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METHOD OF PRODUCING A COLORED ANODIC OXIDE FILM ON ALUMINUM

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ABSTRACT OF THE DISCLOSURE

The subject matter of the specification herein relates to the production of colored anodic oxide films on aluminum surfaces, which, at the same time, have excellent resistance to abrasion and weathering. The method comprises employing an electrolyte comprising an aqueous solution containing 1.5–40% by weight of naphthalenedisulfonic acid and 0.1–3.0% by weight of sulfuric acid at an initial cell voltage of at least 20 volt.

This invention relates to a method of producing an anodic oxide film on aluminum. More particularly, the invention pertains to a method in which aluminum or an aluminum base alloy (hereinafter referred to as aluminum) is anodized in a novel aqueous acidic solution to form a colored anodic oxide film on the aluminum surface.

A method of producing an anodic oxide film in an electrolyte comprising an aqueous sulfuric acid solution to form a dense oxide film on the aluminum surface has been most widely carried out on commercial scale. In the above method, the sulfuric acid solution is ordinarily used at a temperature in the vicinity of room temperature, and in order to maintain said temperature, the electrolyte must be cooled.

Films obtained according to the above method are ordinarily colorless, though they are colored in the case of certain alloys.

Recently a hard anodic oxide film higher in abrasion resistance has come to be obtained by anodizing aluminum at such a low temperature as about 0° C. in an electrolyte comprising an aqueous sulfuric acid solution. The thus obtained film is not only excellent in abrasion resistance but also is colored to metallic grey, greyish brown or dark brown. These colours are attractive for the application of aluminum to architecture and the like. However, in order to maintain the electrolyte temperature at about 0° C., the expenses of apparatus and operation are necessarily increased. Therefore, the development of more practical process for the production of such a film has been desired.

An object of the present invention is to provide a method in which aluminum is anodized in a novel electrolyte to form a colored anodic oxide film on the aluminum surface.

Another object is to provide a method in which a colored anodic oxide film excellent in resistance to abrasion and weather can be obtained at an electrolyte temperature in the vicinity of room temperature.

The present inventors have found that excellent anodic oxide films attaining the above object are obtained by anodizing aluminum in an electrolyte comprising an aqueous solution containing 1.5–40% by weight of naphthalenedisulfonic acid and 0.1–3.0% by weight of sulfuric acid at an initial cell voltage of at least 20 volt.

Naphthalenedisulfonic acid employed in the present invention includes all isomers of naphthalenedisulfonic acids, or the mixture thereof, among which the mixture

containing 1,5-naphthanedisulfonic acid as the main component is preferable. Aluminum alloys employed in the present invention include every alloy which may form thick oxide film by anodizing in an electrolyte containing sulfuric acid.

The colours of the resulting oxide films can be varied by using an electrolyte within the above component range and varying the kind of aluminum alloys employed, working conditions of aluminum, and anodizing conditions. The use of the electrolyte of the present invention makes it possible to obtain, even at a low temperature, such a hard anodic oxide film as produced according to the conventional method using an aqueous sulfuric acid solution. Further, at an electrolyte temperature of about room temperature, e.g. 15–30° C., it is also possible to form a coloured anodic oxide film excellent in resistance to abrasion and weather. However, it is not advantageous economically that aluminum alloy is anodized at an electrolyte temperature of 0° C. It is advantageous economically that the present electrolyte is used at a temperature of 15° to 30° C.

As the concentration of naphthalenedisulfonic acid increases, the cell voltage becomes lower and the colour of the resulting film becomes lighter. On the other hand, as the concentration of said acid decreases, the cell voltage becomes higher and the colour of the resulting film gradually becomes deeper from brown to deep brown and black. In case the concentration of said acid is less than 1.5%, it becomes difficult to obtain a practical, uniform, colored film. Preferable concentration range of naphthalenedisulfonic acid is 5–20% by weight.

In case the sulfuric acid concentration is less than 0.1%, a uniform, colored film is difficultly obtainable, while in case said concentration is more than 3.0%, the colour of the resulting film is getting lighter with increasing the sulfuric acid concentration and, at last, the film becomes colorless, though the cell voltage lowers. Preferable concentration range of sulfuric acid is 0.3–1.5% by weight. In case of electrolyte comprising an aqueous solution containing 10–20% of sulfuric acid and 5–25% of naphthalenedisulfonic acid, the dissolution of the anodic oxide film due to the electrolyte is inhibited during the electrolysis to make it possible to use said electrolyte to anodizing treatment at a high current density. However, the resulting film is colorless or is merely colored to a slight degree, though the colour depends on the kind of the alloy employed. In case the present electrolyte is used, the most preferable result may be obtained by anodizing an aluminum at a current density of 1 to 3 a./dm.^{2}. At an electrolyte temperature of room temperature, i.e. about 20° C., the cell voltage becomes 20–80 v. in case of the anodizing treatment at a current density of 1–3 a./dm.^{2}.

If anodizing is intended to, at the initial voltage of below 20 volt, it is necessary that the anodizing is carried out at lower current density or at higher electrolyte temperature or the amount of sulfuric acid in the electrolyte is increased. However in any of these cases a thick, hard and deep coloured objective film cannot be obtained.

At a constant current density, the cell voltage is gradually increased according to the growth of the thickness of the film. There are some cases where, depending on the kind of the aluminum and aluminum alloys employed, a burning phenomenon is observed when the cell voltage has reached above 60 v. during the anodizing at the same current density. In such cases, the cell voltage is desirably maintained at below a voltage where the burning phenomenon takes place. Accordingly the anodizing is first carried out under a constant current and thereafter under a constant cell voltage in case the burning takes place. The burning phenomenon can also be prevented by elevating the electrolyte temperature.

As the electric current, either of alternating of direct current is used, and, if necessary, the both may be superimposed. The anodizing time is decided according to the current density employed and the desired thickness of the resulting film, but a colored anodic oxide film having sufficient abrasion resistance can be obtained within an anodizing time of 30–60 minutes. The obtained film thickness is usually 15 to 20μ per 1 a. hr./dm.^{2}.

a./dm.^{2} at the end of the anodizing. The film formed by this treatment was sealed in the way similar to that of the Example 1. The film colour was brown and the film thickness was about 35μ.

Several examples of anodizing conditions and the coloured anodic oxide films obtained by a method similar to that of the Example 1 or 2 are shown in the following table.

Ex.	Electrolyte (wt. percent) (remainder: water)	Aluminum and aluminum alloy (A. A. designation)	Alloy composition						Shape	Current density (A./dm.^{2})	Required voltage (v.)	Electrolyte temp. (° C.)	Time (min.)	Film colour
			Si	Mg	Fe	Mn	Cr	Cu						
3	Naphthalenedisulfonic acid, 30; H_2SO_4, 1.8.	1100	Nominal impurities						Sheet	2.0	20-30	15-20	60	Yellowish silver.
4	Naphthalenedisulfonic acid, 18; H_2SO_4, 1.2.	6063-T_5	0.43	0.55	0.17				Extrusions	2.0	20-30	20	60	Do.
5	Naphthalenedisulfonic acid, 15; H_2SO_4, 1.9.	6061-T_4	0.63	0.94	0.17		0.33	0.23	Sheet	3.0	25-60	15-20	60	Brown.
6	Naphthalenedisulfonic acid, 9; H_2SO_4, 0.6.	6351-T_5	0.93	0.70	0.39	0.48			Extrusions	1.0	30-45	20	60	Dark brown.
7	do	6351-T_5	0.93	0.70	0.39	0.48			do	1.5	30-55	20	60	Black.
8	do	6351-T_5	0.93	0.70	0.39	0.48			do	2.0	30-70	20	40	Do.
9	do	Our work-T_5.	0.96	0.67	0.17				do	2.0	28-70	20	60	Brown.
10	do	do	0.42	0.62	0.16		0.24		do	1.8	30-55	20	60	Do.
11	Naphthalenedisulfonic acid, 4.5; H_2SO_4, 0.3.	6351-T_5	0.93	0.70	0.39	0.48			do	*1.5	30-56	25	60	Black.
12	Naphthalenedisulfonic acid, 1.5; H_2SO_4, 0.1.	Our work-T_5.	0.96	0.67	0.16		0.24		do	*1.0	35-56	25	60	Brown.

*Anodizing treatment was effected at a constant current density until the cell voltage had reached 56 v. and thereafter at a constant voltage of 56 v.

In order to illustrate the present invention the following examples are given. But the present invention is not intended to be limited to the examples.

EXAMPLE 1

An aluminum base alloy 6351–T_5 (extrusions) containing 0.93% by weight of silicon, 0.70% by weight of magnesium, 0.39% by weight of iron and 0.48% by weight of manganese was subjected to pretreatments of degreasing, etching and desmutting by a usual method and anodized in an aqueous electrolyte containing 9% by weight of naphthalenedisulfonic acid and 0.6% by weight of sulfuric acid at a temperature of 25° C. at a current density of 2 a./dm.^{2} for 60 minutes under stirring by bubbling air into the electrolyte. The cell voltage increased gradually from 30 v. up to 55 v. at the end of the anodizing. The current used possessed the wave form obtained by full wave rectification of single phase A.C.

The film formed by this anodizing was treated with boiling deionized water to seal the pores of the film. The colour of the film was black and the film thickness was about 35μ.

EXAMPLE 2

An aluminum base alloy 6063–T_5 (extrusions) containing 0.43% by weight of silicon, 0.55% by weight of magnesium and 0.17% by weight of iron was subjected to pretreatments similar to that of the Example 1 and anodized in an aqueous electrolyte containing 9% by weight of naphthalenedisulfonic acid and 0.6% by weight of sulfuric acid at a temperature of 20° C. with an initial current density of 2.4 a./dm.^{2}. Within 37 minutes from the beginning of anodizing the cell voltage increased gradually from 30 v. to 56 v.

Thereafter the alloy was anodized under a constant voltage of 56 v. for 24 minutes. The current density was 1.3

What we claim is:

1. A method of producing a coloured anodic oxide film on aluminum or an aluminum alloy, which comprises anodizing aluminum or an aluminum alloy in an electrolyte consisting essentially of a solution containing 1.5–40% by weight of naphthalenedisulfonic acid and 0.1–3.0% by weight of sulfuric acid, the remainder by weight being water, at an initial cell voltage of at least 20 volt.

2. A method according to claim 1, wherein the anodizing treatment is effected by use of an electrolyte comprising an aqueous solution containing 5–20% by weight of naphthalenedisulfonic acid and 0.3–1.5% by weight of sulfuric acid at a current density of 1–3 a./dm.^{2} and at an electrolyte temperature of 15–30° C.

3. A method according to claim 1, wherein the anodizing treatment is first effected at a constant current density of 1–3 a./dm.^{2} and thereafter at a constant voltage.

4. A method according to claim 2, wherein the anodizing treatment is first effected at a constant current density of 1–3 a./dm.^{2} and thereafter at a constant voltage.

5. A colored anodic oxide film on aluminum or an aluminum alloy produced according to claim 1.

6. A colored anodic oxide film on aluminum or an aluminum alloy produced according to claim 2.

7. A colored anodic oxide film on aluminum or an aluminum alloy produced according to claim 2.

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