

1

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PROCESS AND ELECTROLYTE FOR COLORING ALUMINUM

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ABSTRACT OF THE DISCLOSURE

The instant disclosure teaches a process and electrolyte for coloring aluminum electrolytically which provides a wide variety of colored aluminum articles having good physical properties, with the electrolyte being an aqueous solution consisting essentially of from 0.1 to 1% sulfuric acid, from 3% to saturation of sulfamic acid, and from 0.1 to 10% sulfophthalic acid.

The present invention relates to anodizing aluminum. More particularly, the present invention resides in the production of integral, colored, anodic coatings on an aluminum article by making the aluminum article anode in an electrolytic cell utilizing a particular aqueous acid electrolyte.

Decorative and protective oxide coatings on aluminum have long been made by anodizing in electrolytes consisting of aqueous solutions of sulfuric acid. Such electrolytes are usually employed at or near room temperature and must be cooled to maintain such temperature. The coatings so produced are usually relatively clear or colorless, although on some alloys they may be tinted or colored by some constituents and they are characterized by generally poor abrasion resistance.

Processes have been developed for producing anodic oxide coatings which are more abrasion resistant by anodizing in aqueous sulfuric acid electrolytes at extremely low temperatures, i.e., from about 0 to 30° F. These processes are subject to the inherent disadvantage of requiring expensive refrigeration equipment to maintain the temperatures below 30° F. The coatings so produced, however, in addition to being abrasion resistant are attractively colored for numerous uses of aluminum, i.e., are colored in dark desirable colors, such as dark brown, etc.

It is, therefore, highly desirable to develop a practical process for anodically obtaining relatively dark surface colors and good corrosion resistance.

Accordingly, it is an object of the present invention to provide a practical process as aforesaid for producing an integral, colored, anodic coating on an aluminum article and an electrolytic cell for performing said process.

It is a further object of the present invention to provide a process as aforesaid for anodizing aluminum which yields oxide coatings having relatively dark surface colors.

In addition, it is an object of the present invention to provide a process as aforesaid which yields an integral, colored aluminum article having good physical properties, such as excellent corrosion resistance, abrasion resistance and light stable colors.

It is a still further object of the present invention to provide a process as aforesaid which enables the attainment of a wide variety of desirable, integral, dark surface colors.

Further objects and advantages of the present invention will appear hereinafter.

In accordance with the process of the present invention it has now been found that the foregoing objects and advantages may be readily obtained. The present invention provides a process for coloring aluminum electrolytically,

2

which comprises anodically oxidizing said aluminum at a current density of from 10 to 100 amps per square foot and a voltage of from 10 to 90 volts in an aqueous solution consisting essentially of from 0.1 to 1% sulfuric acid, from 3% to saturation of sulfamic acid, preferably from 5 to 15% sulfamic acid, and from 0.1 to 10% sulfophthalic acid, preferably from 1 to 3% sulfophthalic acid, said bath being maintained at a temperature of from 10 to 90° C.

It has been found in accordance with the present invention that the foregoing process surprisingly achieves all of the objects of the present invention and readily achieves a wide variety of light stable, abrasion and corrosion resistant surface colors having excellent physical characteristics and varying from light silver gray to jet black or a variety of browns and dark olive shades.

It is particularly surprising that the present process attains a wide range of highly desirable dark colors. One particularly unexpected feature of the present invention is the production of integral dark colors of a relatively wide range of sulfamic acid and sulfophthalic acid concentrations but over a very narrow range of sulfuric acid concentrations.

An additional and significant feature of the present invention is that all of the foregoing advantages are obtained at a low cost which renders the process particularly attractive commercially.

It has been found that the process variables of the present invention are important in attaining the desired effect.

The sulfamic acid concentration may be varied over a wide range of from 3% to saturation and preferably should be maintained in the range of 5% to 15%. The sulfuric acid concentration is particularly critical and should be maintained in the range of from 0.1 to 1% by weight and preferably from 0.25 to 0.75% by weight. The sulfophthalic acid concentration can be varied from 0.1 to 10% and preferably is maintained from 1 to 3%.

The aqueous bath is maintained at a temperature of from 10 to 90° C. and preferably from 15 to 30° C.

The time of treatment is not especially critical, with the longer times providing the thicker coatings and darker colors. Generally, at least one minute is used and preferably from 1 to 150 minutes.

The aluminum article is anodically oxidized at a current density of from 10 to 100 amps per square foot and preferably at a current density of 15 to 30 amps per square foot and at a voltage of from 10 to 90 volts, and preferably at a voltage of from 25 to 70 volts.

Naturally, various additional ingredients conventionally used may be added to the anodic oxidation bath to achieve particular results or enhance particular characteristics, such as, for example, metal sulfates.

Any sulfophthalic acid may be employed, e.g., 4-sulfophthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid is preferred.

After the anodic oxidation treatment, the anodized article may if desired be subjected to a conventional hot water sealing step, e.g., immersion in water maintained at or near its boiling point.

The present invention is applicable to anodizing any aluminum article, i.e., high purity aluminum in various commercial grades, and aluminum base alloys.

In the electrolytic cell, the cathode which may be used is not especially critical. Conventionally, lead or preferably stainless steel cathodes may be used.

The present invention and the improvements resulting therefrom will be more readily apparent from a consideration of the following illustrative examples wherein the amounts of all ingredients are given in percent by weight.

Example I

The following example illustrates the wide variety of colors which may be obtained on a number of alloys in accordance with the present invention.

In the following example various aluminum alloys were anodically oxidized for varying periods of time at specified current densities and voltages. The electrolyte used was an aqueous solution consisting essentially of about 0.25% sulfuric acid, about 8% sulfamic acid and about 2% 4-sulfophthalic acid. The bath was maintained at a temperature of 25° C. The cathode used was lead. The voltage was raised to maintain the current density until the maximum voltage was reached. The voltage was then held constant until the anodizing time was completed. Air agitation of the electrolyte was used.

The results are shown in Table I below:

TABLE I

Aluminum Alloy, Aluminum Association Designation	Maximum Voltage, Volts	Time, Minutes	Current Density at Maximum voltage, Amps per square foot	Color
6061-T6	50	20	24	Brown.
6061-T6	65	40	24	Black.
3003	50	20	24	Gray.
3003	65	40	24	Dark gray.
5052	40	30	24	Bronze.
6063-T5	50	20	24	Amber.
6063-T5	60	40	24	Dark amber.
1100	50	30	24	Tan.
1100	60	45	24	Olive.

Example II

The following example illustrates the abrasion resistance of the samples anodized in accordance with the process of the present invention.

Samples anodized in a manner after Example I were tested for abrasion resistance by abrading the surface of the sample with a fine jet of sand. The time necessary to penetrate the anodic coating in ten (10) spots on each specimen was measured. The total time to penetrate the ten (10) spots was then divided by the coating thickness in mils, giving a figure of merit the units of which are seconds per mil. The higher the seconds per mil, the greater the abrasion resistance.

The data is shown in the following table.

TABLE II

Alloy	Processing	Abrasion Resistance, Secs./Mil.
1100	30-min. anodize 165 g./l. H ₂ SO ₄ -12 ASF	25
1100	30-min. anodize 165 g./l. H ₂ SO ₄ -24 ASF	32
1100	30-min. anodize 8% sulfamic acid plus 0.25% H ₂ SO ₄ plus 2% 4-sulfophthalic acid-24 ASF	81

Example III

The following example illustrates the improved, darker colors obtained in accordance with the process of the present invention over (1) anodizing in an aqueous bath containing solely sulfuric acid and (2) anodizing in an aqueous bath containing sulfuric acid and sulfamic acid.

In the following example aluminum alloy 1100 was anodically oxidized in a manner after Example I utilizing treatment conditions and aqueous electrolytes as shown in the following table.

The resulting colors obtained are shown in photovolt readings wherein generally darker colors are indicated by low photovolt readings, i.e., the lower photovolt reading indicates lower reflectivity, hence a darker color.

The results, shown in Table III below, show graphically the darker colors obtained in accordance with the process of the present invention.

TABLE III

Alloy	Processing	Photovolt Reading
1100	30 min. anodize 165 g./l. H ₂ SO ₄ -12 ASF	55
1100	30 min. anodize 165 g./l. H ₂ SO ₄ -24 ASF	50
1100	30 min. anodize 10% sulfamic acid plus 0.25% sulfuric acid-24 ASF	20
1100	30 min. anodize 8% sulfamic acid plus 2% 4-sulfophthalic acid and 0.25% H ₂ SO ₄ -24 ASF	15

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A process for coloring aluminum electrolytically which comprises anodically oxidizing said aluminum at a current density of from 10 to 100 amps per square foot and a voltage of from 10 to 90 volts in an aqueous solution consisting essentially of from 0.1 to 1% sulfuric acid, from 3% to saturation of sulfamic acid, and from 0.1 to 10% sulfophthalic acid, said bath being maintained at a temperature of from 10 to 90° C.
2. A process according to claim 1 wherein the sulfamic acid is present in a concentration of from 5 to 15%.
3. A process according to claim 1 wherein the sulfuric acid is present in a concentration of from 0.25 to 0.75%.
4. A process according to claim 1 wherein the sulfophthalic acid is present in a concentration of from 1 to 3%.
5. A process according to claim 1 wherein said bath is maintained at a temperature of from 15 to 30° C.
6. A process according to claim 1 wherein the current density is from 15 to 30 amps per square foot and the voltage is from 25 to 70 volts.
7. A process according to claim 1 wherein the sulfophthalic acid is 4-sulfophthalic acid.
8. A process according to claim 1 wherein said aluminum is anodically oxidized for from 1 to 150 minutes.
9. An electrolyte for coloring aluminum electrolytically comprising an aqueous solution consisting essentially of from 0.1 to 1% sulfuric acid, from 3% saturation of sulfamic acid and from 0.1 to 10% sulfophthalic acid.

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