



PATENT SPECIFICATION

NO DRAWINGS

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SPECIFICATION AMENDED - SEE ATTACHED SLIP
COMPLETE SPECIFICATION

Improvements in or relating to Anodized Alloys

We, KAISER ALUMINUM & CHEMICAL CORPORATION, a Corporation organised under the laws of the State of Delaware, United States of America of 300 Lakeside Drive, Oakland 12, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

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

The process of anodizing aluminium has been practiced by placing an aluminium 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 aluminium 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 aluminium body. The process is popularly known as *anodizing* and the product is popularly known as *anodized aluminium*, 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.

Colored anodized aluminium has found wide use for architectural purposes, both interior and exterior, as wall panels and curtains walis,

doors, and frames for panels, curtain walls, doors and windows.

Much architectural aluminium is of aluminium alloys in the magnesium-silicon family, and one particularly popular alloy is the aluminium-magnesium-silicon alloy designated by the Aluminium 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.

According to the present invention there is provided a method of producing a black anodic oxide coating on 6063 alloy defined herein, which comprises immersing the alloy in an electrolyte comprising from 25 g/l to 150 g/l sulphophthalic acid and from 0.1 g/l to 15 g/l of sulphuric acid, the alloy being the anode in an electrical circuit which includes the electrolyte, anodizing the alloy in a first stage at a constant current density of from 15 amperes per square foot to 50 amperes per square foot until a preselected voltage in the range from 25 volts to 100 volts is reached, and subsequently anodizing the alloy while maintaining the preselected voltage approximately constant until a black anodic oxide coating is obtained.

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

With the 6063 article immersed in the above-described electrolyte, anodizing is

[Price 4s. 6d.]



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 15 amperes per square foot to 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 25 to 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 25 volts to 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 7.2° C. to 29.4° C. 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 mils to 2.0 mils or more are readily obtainable on an article employed as an anode in the electrolytic process disclosed herein.

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 Aluminium Association specifications for 6063 alloy, shown in Table I in weight per cent.

Table I

Silicon	0.2 —0.6	
Iron	0.35 max	
Copper	0.10 max	
Manganese	0.10 max	
Magnesium	0.45—0.90	
Chromium	0.10 max	90
Zinc	0.10 max	
Titanium	0.10 max	
Others	0.15 max	
Aluminium	Balance	

EXAMPLE 1

A specimen in the form of an extrusion of aluminium alloy containing in weight per cent 0.4 silicon, 0.24 iron, 0.01 zinc, 0.04 copper, 0.60 magnesium, 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 54° C.
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 sulphophthalic acid and 5 g/l of sulphuric acid and maintained at a temperature of 25° C. 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 96° C. and containing 0.6 g/l of sodium lignosulphonate and 0.5 g/l of nickel acetate

to effect sealing of the anodic oxide film that was formed. There resulted a 6063 aluminium alloy covered with a smut-free anodic oxide film that was black in color and approximately 1.5 mils thick.

EXAMPLE 2

An aluminium alloy containing in weight per cent 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 25° C. and containing 53.2 g/l of sulphophthalic acid, 7.78 g/l of sulphuric acid and 4.1 g/l of aluminium 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 mils thick.

EXAMPLE 3

A specimen of aluminium alloy containing by weight per cent 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 to 4 of Example 1. Subsequently the specimen was immersed in an aqueous electrolyte maintained at 25° C. and containing 95.5 g/l of sulphophthalic acid, 9.9 g/l of sulphuric acid, and 4.4 g/l of aluminium 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 aluminium alloy containing, in weight per cent, 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 to 4 in Example 1. The specimen was then immersed as the anode in an aqueous electrolyte maintained at 25° C. and containing 100 g/l of sulphophthalic acid, 5 g/l of sulphuric acid and 0.05 g/l of aluminium 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 con-

stant. 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 aluminium alloy containing, in weight per cent, 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 to 4 of Example 1. Subsequently the specimen was immersed in an aqueous electrolyte maintained at 25° C. and containing 94.6 g/l of sulphophthalic 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 aluminium alloy containing, in weight per cent, 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 to 4 of Example 1. The specimen was then immersed in an aqueous electrolyte maintained at 25° C. and containing 101.2 g/l of sulphophthalic acid, 4.85 g/l of sulphuric acid, and a small but undetermined amount of aluminium 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 aluminium alloy was prepared for anodizing as described in steps 1 to 4 of Example 1, was immersed as an anode in an aqueous electrolyte containing 80.0 g/l of sulphophthalic acid, 3.6 g/l of sulphuric acid and 0.07 g/l of aluminium 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 immersed as the anode in an electrolyte containing 80 g/l of sulphophthalic acid, 3.6 g/l of sulphuric acid, and 0.07 g/l of aluminium ion. Anodizing is effected at a temperature of 18° C., 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 mils 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 aluminium magnesium silicon 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.

WHAT WE CLAIM IS:—

1. A method of producing a black anodic oxide coating on 6063 alloy defined herein, which comprises immersing the alloy in an electrolyte comprising from 25 g/l to 150 g/l of sulphophthalic acid and from 0.1 g/l to 15 g/l of sulphuric acid, the alloy being the anode in an electrical circuit which includes

the electrolyte, anodizing the alloy in a first stage at a constant current density of from 15 amperes per square foot to 50 amperes per square foot until a preselected voltage in the range from 25 volts to 100 volts is reached, and subsequently anodizing the alloy while maintaining the preselected voltage approximately constant until a black anodic oxide coating is obtained.

2. A method as claimed in claim 1, in which the current density in the first stage is maintained constant at from 25 to 40 amperes per square foot.

3. A method as claimed in claim 1 or 2, in which the preselected voltage in the first stage is in the range from 55 to 75 volts.

4. A method as claimed in claim 1, 2 or 3, in which the electrolyte is maintained at a temperature of from 7.2°C. to 29.4°C.

5. A method as claimed in any preceding claim, in which the electrolyte comprises from 70 to 100 g/l of sulphophthalic acid and from 1 to 5 g/l of sulphuric acid.

6. A method of producing a black anodic oxide coating on an aluminium alloy, as described with reference to the foregoing Examples.

7. An anodized alloy article when prepared by a method as claimed in any preceding claim.

8. An article as claimed in claim 8, in which the anodic coating is from 0.30 mils to 2.0 mils thick.

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EXAMPLE 8

Another specimen of 6063 alloy is prepared for anodizing as described in Example 1. The specimen is then immersed as the anode in an electrolyte containing 80 g/l of sulphophthalic acid, 3.6 g/l of sulphuric acid, and 0.07 g/l of aluminium ion. Anodizing is effected at a temperature of 18° C., 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 mils 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 aluminium magnesium silicon 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.

WHAT WE CLAIM IS:—

1. A method of producing a black anodic oxide coating on 6063 alloy defined herein, which comprises immersing the alloy in an electrolyte comprising from 25 g/l to 150 g/l of sulphophthalic acid and from 0.1 g/l to 15 g/l of sulphuric acid, the alloy being the anode in an electrical circuit which includes

the electrolyte, anodizing the alloy in a first stage at a constant current density of from 15 amperes per square foot to 50 amperes per square foot until a preselected voltage in the range from 25 volts to 100 volts is reached, and subsequently anodizing the alloy while maintaining the preselected voltage approximately constant until a black anodic oxide coating is obtained.

2. A method as claimed in claim 1, in which the current density in the first stage is maintained constant at from 25 to 40 amperes per square foot.

3. A method as claimed in claim 1 or 2, in which the preselected voltage in the first stage is in the range from 55 to 75 volts.

4. A method as claimed in claim 1, 2 or 3, in which the electrolyte is maintained at a temperature of from 7.2°C. to 29.4°C.

5. A method as claimed in any preceding claim, in which the electrolyte comprises from 70 to 100 g/l of sulphophthalic acid and from 1 to 5 g/l of sulphuric acid.

6. A method of producing a black anodic oxide coating on an aluminium alloy, as described with reference to the foregoing Examples.

7. An anodized alloy article when prepared by a method as claimed in any preceding claim.

8. An article as claimed in claim 8, in which the anodic coating is from 0.30 mils to 2.0 mils thick.

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