3,682,790
Patented Aug. 8, 1972

3,682,790

PROCESS OF PRODUCING ANODIC OXIDE FILMS ON ALUMINUM

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No Drawing. Filed July 29, 1969, Ser. No. 854,341
Int. Cl. C23b 9/02
U.S. Cl. 204—58 19 Claims

ABSTRACT OF THE DISCLOSURE

An anodic coating on aluminum and its alloys can be obtained by immersing the aluminum as an anode in an aqueous electrolyte containing boric/hydrocarboxylic chelate acid anions to which sulfuric acid or water soluble sulfate or bisulfate salts are added, and passing an electrical current of suitable voltage and current density through the electrolyte solution for a predetermined time.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method of electrolytically coating aluminum or its alloys using an aqueous electrolyte solution.

PRIOR ART RELATING TO THE DISCLOSURE

The production of anodic oxide films on aluminum and its alloys has been accomplished by anodizing in aqueous electrolyte solutions of sulfuric acid, oxalic acid or sulfuric acid and oxalic acid mixtures. Anodizing solutions of boric acid with or without sulfuric acids are known to give anodic coatings. The anodic coatings produced, however, are barrier layer or "high resistance" coatings of no more than about one micron in thickness. Barrier layer coatings are not useful in architectural applications.

Similarly, anodizing solutions of oxalic acid with sulfuric acid are known to give anodic coatings. For example, see U.S. Patent 3,252,875.

Processes for producing anodic films on various metals are discussed in detail in Young, "Anodic Oxide Films," Academic Press, 1961.

SUMMARY OF THE INVENTION

This invention has as one of its objects the production of anodic oxide coatings on aluminum and its alloys.

A further object of this invention is a method of producing corrosion resistant anodic oxide films on aluminum and its alloys using an electrolyte solution comprising boric/hydroxycarboxylic chelate acid anions to which a minor amount of sulfuric acid or water soluble sulphate or bisulfate salts are added.

The electrolyte containing boric/hydroxycarboxylic chelate acid anions to which sulfuric acid or water soluble sulphate or bisulfate salts are added in small amounts results, on passing an electric current through the electrolyte, in colored "porous" or "low-resistance" anodic coatings which grow at constant voltage to the desired thickness. For practical reasons, a thickness up to 1.5 mils is sufficient. Kinetics for the coating using the anodizing electrolyte of this invention are not well understood; however, when boric acid is mixed with the hydroxycarboxylic acids set forth herein the resulting hydrogen ion concentration of the electrolyte solution is much higher because of the formation of a complex ortho boric chelate of boric acid and the hydroxycarboxylic acid. The chelate acid anions in the electrolyte solution, from whatever source obtained, make up the major portion of the electrolyte solution.

Hydroxycarboxylic acids useful in the anodizing solution of this invention include those having more than 2 carbon atoms, specifically alpha hydroxycarboxylic acids such as malic acid, tartaric acid, mandelic acid, 2-hydroxybutanoic acid, and 2-hydroxy, 2-methylpropanoic acid; beta hydroxycarboxylic acids such as 2-hydroxypropanoic acid, 2-methyl, 2-hydroxypropanoic acid, citric acid; polyhydroxy carboxylic acids such as glyceric acid, 2,3,4-trihydroxybutanoic acid and gluconic acid; and gamma hydroxycarboxylic acids. Mixtures of the hydroxycarboxylic aicds can also be used.

Sulfuric acid or water soluble sulfate or bisulfate salts, or mixtures thereof, are added to the electrolyte solution in relatively small quantities, i.e. as little as 0.001 gm. per liter calculated as sulphate. The concentration of sulfuric acid or sulfate or bisulfate salts can be as high as 5.0 gms./liter if desired, although this is not necessary. Water soluble sulphate salts such as alkali metal sulfates or bisulfates or ammonium sulphate or bisulfate can be used.

The concentration of boric acid used to form the chelate in the anodizing solution may range from 0.2 Molar up to the solubility limit of boric acid in aqueous solutions and preferably from 0.2 to 1.0 Molar.

The concentration of hydroxycarboxylic acid used to form the chelate in the anodizing solution ranges preferably from 0.2 to 2.0 Molar.

Aluminum or its alloys are immersed in the anodizing electrolyte solution previously described. Stainless steel or other suitable materials are used as the cathode. The anodizing process is carried out using DC current.

The electrolyte solution described may be employed over a wide range of operating conditions (voltage, current density, temperature). A DC voltage of up to 150 volts is normally applied to maintain a predetermined current density. Normally a current density ranging from 12 to 36 amps/sq. ft. is used. The current density is maintained constant until a predetermined peak voltage is reached, at which time the current density is allowed to fall. The peak voltage may be the final voltage. The temperature of the anodizing electrolyte solution is usually maintained between 60 and 90° F.

Time of treatment depends upon current density, thickness of coating desired and color of the coating desired.

The colors of the anodic film produced by the above process are various shades of grey and bronze.

Table I illustrates the operating conditions employed in anodizing an aluminum 6063 alloy using anodizing electrolyte solutions of several different hydroxycarboxylic acids at different concentrations. The thickness and color of the anodic films are described.

plex, and 0.001 to 5.0 grams per liter sulfuric acid, and

passing a direct electrical current of up to 150 volts and a current density of from 12 to 36 amps. per sq. ft. through the electrolyte solution between the anode and cathode at an electrolyte solution temperature of 60 to 90° F. to obtain a bronze-colored coating on the aluminum anode.

TABLE I

	Aluminum, designation	Boric acid, g./l.	Hydroxy carboxylic acid	Grams/liter	$SO_4^{=}$	Grams/liter	Voltage, volts D.C.	Temp., °F.	Current, amps/sq. ft.	Time, mins.	Thickness, mils	Color
1	6063 Alloy	19.4	Citric acid monohydrate.	60.0	Na_2SO_4	1.8–3.0	0–100	70	24	30	0.5–0.8	Medium to dark bronze.
2	do	30.0	do	60.0	H_2SO_4	0.7–2.0	0–120	70	24	30	0.4–0.6	Light to dark bronze.
3	do	30.0	(d)tartaric acid		H_2SO_4	1.0	0–120	70	24	15	0.3	Medium bronze.
4	do	27.7	(dl)malic acid	60.0	H_2SO_4	0.1–0.7	0–120	70	24	30	0.2	Light brown.
5	do	27.7	do	60.0	H_2SO_4	0.8–1.0	0–80	70	24	30	0.4–0.6	Light to dark bronze.
6	do	30	Gluconic acid	60.0	H_2SO_4	0.5	0–55	70	24	13	0.2	Medium bronze.
7	do	27.7	(dl)mandelic acid	60.0	H_2SO_4	0.6–1.2	0–120	70	24	30	0.2	Gray.
8	do	27.7	do	60.0	H_2SO_4	1.3–2.7	0–52	70	24	30	0.4–0.9	Light to dark brown.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing a low-resistance porous, bronze-colored anodic coating on aluminum comprising:

providing at least one cathode,

immersing the aluminum as anode in an aqueous electrolyte consisting essentially of boric hydroxycarboxylic chelate acid anions formed in equilibrium with boric acid and a hydroxycarboxylic acid capable of forming a complex boric chelate with a resulting increase in the hydrogen ion concentration of the electrolyte and at least 0.001 gram per liter sulfate ions from sulfuric acid, water soluble sulfate or bisulfate salts, and

passing a direct electrical current through the electrolyte solution between the anode and cathode to obtain a colored anodic coating on the aluminum anode.

2. The method according to claim **1** wherein the aqueous electrolyte solution comprises at least 0.2 Molar boric acid, 0.2 to 2.0 Molar hydroxycarboxylic acid and at least 0.001 gm. per liter sulfate.

3. The method according to claim **1** wherein the electrical current is passed through the electrolyte solution at a current density ranging from about 12 to 36 amps./sq. ft.

4. The method according to claim **1** wherein the hydroxycarboxylic acid is one selected from the group consisting of citric acid, tartaric acid, malic acid, gluconic acid and mandelic acid.

5. The method according to claim **1** wherein the hydroxycarboxylic acid is citric acid.

6. The method according to claim **1** wherein the hydroxycarboxylic acid is tartaric acid.

7. The method according to claim **1** wherein the hydroxycarboxylic acid is malic acid.

8. The method according to claim **1** wherein the hydroxycarboxylic acid is gluconic acid.

9. The method according to claim **1** wherein the hydroxycarboxylic acid is mandelic acid.

10. A method of producing a porous, bronze-colored anodic coating on aluminum comprising:

providing at least one cathode,

immersing the aluminum as anode in an aqueous electrolyte solution consisting essentially of from 0.2 to 1.0 Molar boric acid, 0.2 to 2.0 Molar hydroxycarboxylic acid selected from the group consisting of citric acid, tartaric acid, maleic acid, gluconic acid and mandelic acid, the boric acid and hydroxycarboxylic acid forming a boric/hydroxycarboxylic complex, and 0.001 to 5.0 grams per liter sulfuric acid, and

11. An aqueous anodizing electrolyte consisting essentially of boric/hydroxy carboxylic chelate acid anions formed in equilibrium with boric acid and a hydroxycarboxylic acid capable of forming a complex boric chelate with a resulting increase in the hydrogen ion concentration of the electrolyte and at least 0.001 gram per liter sulfate ions from sulfuric acid, water soluble sulfate or bisulfate salts.

12. The electrolyte solution of claim **11** wherein the hydroxycarboxlic acid is one selected from the group consisting of citric acid, tartaric acid, malic acid, gluconic acid and mandelic acid.

13. The electrolyte solution of claim **11** wherein the concentration of boric acid ranges from 0.2 Molar up to the limit of its solubility in an aqueous solution, the concentration of hydroxycarboxylic acid ranges from 0.2 to 2.0 Molar and the concentration of sulfate ion ranges from 0.001 to 5.0 grams per liter.

14. The solution according to claim **11** wherein the hydroxycarboxylic acid is citric acid.

15. The solution according to claim **11** wherein the hydroxycarboxylic acid is tartaric acid.

16. The solution according to claim **11** wherein the hydroxycarboxylic acid is malic acid.

17. The solution according to claim **11** wherein the hydroxycarboxylic acid is gluconic acid.

18. The solution according to claim **11** wherein the hydrocarboxylic acid is mandelic acid.

19. Anodized aluminum having a low resistance, porous, bronze-colored anodic coating produced by the method of claim **1**.

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