatic dicarboxylic acids, such as, for example, oxalic, malonic, succinic, and maleic acids.

The foregoing acids are employed in the anodizing bath in concentrations ranging from about 0.5 percent by weight up to the limit of solubility.

The preferred organic acid is oxalic acid.

The color control component of the bath is a metal salt of one of the foregoing organic acids, and in general, is a salt of the same acid that constitutes the voltage component, but it may also be a salt of a specifically different acid. Metals which have been found to induce desirable colors to the anodic film are the common metals of Groups IB, VIIB and VIII of the periodic system, namely iron, nickel, cobalt, copper and manganese. The preferred metal is iron, and the preferred metal salt is ferric oxalate. The concentration of metal salt ranges from about 0.1 percent by weight up to the limit of solubility.

The colors produced by the method of the invention are integral with the anodic coating. The color may arise from several sources. For example, where the oxalic acid reacts during anodizing, one of the reaction products will be colloidal carbon, some of which remains in the coating lending a yellow tint to the oxide film. Where iron salts are employed, iron from the electrolyte is incorporated in the film, probable in the form of oxides of iron, or of combined iron and aluminum oxides. The color imparted by iron is reddish brown. Manganese constituents tend to turn the coating dark or black.

In contrast to the transparent types of coatings produced with conventional sulfuric acid electrolytes, the baths of the present invention produce opaque types of coatings. This may be due to entrapment of aluminum particles, and oxidation products or partly oxidized products, insoluble or slightly soluble, from other constituents of the alloy or the film.

The method and electrolyte of the invention may be employed for the decorative hard coat anodization of aluminum metal, and of aluminum base alloys, for example in the form of sheet, extrusions, or honeycomb. Examples of sheet alloys which can be coated include Nos. 1100, 3003, 3004, 5005, 5052, 5257, 5457, 5657, 5252, and 6061. Examples of extrusion alloys include 6061, 6063, 6463, and 6351. The application of the hard coat to aluminum honeycomb increases its crush strength greatly, by as much as 40 percent.

The general procedure employed in the practice of the invention includes the preparatory steps of degreasing the article to be treated in a conventional bath of a nonsilicated alkaline cleaning agent, rinsing in tap water, etching for 5 minutes in sodium hydroxide-sodium gluconate solution at about 150° F., desmutting for 2 minutes in 1—1 nitric acid and rinsing in water. This is then followed by anodizing in the electrolyte of the invention, and subsequent sealing, if desired.

The preferred anodizing electrolyte according to the invention is an aqueous solution of sulfuric acid, oxalic acid, and ferric oxalate, having the following composition range, by weight:

Sulfuric acid	0.05%—4.5%
Oxalic acid	0.50%—9.0%
Ferric oxalate	0.50%—16%

The voltage range encountered will be dependent upon the resistance of the system to the passage of current. The current density applicable is of the order of 48 amperes per square foot. At this current density the required voltage will range from about 25 volts initially to as high as 250 volts for heavy films on some aluminum alloys. A 1 mil hard anodic film can be produced on most alloys in 15 minutes. The color of the anodized part will depend upon the method of pretreatment,

the alloy and temper, the nature and concentration of the electrolyte, the anodizing time, the applied voltage, and the thickness of the coating.

The importance of having all three components present in the electrolyte is shown by the fact that, if ferric oxalate is added to a bath of oxalic acid alone, the film-forming efficiency goes down almost to zero. Upon adding 1 percent H_2SO_4 , it goes to 100 percent, because the mineral acid addition starts the dissolution of the oxide film once more.

In accordance with another aspect of the invention, it was found that a uniquely different appearance can be imparted to the anodic coating by the use of a preanodizing step in conventional concentrations of sulfuric acid before completing the anodization utilizing the novel bath of the invention. Thus, for example, the preanodizing step may be carried out by anodizing for 3 minutes in 10–30 percent sulfuric acid at 12–20 amperes per square foot current density at 70° F., followed by a water rinse. The article is then anodized using the bath of the invention, as previously described. This results in a unique gloss finish in the colored article.

The surface of aluminum and aluminum alloys is not homogeneous and conventional anodizing electrolytes tend to select spots of low resistance as nucleation sites for conversion of metal to oxide. The novel bath and process of the invention disregard the heterogeneity of the metal surface and result in uniform anodic coatings. This homogeneous response for a given alloy is improved still further by the aforementioned preanodizing step, whereby nucleation sites are established very homogeneously by forming only enough oxide by conventional sulfuric acid anodizing. These sites are then immediately utilized in further anodization with the electrolyte mixture of the invention.

The preferred range of temperature in hard coat anodizing according to the invention is from about 50° F. to about 80° F., and the preferred temperature is 70° F. $\pm$ 2° F. The bath temperature affects conductivity, film-forming efficiency, and the color and reflectivity of the finished article.

Where ferric oxalate is employed, a certain amount of depletion of the electrolyte occurs during use as the result of the reduction of ferric iron to ferrous iron, forming a precipitate of ferrous oxalate which is insoluble in the electrolyte. The ferrous oxalate may be removed either by filtration or by oxidation to ferric oxalate by periodic additions to the bath of hydrogen peroxide.

The anodizing bath of the invention exhibits good throwing power, permitting the formation of anodic coatings of uniform thickness in the crevices and recesses of irregularly shaped objects which are at different distances from the cathode.

The anodic coatings produced according to the invention exhibit superior hardness qualities. Presently, there is no accepted method of measuring the hardness of anodic coatings. The hardness of coatings produced by the baths of the invention was tested using the Tukon Microhardness Tester. Samples having various coatings were mounted and polished in cross section. The hardness measurements were made with a 100 gram load using a diamond indenter which had an included longitudinal angle of 172°30' and an included transverse angle of 130°0'. The K_{100} (Knoop hardness, 100 grams load) values using the preferred bath are shown in table I. The hardness values depend upon the alloy treated and the thickness of the coating. As the purity of the metal increases, so does the hardness of the oxide formed. The hardness obtained in films produced by the method of the invention is superior to that produced by other known methods. The Knoop values range from about 400 to as high as 624 in the case of pure aluminum (99.99 percent).

The apparent densities of coatings obtained with various alloys are also shown in table I. They were measured by cutting specimens about 3 inches $\times$ 3 inches, measuring, cleaning in acetone, weighing, stripping with a boiling solution of 20g CrO_3 and 35 ml. H_3PO_4 in 965 ml. distilled water, weighing and calculating density. The apparent density increases as coating thickness increases.

TABLE 1

Hardness of Anodic Coatings

Alloy	Thickness (mils)	Apparent Density	K ₁₀₀ Hardness
3003-H14	2.69	—	385
3003-H14	1.05	2.32	451
3003-H14	1.58	2.12	473
5657-H25	0.99	2.89	458
5657-H25	2.14	2.62	508
5657-H25	3.39	2.56	537
6463-T6	1.03	2.65	492
6463-T6	2.22	2.57	506
5005-0	1.77	2.63	437
5005-0	2.90	2.52	481
5052-H38	2.19	—	528
5052-H38	1.09	2.61	493
99.99% Al	1.20	2.63	512
99.99% Al	2.09	2.55	576
99.99% Al	3.45	2.49	624

Film thicknesses shown in Table 1 were computed to within about 10 percent of the true value by applying the formula:

$$D=kTC$$

where

k is the anodizing constant 0.0014

T is the anodizing time in minutes

C is the current density in amperes per square foot

D is the thickness in mils.

As explained previously crazing may occur with conventional anodizing methods where there is a difference in thermal expansion between the oxide film and the metal. One type of crazing appears around certain grains, certain imperfections, scratches and microconstituents where there is preferential anodizing at these sites, with adjacent areas anodizing at different rates. The edges which are growing fastest tend to crack.

Much of this type of crazing can be prevented, in accordance with the invention, either by preanodizing in sulfuric acid, which will start all the grains anodizing at a uniform rate, or by lowering the current density during hard coating.

Other types of crazing occur during conventional hard coating by heat buildup within the article or where the radius of curvature is too small for the coating to form properly. Both the latter types of crazing are minimized by the method of the invention. This, in turn, results in greatly improved corrosion resistance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the practice of the invention, but are not to be considered as limiting.

EXAMPLE 1

A 1 inch $\times$ 3 inch sample of 99.99 percent aluminum sheet was degreased in alkaline detergent, rinsed in tap water, etched with caustic soda 5 minutes at 150° F., rinsed for 2 minutes, and desmutted in 1—1 nitric acid, and rinsed in tap water. The sample was then anodized for 15 minutes in a bath having the composition:

Material	Quantity	% by Weight
Distilled water	1,000 ml.	87
Ferric oxalate		
$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$	80 g.	7.0
Oxalic acid $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	60 g.	5.0
Sulfuric acid H_2SO_4	12 g. (6.6 ml.)	1.0
Totals	1,152 g.	100.0

The anodizing temperature was 70° F. the current density was 48 amperes per square foot. The voltage ranged from 25 to 35

volts direct current. A reddish brown coating was obtained. The coating had a thickness of 1.20 mils, a density of 2.63, and a Knoop hardness of 512.

EXAMPLE 2

To illustrate the effect of preanodizing, a sample similar to that of example 1 was degreased, bright dipped in a conventional phosphoric acid-nitric acid solution, and preanodized for 3 minutes in a 17 percent by weight sulfuric acid electrolyte at a current density of 15 amperes per square foot, at a temperature of 70° F. It was then anodized as in example 1. The product had a reddish brown color and exhibited a high degree of gloss.

EXAMPLE 3

An extrusion of 6063-T6 alloy was hard coated following the preanodizing and hard coat anodizing procedures of example 2. The anodizing time was 22 minutes, the voltage range was 38 to 62 volts. The product had a glossy light amber shade, film thickness 1.7 mils.

EXAMPLE 4

A preanodized sheet of alloy 5052 was further anodized for 15 minutes, at current density 48 amps. per sq. ft., voltage range 30 to 33 volts DC, electrolyte temperature 31° C. in a bath having the composition:

Material	Quantity
Water	5,000 ml.
Ferric oxalate	400 g.
Malonic acid	13.25 g.
Sulfuric acid	33 ml.

The anodizing produced a dark brownish and very hard film on the aluminum surface.

EXAMPLE 5

A preanodized extrusion of 5052 alloy was further anodized for 15 minutes, at current density 48 amps. per sq. ft., voltage range 33 to 36 volts DC, electrolyte temperature 21° C., in a bath having the composition:

Material	Quantity
Water	5,000 ml.
Ferric oxalate	400 g.
Malonic acid	39.75 g.
Sulfuric acid	33 ml.

A deep brown-grey oxide film was formed showing exceptional hardness.

EXAMPLE 6

A preanodized sheet of alloy 5052 was further anodized for 13 minutes, at current density 48 amps. per sq. ft., voltage range 36 to 40 volts DC, electrolyte temperature 20.5° C. in a bath having the composition:

Material	Quantity
Water	1,000 ml.
Ferric oxalate	80 g.
Succinic acid	60.5 g.
Sulfuric acid	6.6 ml.

A hard brown-grey anodic coat was produced on the alloy.

EXAMPLE 7

A preanodized sheet of alloy 5052 was further anodized for 24 minutes, at current density 48 amps. per sq. ft., voltage range 27.5 to 37 volts DC, electrolyte temperature 20°–22° C., in a bath having the composition:

Material	Quantity
Water	400 ml.
70% Hydroxyacetic acid	573 ml.
Ferric oxalate	80 g.
Sulfuric acid	27 ml.

The electrolyte produced a dark grey anodic film which was found to be very hard.

EXAMPLE 8

A sheet of alloy 1100 was anodized for 20 minutes, at current density 48 amps. per sq. ft., electrolyte temperature 20°-22 C., voltage range 34 to 45 volts, DC, in the following bath:

Material	Quantity
Water	971 ml.
Ferric oxalate	80 g.
70% Hydroxyacetic acid	217 g.
Sulfuric acid	6.6 ml.

A dark grey-brown oxide film of high hardness was produced.

EXAMPLE 9

A sheet of alloy 1100 was anodized for 15 minutes, at current density 48 amps. per sq. ft., electrolyte temperature 70° F., voltage range 40 to 60 volts, DC, in the following bath:

Material	Quantity
Ferric glycolate	5% by weight
Glycolic acid	6%
Sulfuric acid	1%
Water	balance.

A dark grey hard coating was obtained, thickness 1 mil.

In employing the oxalates of such metals as copper, nickel, cobalt, and manganese, the problems presented by reason of limited solubility, and of compatibility with the sulfuric acid electrolyte are controlled by using the metal in its lower valence state, i.e. cuprous, cobaltous, nickelous or manganous oxalates. In order to obtain compatibility, the metal oxalate is brought into solution in water by adding an amount of ammonium hydroxide solution (28-30 percent NH_3) sufficient to form a clear solution of the metal ammonium complex oxalate, and then the solution is reneutralized with oxalic acid until slightly acidic. The practice of the invention in regard to these salts is illustrated by the following examples:

EXAMPLE 10

A sheet of alloy 1100 was anodized for 15 minutes at current density 48 amps. per sq. ft., electrolyte temperature 70° F., voltage range 35 to 50 volts, DC, in the following bath:

Material	Quantity
Cuprous oxalate	9% by weight
Oxalic acid	9%
Sulfuric acid	1%
Water	balance.

The cuprous oxalate was dissolved in NH_4OH and the solution slightly acidified with oxalic acid.

There was produced a hard brownish coating having a thickness of 1 mil.

EXAMPLE 11

A sheet of alloy 1100 was anodized for 15 minutes, at current density 48 amps. per sq. ft., electrolyte temperature 70° F., voltage range 35 to 45 volts, DC, in the following bath:

Material	Quantity
Cobaltous oxalate	3.2% by weight
Oxalic acid	9%
Sulfuric acid	1%
Water	balance.

The cobaltous oxalate was dissolved in NH_4OH and the solution slightly acidified with oxalic acid. A coating 1 mil-thick was obtained.

EXAMPLE 12

A sheet of alloy 1100 was anodized for 15 minutes, at current density 48 amps. per sq. ft., electrolyte temperature 70° F., voltage range 42 to 60 volts, DC, in the following bath:

Material	Quantity
Manganous oxalate	3.2% by weight
Oxalic acid	9%
Sulfuric acid	1%
Water	balance.

The manganous oxalate was dissolved in NH_4OH to a clear blue solution, which was slightly acidified with oxalic acid. A film 1 mil-thick was obtained.

EXAMPLE 13

A sheet of alloy 1100 was anodized for 15 minutes, at current density 48 amps. per sq. ft., electrolyte temperature 70° F., voltage range 35 to 50 volts, DC, in the following bath:

Material	Quantity
Nickelous oxalate	3.3% by weight
Oxalic acid	9%
Sulfuric acid	1%
Water	balance.

The nickelous oxalate was dissolved in NH_4OH to a clear solution and acidified slightly with oxalic acid. The coating formed was 1 mil-thick.

EXAMPLE 14

An anodizing electrolyte was prepared having the composition:

Water	1,000 ml.
Ferric oxalate	80 g./l.
Oxalic acid	60 g./l.
Sulfuric acid	12 g./l.

and a panel of aluminum alloy 1100 was anodized in this electrolyte with alternating current, at 20°-25° C., 10 volts, and 48 amperes per square foot current density for 25 minutes. The resulting oxide film had a light gold color.

EXAMPLE 15

Employing the following electrolyte:

Water	1,000 ml.
Ferric oxalate	80 g./l.
Oxalic acid	20 g./l.
Sulfuric acid	9.75 g./l.

three samples of aluminum alloy 1100 were electrolyzed with 60-cycle alternating current at 23-30 volts and at a current density of 48 amperes per square foot, and a temperature of 20° C. The samples were anodized for 10, 20, and 30 minutes, being used as both electrodes. The results are summarized as follows:

Anodizing Time (min.)	Voltage	Color	Total Reflectance
10	22-24	gold	33
20	22-28	light bronze	23
30	22-30	bronze	19

There is also included within the contemplation of the present invention a composition adapted to form components of an aluminum anodizing bath when dissolved in water, and which bath can be utilized in the practice of the invention.

Said composition is a dry mixture of an organic acid and the metal salt of an organic acid. A preferred embodiment of such a mixture is one which consists essentially of from about 0.5 to about 9.0 parts by weight of oxalic acid and from about 0.5 to about 8.0 parts by weight of ferric oxalate.

EXAMPLE 16

A sample of 6063-T4 extrusion 0.125 inches thickness was anodized for 30 minutes at a current density of 48 amps. per square foot in a bath containing 30 g./l. sulfamic acid, 20 g./l. oxalic acid and 80 g./l. ferric oxalate at a temperature of 27° C. A voltage range of 77-123 was observed. A uniform coating of medium gold resulted.

EXAMPLE 17

A sample of 6063-T4 extrusion 0.125 inches thickness was anodized for 45 minutes at a current density of 48 amps. per square foot in a bath containing 6.1 g./l. sulfuric acid, 30 g./l. sulfamic acid and 80 g./l. ferric oxalate at a temperature of 20° C. A voltage range of 39 to 85 volts was observed. A uniform black color resulted.

EXAMPLE 18

The results of using hydrofluoric acid as the mineral acid component of the electrolyte are shown in the following table II:

Table II

Concentrations used and data obtained when hydrofluoric acid was substituted for sulfuric acid; material anodized was 6063-T4 extrusion:

Concentration (g./l.)						
HF	Oxalic	Ferric oxalate	Time (min.)	Temp., °C.	Volts	Results
1.0.....	20	80	15	23	67-71	Uniform golden brown.
5.0.....	20	80	15	20	43-64	Light gold.
10.0.....	20	80	15	20	24-29	Bright polished.

EXAMPLE 19

A 1 inch × 3 inch sample of aluminum sheet, after degreasing and desmutting as described in example 1, was anodized for 18 minutes at a temperature of 63° F. and current density of 35 amperes per square foot in an aqueous anodizing solution having the composition:

Boric acid	1 g. per l.
Oxalic acid	75 g. per l.
Ferric oxalate	50 g. per l.
Distilled water	1,000 ml.

A uniform golden-colored oxide coating was formed, having a film thickness of 0.80 mil.

While present preferred embodiments of the invention have been described, it will be apparent that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

5 What is claimed is:

1. In the method of producing a selectively colored, hard, and opaque oxide coating on aluminum and aluminum alloys by anodizing thereof in an aqueous acidic electrolyte containing an inorganic acid and an organic acid at an electrolyte temperature of about 50-80° F., the improvement comprising the addition of a metal salt of said organic acid in greater amounts by weight than said inorganic acid to form a three-component electrolyte in which:

15 a. said inorganic acid is selected from the group consisting of sulfuric acid in an amount from about 0.05 percent to about 4.5 percent by weight, sulfamic acid in an amount from about 0.5 percent to about 5 percent, hydrofluoric acid in an amount from 0.001 percent to about 0.5 percent, and boric acid in an amount from about 0.5 percent to about 2 percent;

20 b. said organic acid is from about 0.5 percent by weight up to a percentage represented by the limit of its solubility therein of an acid selected from the group consisting of aliphatic alpha-hydroxy monocarboxylic acids and aliphatic dicarboxylic acids; and

25 c. said salt is from about 0.1 percent by weight up to a percentage represented by the limit of its solubility therein of a metal salt of an organic acid selected from the group consisting of aliphatic alpha-hydroxy monocarboxylic acids and aliphatic dicarboxylic acids, said metal being selected from the group consisting of iron, nickel, cobalt, copper and manganese;

30 Said metal salt of said organic acid being substantially the sole source of said metal and of the anion of said organic acid, whereby said oxide coating is uniformly colored and abrasion-resistant.

35 2. The method of claim 1 in which the acid in (b) is an aliphatic alpha-hydroxy monocarboxylic acid and the metal salt is a metal salt of an aliphatic dicarboxylic acid.

40 3. The method of claim 1 in which the acid in (b) is an aliphatic dicarboxylic acid and the metal salt is a metal salt of an aliphatic dicarboxylic acid.

4. The method of claim 1 in which the acid in (b) is hydroxyacetic acid.

45 5. The method of claim 1 in which the acid in (b) is oxalic acid.

6. The method of claim 1 in which the acid in (b) is malonic acid.

50 7. The method of claim 1 in which the acid in (b) is succinic acid.

8. The method of claim 1 in which the metal salt is ferric oxalate.

9. The method of claim 1 in which said anodizing electrolyte consists essentially of approximately 80 gm. ferric oxalate, 60 gm. oxalic acid and 12 gm. sulfuric acid for each 1,000 ml. of water.

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