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3,328,274

METHOD OF ANODIZING ALUMINUM

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No Drawing. Continuation of application Ser. No. 314,497, Oct. 7, 1963. This application Nov. 25, 1966, Ser. No. 597,164

2 Claims. (Cl. 204—58)

This application is a continuation of our copending application Ser. No. 314,497 filed Oct. 7, 1963, now abandoned.

This invention relates to a method for producing an integrally colored black anodic oxide coating on specific aluminum alloys, and the product resulting from this process.

The process of anodizing aluminum has been practiced by placing an aluminum body in an electrolyte as the anode in an electrical circuit which includes that electrolyte. When a current is passed through the cell thus formed, the aluminum is oxidized by oxygen liberated at the anode during electrolysis to produce what is known as an anodic oxide coating or an anodized coating on the aluminum body. The process is popularly known as *anodizing* and the product is popularly known as *anodized aluminum*, and it is characterized by a pleasing, lustrous appearance.

The usual electrolyte for commercial anodizing is sulphuric acid. Recently, however, mixed acid electrolytes containing both sulphuric acid and certain organic acids have produced integrally colored anodic oxide coatings ranging in color from light gold or bronze to black. Integrally colored coatings are those in which the anodic oxide itself is colored in contrast to those coatings that are dyed. Integrally colored coatings are characterized by being light-fast and by freedom from bleeding or other loss of color.

To obtain a specific color, the electrical program for anodizing, the composition of the alloy and the composition of the electrolyte must be carefully selected.

Colored anodized aluminum has found wide use for architectural purposes, both interior and exterior, as wall panels and curtain walls, doors, and frames for panels, curtain walls, doors and windows.

Much architectural aluminum is of aluminum alloys in the magnesium silicide family, and one particularly popular alloy is the aluminum-magnesium silicide alloy designated by the Aluminum Association as 6063. Unfortunately, although 6063 has very desirable properties, heretofore no means for producing integrally colored black anodic oxide coating on 6063 has been available. As may be expected, black is a very popular color for use in integrally colored anodic oxide coatings. Accordingly it is an object of this invention to provide a method for producing an integrally colored black anodized 6063 article.

In accordance with this invention, a black anodized 6063 article is produced by proper selection of both the electrolyte in which anodizing is effected and by proper selection of the electrical program to which the article is subjected. The process for anodizing first requires that the 6063 alloy be immersed as the anode in an electrolyte consisting essentially of sulfophthalic acid and sulphuric acid, said electrolyte containing at least about 25 grams per liter of sulfophthalic acid and at least 0.1 g./l. of sulphuric acid, although it may contain as much as 150 g./l. of sulfophthalic acid or more, greater quantities up to the limit of solubility being effective but unnecessary to obtain the desired effect, and as much as 15 g./l. of sulphuric acid or more. Preferably, the electrolyte contains

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from about 70 to 100 g./l. of sulfophthalic acid and from about 1 to about 5 g./l. of sulphuric acid. The electrolyte also may contain normal impurities and a certain amount of aluminum ion which is present after a short period of operation due to dissolving of the aluminum being anodized by the electrolyte.

With the 6063 article immersed in the above-described electrolyte, anodizing is effected by forming a direct current circuit which includes both the 6063 article and the electrolyte. The former is the anode with respect to the cell containing the electrolyte and a cathode of suitable material, such as type 302 stainless steel. The anodizing process in accordance with this invention, is effected in two distinct stages.

The first stage of the anodizing process is effected at a current density of from about 15 amperes per square foot to about 50 amperes per square foot, but whatever current density is selected, it is held approximately constant during the first stage of the anodizing period. Preferably, a current density of from about 25 to about 40 amperes per square foot is employed. As the anodic oxide coating builds up in thickness, the electrical resistance of the cell increases so that it is necessary to raise the voltage continuously in order to maintain the current density approximately constant. The first stage of the program is called the constant current density stage of the process.

When a certain pre-selected voltage is reached the second stage of the process is begun, in which the voltage is maintained approximately constant and the current density is permitted to decay. The second stage is termed the constant voltage portion of the program.

The constant voltage electrolysis is continued for a time sufficient to produce a black anodic oxide coating of the desired thickness on the article, and the time required is variable depending upon the alloy composition of the article, the temperature of the electrolyte, the magnitude of the current density in the first stage of the process, and the magnitude of the voltage selected as the constant voltage for the second stage of the process. The constant voltage stage may be effected at voltages varying from about 25 volts to about 100 volts or more, but preferably it is effected at voltages of from 55 to 75 volts.

Several generalities may be borne in mind as guides for selecting variables within the scope of the process described herein. One is that at higher current densities the peak voltage will be reached more quickly and a dark coating will be obtained more rapidly so that the process may be effected in a shorter length of time. Another is that higher maximum voltages will provide dark colors sooner and will also result in a process effected in a shorter length of time. Another variable which may be adjusted to suit the need of the processor is the temperature. At lower temperatures black coatings may be produced which are thinner and which are produced in shorter periods of time than at higher temperatures. In this respect, the temperature at which the process may be effected may be varied from very low temperatures to normal room temperatures but preferably from temperatures of from about 45° F. to about 85° F. which is a temperature range that may be maintained readily with ordinary equipment. Depending upon the composition of the alloy, the composition of the electrolyte and the processing conditions selected, black anodic oxide coatings may be produced in a wide range of thicknesses, and thicknesses from 0.30 mil to 2.0 mils or more are readily obtainable.

The following examples illustrate several processes embodying this invention and are presented here as illustrative of the invention rather than limiting in any way. Although the alloys used are of varying composition, all are within the composition limits of the Aluminum Asso-

ciation specifications for 6063 alloy, shown in Table I in weight percent.

TABLE I

Silicon	0.2-0.6
Iron, max.	0.35
Copper, max.	0.10
Manganese, max.	0.10
Magnesium	0.45-0.90
Chromium, max.	0.10
Zinc, max.	0.10
Titanium, max.	0.10
Others, max.	0.15
Aluminum	Balance

Example 1

A specimen in the form of an extrusion of aluminum alloy containing in weight percent 0.4 silicon, 0.24 iron, 0.04 copper, 0.60 magnesium, 0.01 zinc and 0.01 titanium and normal impurities, was prepared for anodizing by the following operations:

- (1) etched for 10 minutes in 5% NaOH solution maintained at 130° F.
- (2) washed with water to remove NaOH.
- (3) desmutted by immersion in a 35% by weight nitric acid solution.
- (4) washed in water to remove nitric acid.

Following the preparatory operations, the specimen was anodized by immersing it in an aqueous electrolyte containing 100 g./l. of sulfophthalic acid and 5 g./l. of sulphuric acid and maintained at a temperature of 77° F. Anodizing was begun by passing a direct current through the specimen at a current density of 27 amperes per square foot until a preselected peak voltage of 60 volts was reached. After 14.8 minutes of anodizing, while the voltage was raised continuously to maintain the current density at 27 amperes per square foot, the peak voltage of 60 volts was reached after which the anodizing was continued at a constant voltage of 60 volts for a total anodizing time of 81.5 minutes. The sample was removed from the electrolyte, washed in water, and immersed for 10 minutes in an aqueous bath maintained at 205° F. and containing 0.6 g./l. of sodium lignosulfonate and 0.5 g./l. of nickel acetate to effect sealing of the anodic oxide film that was formed. There resulted a 6063 aluminum alloy covered with a smut-free anodic oxide film that was block in color and approximately 1.5 mils thick.

Example 2

An aluminum alloy containing in weight percent 0.40 silicon, 0.22 iron, 0.04 copper, 0.63 magnesium, 0.01 zinc and 0.01 titanium was prepared for anodizing in accordance with steps 1, 2, 3 and 4 described in Example 1. The specimen was then immersed in an aqueous electrolyte at 77° F. and containing 53.2 g./l. of sulfophthalic acid, 7.78 g./l. of sulphuric acid and 4.1 g./l. of aluminum ion which resulted from previous use of the electrolyte. Anodizing in the first stage was effected at 27 amperes per square foot for a period of 8.5 minutes at which time the peak voltage of 60 volts was attained. Subsequently, the anodizing was effected at a constant voltage of 60 volts for a total anodizing time of 35 minutes. The specimen was washed and sealed in accordance with the procedure set forth in Example 1 and upon examination it was found to be coated with a dense black anodic oxide film 0.7 mil thick.

Example 3

A specimen of aluminum alloy containing by weight percent 0.41 silicon, 0.24 iron, 0.04 copper, 0.61 magnesium, 0.01 zinc and 0.01 titanium was prepared for anodizing in accordance with steps 1 through 4 of Example 1. Subsequently the specimen was immersed in an aqueous electrolyte maintained at 77° F. and containing 95.5 g./l. of sulfophthalic acid, 9.9 g./l. of sulphuric acid, and 4.4 g./l. of aluminum ion. Anodizing was conducted at a current density of 27 amperes per square

foot and after a period of 14 minutes the preselected peak voltage of 60 volts was attained whereafter anodizing was continued at a constant voltage of 60 volts for a total anodizing time of 76 minutes. The specimen was washed and sealed in accordance with Example 1 and found to be coated with a dense black anodic oxide film 1.8 mils thick.

Example 4

An aluminum alloy containing, in weight percent, 0.40 silicon, 0.24 iron, 0.04 copper, 0.63 magnesium, 0.01 zinc, and 0.01 titanium was prepared for anodizing in accordance with steps 1 through 4 in Example 1. The specimen was then immersed as the anode in an aqueous electrolyte maintained at 77° F. and containing 100 g./l. of sulfophthalic acid, 5 g./l. of sulphuric acid and 0.05 g./l. of aluminum ion. Anodizing was conducted at an initial current density of 27 amperes per square foot for a period of 12 minutes at which time the voltage had been raised to 60 volts in order to maintain the current density constant. Subsequently anodizing was continued at a constant voltage of 60 volts for a total anodizing time of 89 minutes. The specimen was washed and sealed in accordance with Example 1 and found to have a black coating 1.78 mils thick.

Example 5

A specimen of an aluminum alloy containing, in weight percent, 0.40 silicon, 0.24 iron, 0.04 copper, 0.63 magnesium, 0.01 zinc, and 0.01 titanium was prepared for anodizing in accordance with steps 1 through 4 of Example 1. Subsequently the specimen was immersed in an aqueous electrolyte maintained at 77° F. and containing 94.6 g./l. of sulfophthalic acid and 4.5 g./l. of sulphuric acid. The specimen was anodized at an initial current density of 27 amperes per square foot for a period of 14.5 minutes at which time a predetermined voltage of 60 volts was reached. Anodizing was continued for a total of 75.8 minutes after which the specimen was removed from the anodizing tank and washed and sealed in accordance with Example 1. The alloy was found to have a black coating 1.75 mils thick.

Example 6

A specimen of aluminum alloy containing, in weight percent, 0.40 silicon, 0.24 iron, 0.04 copper, 0.66 magnesium, 0.01 zinc and 0.01 titanium was prepared for anodizing in accordance with steps 1 through 4 of Example 1. The specimen was then immersed in an aqueous electrolyte maintained at 77° F. and containing 101.2 g./l. of sulfophthalic acid, 4.85 g./l. of sulphuric acid, and a small but undetermined amount of aluminum ion. Anodizing was effected at an initial current density of 27 amperes per square foot for a period of 16.8 minutes at which time the preselected voltage of 60 volts was reached. Anodizing was continued at 60 volts for a total time of 67 minutes after which the specimen was removed from the electrolyte, washed, and sealed in accordance with Example 1. The specimen was found to have a black coating 1.6 mils thick.

Example 7

A specimen of 6063 aluminum alloy was prepared for anodizing as described in steps 1-4 of Example 1, was immersed as an anode in an aqueous electrolyte containing 80.0 g./l. of sulfophthalic acid, 3.6 g./l. of sulphuric acid and 0.07 g./l. of aluminum ion. Anodizing was effected at an initial current density of 40 amperes per square foot until a peak preselected voltage of 72 volts was attained after which the anodizing process was continued at 72 volts for a total anodizing period of 45 minutes. After washing and sealing in accordance with Example 1, the alloy was found to have a black coating the thickness of which was not determined.

Example 8

Another specimen of 6063 alloy is prepared for anodizing as described in Example 1. The specimen is then

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immersed as the anode is an electrolyte containing 80 g./l. of sulphophthalic acid, 3.6 g./l. of sulphuric acid, and 0.07 g./l. of aluminum ion. Anodizing is effected at a temperature of 65° F., and at an initial current density of 36 amperes per square foot until a preselected voltage of 96 volts was reached, approximately 10 minutes from the start of anodizing. Further anodizing at approximately 96 volts is continued for a total anodizing time of 25 minutes. After washing and sealing in accordance with Example 1, the alloy is found to have a black coating 0.7 mil thick.

As described in the specification and as illustrated in the foregoing examples, the present invention provides a method for obtaining what was heretofore an unobtainable although highly desirable product—6063 aluminum magnesium silicide alloys that are anodized to have an inherently colored black anodic oxide coating on the surface thereof. This process and the product therefrom are obtainable by use of electrolytes and electrical programs described above, which, when employed together will produce the novel product of this invention.

We claim:

1. The method for producing a black anodic oxide coating on an alloy consisting by weight essentially of from 0.2 to 0.6% silicon, up to 0.35% iron, up to 0.10% copper, up to 0.10% manganese, from about 0.45 to about 0.9% magnesium, up to about 0.10% chromium, up to about 0.10% zinc, up to about 0.10% titanium and up to 0.15% others, and the balance aluminum which comprises immersing said alloy in an aqueous electrolyte maintained at a temperature of from about 45° F. to about 85° F.

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and consisting essentially of from about 25 g./l. to about 150 g./l. of sulfophthalic acid and from about 0.1 g./l. to about 15 g./l. of sulfuric acid, as the anode in a direct current electrical circuit which includes said electrolyte, anodizing said alloy at approximately constant current density of from about 25 amperes per square foot to about 40 amperes per square foot until a preselected voltage of from about 55 to about 75 volts is reached, and subsequently anodizing said alloy while maintaining said preselected voltage approximately constant until a black anodic oxide coating is obtained.

2. The method of claim 1 in which the sulfophthalic acid is present in the electrolyte in an amount of from about 70 g./l. to about 100 g./l. and the sulfuric acid in an amount of from about 1 g./l. to about 5 g./l.

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