

PATENT SPECIFICATION

NO DRAWINGS



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COMPLETE SPECIFICATION

Improvements in or relating to the Anodizing of Aluminium

We, KAISER ALUMINUM & CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 300 Lakeside Drive, Oakland, 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 process for producing integrally colored anodically oxidized aluminium and to the product that results from this process.

Processes for the production of integrally colored anodically oxidized aluminium are now well known. Patent Specification No. 850576, for example, discloses one such process in which aluminium may be produced with integral colors ranging from light bronze to black with an infinite number of intermediate shades of bronze and brown between. Anodic oxide coatings are glasslike, and the appearance of an anodized aluminium article is influenced by the condition of the metal surface beneath the oxide coating, as well as by the condition of the surface of the glassy oxide. For example, aluminium with brushed, sand-blasted, polished or other specially treated surfaces will produce different appearances on anodized products made from them; also, mechanically polishing the anodic oxide surface will impart a higher gloss to the surface.

The richer, more lustrous and more desirable shades are obtained when a brighter surface appearance exists prior to anodizing and as a consequence the more desirable shades have consistently been more expensive because additional work is required to prepare them. Buffing, chemical brightening, brushing and other surface conditioning processes usually require labor and material that add materi-

ally to the expense of the aluminium product being prepared.

In this specification and the following claims the term *aluminium* is used, and it is intended that it include aluminium base alloys as well as pure aluminium. This invention includes anodizing any aluminium material that is capable of accepting colorless and integrally colored anodic oxide coatings and it is intended that all such aluminous materials be included within the scope of this invention. It is also intended that the term *integrally coloured anodic oxide coatings* means those coatings that are formed with a colour by anodizing alone, in contrast to coatings that are prepared colourless and subsequently dyed, pigmented, or otherwise treated to have a colour imparted to them. The term *colourless* includes those coatings that are the ordinary glass-like anodic oxide coatings such as those produced in sulphuric acid electrolytes for many years. Colourless coatings include those that have slight casts of white, grey or gold resulting from reaction products of alloying ingredients. For example, when aluminium containing significant amounts of chromium is anodized, even in sulphuric acid, the coating may have a gold-like cast and when aluminium containing high amounts of silicon is anodized, even in sulphuric acid, the coating may have a grey cast. These coatings are intended to be classified as "colourless coatings" in that they do not have dark, dense and definite colours but instead could be characterized as having a coloured cast. Also colourless coatings showing a deeply etched aluminium subsurface have been characterized as white coatings, and these too are considered colourless within the context of this invention. Additionally, the term *anodized* has become part of the aluminium processing art to refer to aluminium articles that have an anodic oxide coating on their surface.

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When this term is used in the specification it should be intended to describe an article with such a coating on its surface or to describe the process for producing such a coating.

5 According to the present invention, a process for producing a coloured anodized aluminium article is provided, which comprises anodizing the article in an aqueous sulphuric acid electrolyte to produce a colourless anodic oxide coating on its surface and subsequently anodizing the article in an aqueous electrolyte containing 0.1% to 4% by weight of sulphuric acid and sulphosalicylic acid, sulphophthalic acid, sulphoresorcinol or ligno sulphonic acid in an amount of at least 20 g/l to produce an integrally coloured anodic oxide coating on the surface of the article.

10 The process of the present invention results in integrally coloured anodic oxide coatings on aluminium in shades which are particularly rich and lustrous and which are comparable to or superior to shades previously available only by expensive mechanical or chemical polishing of the metal prior to anodic oxidation, or by mechanical polishing of the anodic coating.

15 The invention also relates to the product from the process which is a lustrous, richly colored article consisting of aluminium covered with two anodic oxide coatings, the outermost of which is a colorless, transparent anodic oxide coating and the innermost of which is an integrally colored anodic oxide coating.

20 The process of the present invention is always effected by placing a colorless, transparent coating on the article after which the integrally colored coating is made. This method produces the second coating, that is the integrally colored coating as the innermost coating beneath the colorless coating in that anodic oxide coatings are formed at the aluminium surface and grow outwardly from there. When the order is reversed, that is when the integrally colored anodic oxide coating is formed first, and the transparent oxide coating is formed second, the product is produced with a dull, lackluster, almost dusty appearance. Although for some purposes such a dull appearance might be desirable, the process of the present invention is for the purpose of producing a brilliant, lustrous and richly colored anodic oxide coating.

25 The colorless anodic oxide coating, which is the first produced, may be applied to the aluminium article by any of the anodizing methods known to the aluminium anodizing art which makes use of aqueous solutions of sulfuric acid. Anodizing is effected by making the aluminium article the anode, usually in a direct-current circuit which includes the aluminium article, the electrolyte, and an inert cathode of material such as lead or stainless steel. The electrolyte is maintained at about

room temperature and anodizing is effected by passing current at a density of about 12 amperes per square foot through the electrolyte for a time sufficient to produce a coating of the desired thickness. Although the above describes a typical process for producing a colorless coating, the range of suitable conditions and ingredients is large, the only essential requirement being the use of an aqueous sulphuric acid electrolyte to produce a colorless anodic oxide coating. The anodizing conditions may be adjusted or modified over wide ranges. For example, the anodizing process may be effected at temperatures from the freezing point of electrolyte to about 90°F., and at current densities ranging from less than 5 amperes per square foot up to perhaps 25 or 30 amperes per square foot. The voltage employed is that required to obtain the desired current density and it may range up to 60 volts or higher. For the purposes of this invention the time required may be very short, one minute or less, for producing the colorless coating because, as will be shown, the existence of a colorless coating prior to forming an integrally colored coating causes the improved appearance, and whether the colorless coating is thick or thin does not significantly alter the improved appearance.

The integrally colored anodic oxide coating, the second anodizing process employed in this invention, is effected by removing the article from the first anodizing bath, rinsing it to prevent contamination of the second anodizing bath, immersing it in the second anodizing bath as the anode in an electric circuit and passing current through the circuit which includes the aluminium article, the electrolyte and an inert cathode. The colour-anodizing electrolyte used is an aqueous solution including sulfuric acid and any of certain organic acids effective to produce such integrally coloured coatings, namely sulphosalicylic acid, which is described in the above-cited Specification No. 850576, sulphophthalic acid, sulphoresorcinol or lignosulfonic acid.

The organic acid is present in the colour-anodizing electrolyte in a concentration ranging from 20 grammes per litre to the limit of solubility of the acid, but it is preferred to use concentrations in the range of 50-100 grams per litre as these have proved to be the most effective concentrations. The sulfuric acid concentration varies from 0.1 to 4% by weight, but it has been found that sulfuric acid in quantities amounting to from about 0.1 to about 1% by weight of the electrolyte is very effective.

Anodizing is usually effected in an electrolyte maintained at about room temperature although temperatures up to 90°F. and as low as the freezing point of the electrolyte may be used. Current densities up to 100 amperes per square foot may be used, preferably em-



ploying a constant current density throughout the anodizing period or until some predetermined maximum voltage is reached after which that voltage is maintained constant until the anodizing process is completed. The voltage employed is that required to produce the current density desired, usually not over 120 volts and preferably not over 75 volts. As with the colorless anodizing process, the integrally colored anodizing process may be effected over wide ranges of processing conditions depending upon the results that are desired.

Although substantially any aluminium alloy may be produced with an integrally colored anodic oxide coating, the composition of the alloy employed affects the color that is produced in the anodic oxide coating. If it is desired that the color be dark per unit of coating thickness lower concentrations of organic acid may be used while if it is desired that a thick coating without too dense a color be produced higher concentrations of the organic acid may be employed. It is therefore evident that depending upon the color

of the coating desired and the composition of the aluminium article being anodized, wide variations in electrolyte concentration and processing conditions may be made.

In order to illustrate several preferred embodiments within the scope of this invention, the following examples are presented. It should be understood that Examples 1 to 3 represent typical embodiments of the invention and are not intended to limit the invention or to restrict the scope of the claims to the materials or conditions illustrated; Example 4 is given for comparison purposes to show that the benefits of the invention are obtained only if the two anodizing steps are carried out in the order specified.

EXAMPLE 1

In Example 1 conventional integrally colored anodizing was contrasted with the process of the present invention employing an alloy designated as Alloy No. 5005 by the Aluminium Association and having the following exact composition:

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Bal.
	0.09	0.61	0.05	0.01	0.66	0.08	0.02	0.01	Al.

The aluminium alloy described above was rolled into a sheet 0.125 inch thick and portions of that sheet were racked for anodizing and treated as follows. Between each step noted below a cold water rinse was used to prevent contamination of each solution with the one previously used:

1. Cleaned by immersion for 5 minutes in a 5% by weight aqueous solution of a proprietary non-etching alkaline cleaner (Oakite 61A—"Oakite" is a Regd. Trade Mark) at 140°F.

2. Dipped for 30 seconds in 30% by weight aqueous nitric acid solution at 70°F.

3. Etched for 10 minutes in a 5% by weight aqueous solution of caustic soda at 130°F.

4. Dipped for 2 minutes in 30% by weight aqueous nitric acid solution at 70°F.

5. Anodized in an aqueous electrolyte containing 15% by weight of sulfuric acid and maintained at 70°F. employing a current density of 12 amperes per square foot for 18 minutes.

6. Anodized at 20 amperes per square foot in an aqueous electrolyte containing 47 grams per liter of sulfosalicylic acid and 4.7 grams per liter of sulfuric acid maintained at 77°F. In three minutes the anodizing potential reached 60 volts and anodizing was then continued at 60 volts until 10 ampere-hours per square foot of electricity had passed through

the cell. The total time required for this anodizing step was 52 minutes.

7. The aluminium article was then sealed by immersing it in an aqueous sealing solution containing 1 gram per liter of sodium lignosulfonate and 0.5 gram per liter of nickel acetate for a period of 20 minutes at 200°F.

The identical process was effected on another piece of 5005 aluminium sheet having the same composition and dimensions, and the same treatments as the one described above with the single exception that step 5, colorless anodizing in sulfuric acid electrolyte, was omitted. A comparison of specimen 1 which was treated by all 7 of the above-described treatments with specimen 2 which was treated with all but the colorless anodizing treatment revealed a clearly discernible difference in the appearance of the specimens. The specimens had approximately the same intensity of shade but specimen 1 was lustrous and glossy, and it had a richer, more appealing color.

EXAMPLE 2

Example 2 illustrates that the process as effected on the sheet material of Example 1 is equally effective on aluminium extrusions, which are alloys frequently difficult to produce with attractive colored anodic oxide finishes. In Example 2, an alloy nominally identified by the Aluminium Association as 6463 was employed. This alloy had the following composition:

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Bal.
0.41	0.10	0.18	0.004	0.48	0.00	0.02	0.01	Al.

5 A specimen of this material was treated with the steps enumerated 1—5 in Example 1, after which it was anodized at 24 amperes per square foot in a bath of the same composition as the one described in step 6 of Example 1 which was maintained at 77°F. The anodizing potential reached 50 volts in 2 minutes after which anodizing was continued at 50 volts until 10-ampere hours per square foot of electricity had passed. The total time for anodizing was 51 minutes. Following anodizing, the specimen was sealed as set forth in step 7 in Example 1.

10 A second specimen of 6463 alloy was treated exactly as the first except that step 5, anodizing in sulfuric acid to produce a colorless anodic oxide coating, was omitted. The appearance of specimen 1 was noticeably different from that of specimen 2. Specimen 2 was a pleasant medium bronze with moderate gloss while specimen 1 was a very bright golden bronze with high luster and rich tone.

25 EXAMPLE 3

In Example 3, three specimens of the same 5005 aluminium alloy employed in Example 1 were anodized in a two-stage process which was identical in all respects to the process set forth in Example 1 except that in step 5, sulfuric acid anodizing to produce a colorless coating, the anodizing time was effected in one instance for 6 minutes, in one instance for 12 minutes and in one instance for 18 minutes. The 6-minute, 12-minute and 18-minute sulfuric acid anodized samples all followed by the same integral color anodizing process, were almost identical in appearance. All had about the same gloss, color and general rich appearance of the resultant colored coating. Example 3 indicates that colorless anodic oxide coatings of various thicknesses are effective to produce improved appearance and luster on aluminium articles.

45 EXAMPLE 4

In Example 4 a specimen of 5005 alloy having the composition set forth in Example 1 was employed in a process wherein all of the steps set forth in Example 1 were employed as set forth in Example 1 with the following exceptions:

Step No. 6 was performed after step 4

55 followed by step 5, that is the sulfuric acid anodizing to produce a colorless coating was effected on an aluminium article that had already been anodized to produce an integrally colored coating on its surface. However, the peak voltage in step 6 was reached in 7 minutes and the total anodizing time was 44 minutes, and these conditions are different from those in Example 1 in order to obtain the same number of ampere hours per square foot of electricity, the true criterion of how much anodizing is done.

65 The process set forth in this example reversed the order of colorless and color anodizing and the result was a colored anodic oxidized article that was very dull in appearance. Example 4 thereby illustrates that the process of this invention must employ the colorless anodizing step first if a lustrous color is to be produced.

WHAT WE CLAIM IS:—

1. A process for producing a coloured anodized aluminium article, which comprises anodizing the article in an aqueous sulphuric acid electrolyte to produce a colourless anodic oxide coating on its surface and subsequently anodizing the article in an aqueous electrolyte containing 0.1% to 4% by weight of sulphuric acid and sulphosalicylic acid, sulphophthalic acid, sulphoresorcinol or lignosulphonic acid in an amount of at least 20 g/l, to produce an integrally-coloured anodic oxide coating on the surface of the article.

2. A process according to claim 1, wherein the electrolyte for producing the integrally-coloured anodic oxide surface contains sulphosalicylic acid, sulphophthalic acid, sulphoresorcinol or lignosulphonic acid in an amount from 50 g/l to 100 g/l.

3. A process according to claim 1, for producing a coloured anodized aluminium article, substantially as described with reference to any of the foregoing Examples 1 to 3.

4. A coloured anodized aluminium article, when prepared by a process according to any of claims 1 to 3.

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2. A process according to claim 1, wherein the electrolyte for producing the integrally-coloured anodic oxide surface contains sulphosalicylic acid, sulphophthalic acid, sulphoresorcinol or lignosulphonic acid in an amount from 50 g/l to 100 g/l.

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4. A coloured anodized aluminium article, when prepared by a process according to any of claims 1 to 3.

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