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[54] PROCESS FOR INTEGRAL COLOR ANODIZING

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[58] Field of Search ..... 204/58, 35, 38 A

[56] References Cited

FOREIGN PATENTS OR APPLICATIONS

1,022,927 3/1966 Great Britain 204/58

662,063 4/1963 Canada 204/58

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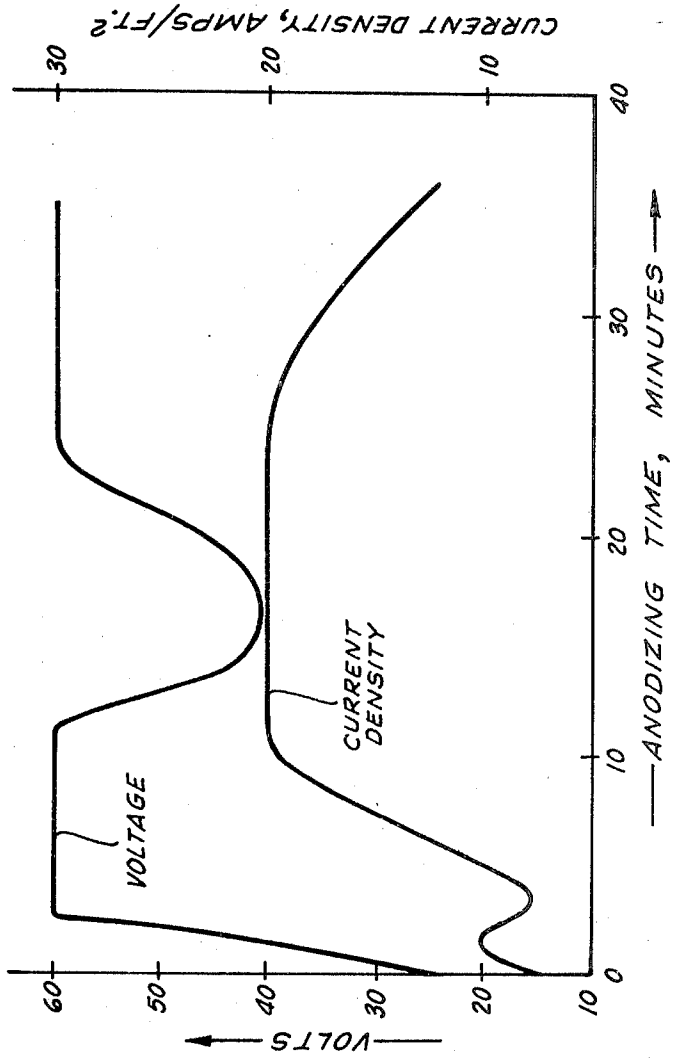
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[57] ABSTRACT

A process for integral color anodizing of aluminum and aluminum alloys wherein the aluminum piece is subjected as an anode to electrolysis in an aqueous solution containing sulfuric acid, and at least one compound selected from the group consisting of molybdates, tungstates, vanadates and manganates, a portion of which exists in a polyacid species.

4 Claims, 1 Drawing Figure



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PROCESS FOR INTEGRAL COLOR ANODIZING

BACKGROUND OF THE INVENTION

In many circumstances it is desirable to have a colored or hued surface on aluminum articles, particularly in architectural applications where aesthetic considerations are quite important. Several processes have been developed to produce colored oxide coatings; however, only one has met with any real commercial success, that being the integral color anodizing process basically described in U.S. Pat. No. 25,566, assigned to the present assignee. Methods such as dyeing a previously anodized surface with organic dyes or introducing metallic salts or oxides into a previously prepared anodic oxide coating suffer from the inherent disadvantage of requiring additional process coloring steps after the aluminum article has been anodized, which increase the cost as well as the inconvenience of the process. The dyeing of the anodic oxide coating has the additional disadvantage of producing a color which fades when exposed to ultraviolet light and also a color which is difficult to reproduce from batch to batch. The color anodizing process described in U.S. Pat. No. Re. 25,566 involves the anodization of the aluminum article in an aqueous electrolyte containing sulfosalicylic acid and sulfuric acid. Other sulfonic acids such as sulfophthalic acid have also been proven to be efficient in producing integral color anodized coatings. In general, the colors produced are uniform, reproducible and have a high aesthetic appeal necessary for architectural applications. In addition, these integrally colored anodic oxide coatings are also lightfast and highly abrasion resistant. However, the color ranges obtainable with the prior art electrolytes were generally dependent upon the alloy anodized.

SUMMARY OF THE INVENTION

The present invention is related to a novel electrolytic bath and the process of forming integrally colored anodic oxide coatings on the surface on an aluminum article. More particularly the invention is directed to the anodizing of aluminum and aluminum alloys in an aqueous electrolyte containing sulfuric acid and a free polyacid species selected from the group consisting of molybdic, tungstic, vanadic and manganic acids. The process is advantageously operated by subjecting the aluminum surface as the anode in an electrolytic cell to a current density between 10 and 50 a./sq.ft. until a final peak voltage across the cell between 40 and 80 volts is reached and then maintaining this peak voltage at a substantially constant level until the desired color density and oxide thickness is obtained.

DETAILED DESCRIPTION

In accordance with the present invention, it has been found that an aqueous solution of sulfuric acid and at least one soluble compound selected from a group consisting of molybdates, tungstates, vanadates and manganates a portion of which is in the polyacid form can be advantageously utilized in an electrolyte for the integral color anodizing of aluminum and aluminum alloys. Moreover, it has been found that the electrolyte produces a full range of lightfast architecturally desirable colors which are considerably more independent of the alloy composition of the workpieces than prior art electrolytes.

The sulfuric acid concentration can range from 0.1–1.5 percent. However, it is preferred to maintain this level between 0.1 and 0.8 percent by weight. The soluble molybdates, tungstates, vanadates, and manganates can range from 0.03 gram-mols/liter up to the limit of solubility; however, it is preferred to maintain the content of these compounds between 0.03 and 0.5 gram-mols/liter. At least 0.01 gram-mols/liter of the compounds must exist in free polyacid form. The term "polyacid" is used herein to include the dimers and trimers up to and including the higher molecular weight species. Although any molybdate, tungstate, vanadate and manganate or combinations thereof which are soluble within the limits set forth above can be utilized, it is preferred to use potassium, sodium and ammonium compounds, particularly the latter. The basic integral color range of light gold to black is obtainable with almost any aluminum alloy with the electrolytes of the present invention.

In the process of the present invention, the aluminum article is preferably subjected as the anode to a substantially constant current density between 5 and 50 a./ft. until a final peak voltage between 30 and 110 volts is reached and this final peak voltage is maintained at a substantially constant level until the desired integrally colored anodic oxide coatings are obtained. Integral color generation is very slow at peak voltages below 50 volts. Bath temperatures may range from 0° to 100° C., although for commercial applications it may be desirable to maintain these temperatures between 15° and 35° C. Other anodizing programs can be employed but the "constant current density followed by a constant voltage" program is the most efficient.

Electrolytes containing sulfuric acid and a molybdate or tungstate compound when subjected to electrolysis have a tendency to form high molecular weight polyacids. To a certain extent these polyacids tend to be somewhat colloidal in nature and thus incorporate themselves into the anodic oxide coating during anodizing in colloidal as well as anionic form. This incorporation introduces an additional advantage with the polymolybdic acid in that this incorporation tends to modify the basic integral color obtained during the anodizing process. The molybdates tend to give dark green and dark blue anodic oxide coatings. However, with polytungstic acid the incorporation phenomenon does not substantially change the basic integral color of light gold to black.

However, as the anodizing process proceeds the buildup of this colloidal species tends to reduce the efficiency of the electrolyte. To overcome this tendency to produce large amounts of high molecular weight species, it has been found that small quantities of oxalic acid, when introduced into the electrolyte will apparently complex with these compounds to form oxalato-molybdic acid and oxalato-tungstic acid and thus reduce the quantity of colloidal material in the electrolyte. However, the oxalic acid concentration should never equal or exceed the amount necessary to complex all of the polymolybdic and polytungstic acids for this removes the effectiveness of these compounds in the electrolyte and the electrolyte tends to behave as if only oxalic acid and sulfuric acid were present. At least an excess of 0.01 gram-mols/liter of free polymolybdic acid or polytungstic acid (i.e., not complexed with oxalic acid) must be in solution in the electrolyte at all times. During the course of anodizing, the concentration of free polymolybdic acid in solution is reduced due to the incorporation of this material into the anodic oxide coating and due to the reduction at the cathode of the dissolved compound during anodizing. However, during anodizing the complexed oxalic acid is oxidized to carbon dioxide and the complexed molybdate is reduced to approximately the +5 valence state, i.e., to the desired polymolybdic acid; and therefore free polymolybdic acid is continually released to the bath. If the polymolybdic acid is complexed with oxalic acid, the bath can be utilized almost to the point of complete exhaustion of the molybdate concentration in the bath.

Anodizing in a sulfuric acid polymolybdic acid electrolyte produces oxide coatings which can range from light golds to browns to blacks and also to greens and blues. However, when these anodized articles are sealed in an aqueous solution the greens and blues tend to disappear, leaving the anodic oxide coating ranging in color from light gold to black depending on the base color. It has been found that if these anodic oxide coatings are sealed in a nonaqueous solution such as a mixture of mineral oil and stearic acid or in a lanolin bath that the green and blue colors can be sealed into the anodic oxide coating and thus rendered permanent. These green and blue colors are lightfast and the nonaqueous sealed anodic oxide coatings have a corrosion and abrasion resistance comparable to those coatings which have been sealed in an aqueous solution. The oxide coating produced in a sulfuric acid polytungstic acid tend to become darker upon aqueous sealing. The

nonaqueous sealing bath mentioned above also functions efficiently with all of the sulfuric acid, polyacid produced anodic oxide coatings.

In the preferred embodiment of the present invention, the electrolyte is prepared by adding about 20 grams/liter ammonium molybdate and about 5 grams/liter sulfuric acid to water which produces a clear and colorless solution. Apparently the sulfuric acid converts the ammonium molybdate to a molybdic acid of the formula H_2MoO_4; however, this is recognized as only a barrier layer electrolyte which does not produce integral colored coatings. A workpiece, which can be aluminum or any conductive material, is immersed in this electrolyte and subjected to anodization which transforms (at the cathode) this molybdic acid solution into a blue polymolybdic acid solution which is the form needed to produce the integral colored anodic oxide coatings. The exact form of this polymolybdic acid species is not known, but it is believed to have an average oxidation state of probably closer to +5 than to +6. Having generated the proper acidic species of polymolybdic acid, the electrolyte is ready for anodizing. Anodizing in a polymolybdic acid electrolyte has the unique feature that the peak voltage is reached twice during the anodizing process. With a constant current density, constant-voltage program, the anodizing is advantageously carried out employing a constant-current, constant-voltage power supply whereby the desired current and peak or maximum voltage can be preset and automatically controlled at the desired levels. As illustrated in the drawing, a constant current density, constant-voltage anodizing program, results in the voltage reaching a peak value twice during the program. For example, in the anodizing operation the maximum voltage is first set at the desired peak level such as 60 volts. After a short run in period at low-current density and low voltage, the current density is set at the desired level such as 20 a./sq.ft. Thereafter no operator attention need be given to the anodizing. The voltage and current density will rise rapidly but the voltage will usually reach the maximum preset value before the current density will reach the preset value. The voltage will remain at the peak value for a few minutes then decrease to a minimum value of about 40 volts during which time current density will reach the desired maximum level. The voltage will rise during the constant current density stage until the peak value is reached a second time and thereafter remain at that value until the desired current quantity has passed through the workpiece. As shown in the drawings, the current density decays from the maximum value during the constant voltage period.

The peculiar features of the aforedescribed current density voltage relationships are a consequence of both the manner in which the current density and voltage controls are applied and the particular anodic reaction mechanisms resulting from the use of polymolybdic acid containing electrolytes. The color of the anodic oxide coating can be controlled in part by selecting a termination time during the final constant-voltage period. In the operation as described above, the anodizing program is substantially automatic and self-regulated with the consequent benefits of improved uniformity and reproducibility of color. Manual control may be employed and the program may be adjusted to produce the coating thickness and color desired.

To prepare a sulfuric acid polytungstic acid electrolyte, the pretreatment given above to form the polymolybdic species is necessary. However, with vanadate and manganate compounds the pretreatment is unnecessary because the proper polyacid species is obtained by merely adding the compound to the sulfuric acid solution. The vanadate- and manganate-containing electrolytes do not have a tendency to form the higher molecular weight species or colloidal species and thus little or no polyacid material is incorporated into the oxide coating.

The examples in the table are given to illustrate embodiments of the present invention.

Alloy	Electrolyte	Temperature, ° C.	Constant current density, amps/ft.²	Final peak voltage	Time to final peak voltage, minutes	Total anodizing time, minutes	Color
1100	1	25	20	60	30	30	Light brown-green.
	1	25	20	60	30	35	Dark brown-green.
	1	25	20	60	30	38	Blue-black.
1199	2	25	30	70	39	78	Dark brown-green.
	2	25	25	70	34	50	Light brown-green.
	4	25	20	70	15	40	Blue-black.
5005	3	25	20	70	18.5	90	Dark blue.
	3	25	20	70	15	49	Dark blue-green.
	3	25	20	70	20	20	Brown-green.
	2	25	20	70	34	57	Blue-black.
	2	25	30	70	20	29	Brown-green.
	2	25	25	70	28	30	Do.
	5	25	20	80	10	20	Brown.
	5	25	20	90	15	40	Black.
	5	25	5	90	20	30	Light brown.
	5	25	20	110	15	20	Black.
6061	2	25	20	70	24	40	Blue-black.
	2	25	20	70	23.5	26	Dark blue.
	2	25	20	70	18	18	Dark blue-brown.

NOTE:
Electrolyte 1—20 gms./liter ammonium paramolybdate, 5 gms./liter sulfuric acid, balance water.
Electrolyte 2—66 gms./liter ammonium paramolybdate, 5 gms./liter sulfuric acid, 45 gms./liter oxalic acid, balance water.
Electrolyte 3—17.6 gms./liter ammonium paramolybdate, 3 gms./liter sulfuric acid, 20 gms./liter oxalic acid, balance water.
Electrolyte 4—72.7 gms./liter ammonium paramolybdate, 8 gms./liter sulfuric acid, 45 gms./liter oxalic acid, balance water.
Electrolyte 5—16.5 gms./liter sodium tungstate, 5 gms./liter sulfuric acid, 5 gms./liter oxalic acid, balance water.

Each of the specimens were cleaned in an inhibited alkaline cleaner, etched in a NaOH solution, desmutted in a nitric acid solution and anodized as shown in the table. All reported colors are for the unsealed specimen except as otherwise noted. The compositions of the above aluminum alloys are given in *Metals Handbook*, Eighth Edition, Volume I, page 917.

What is claimed is:

1. A process for forming an integrally colored oxide coating on an aluminum article comprising anodizing said aluminum article as the anode in an aqueous electrolyte consisting essentially of from about 0.1 to about 0.8 percent sulfuric acid, at least 0.03 gram-mols/liter of a compound selected from a group consisting of molybdates, vanadates, tungstates and

manganates, at least 0.01 gram-mols/liter of said compound existing as a free polyacid species, and the balance water.

2. The process according to claim 1 wherein the sulfuric acid concentration is from about 0.1 to 0.8 percent by weight and the concentration of a compound selected from the group consisting of molybdates, vanadates, tungstates and manganates is from about 0.03 to 0.5 gram-mols/liter.

3. The process according to claim 2 wherein the compound is selected from the group consisting of molybdates and tungstates.

4. The process according to claim 3 wherein a portion of a compound selected from the group consisting of molybdates and tungstates is complexed with oxalic acid.

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