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METHOD AND MATERIAL FOR ELECTROLYTICALLY BRIGHTENING ALUMINUM SURFACES

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This invention relates to bright aluminum and aluminum alloy surfaces and a method for the production thereof. More particularly the invention relates to an improved electrolyte and electrobrightening process for the treatment of aluminum and aluminum base alloys to produce thereon durable bright surfaces of high specular reflectivity.

Highly polished or brightened aluminum surfaces are required for various decorative purposes and perhaps the major application thereof resides in the manufacture of reflectors, for the reflection of any kind of radiant energy, but particularly, for light reflection of either the diffuse or specular type. Bright surfaces of the diffusely reflecting type may be produced by chemical etching, but surfaces which are highly specularly reflective more often require mechanical buffing or polishing and/or electrobrightening. Mechanical buffing alone provides a highly polished surface, but there is a distortion of the grains of the metal. This invention is primarily directed to an improved electrolyte and electrobrightening method for increasing the specular reflectivity of bright aluminum surfaces and also the preservation of such reflectivity.

Various commercial processes have been developed for electrobrightening aluminum to produce surfaces of high specular reflectivity, perhaps the most notable of which is that described in U. S. Patent 2,108,603 to R. B. Mason which comprises an electrolytic brightening step performed under certain conditions of temperature, current density and concentrations in which the aluminum article is the anode and the electrolyte is a solution of fluoboric acid. The brightened surface is then usually given a protective anodic oxide coating in a suitable electrolyte, and such coating, if porous, is subjected to a sealing treatment to render it impervious. Other brightening electrolytes having similar characteristics are known, but less commonly used.

In all existing methods of electrobrightening, however, a thin soft film is formed on the brightened surface which is said to consist essentially of aluminum oxide. Such film, although at times initially transparent, due to handling or rubbing of the surface causes smudges thereon which are highly undesirable and which adversely affect to a substantial degree the reflectivity of the surface. A subsequently formed anodic oxide coating is deposited beneath the soft permeable film and when the coating is sealed, for example, by the conventional hot water treatment, the tendency for this superficial film to smudge is increased. The

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removal of such a film, whether from the subsequently formed oxide coating or from the brightened metal surface before anodizing, is imperative and has entailed additional and time consuming operations which have significantly increased the cost of commercial production of durable bright aluminum surfaces of high specular reflectivity. For example, in the electrobrightening process employing a hydrofluoboric acid electrolyte, the electrolytically brightened article prior to deposition of an anodic oxide coating is subjected to a chemical dip treatment in a solvent for aluminum oxide, preferably, for example, an alkaline solvent, such as a solution of an alkali carbonate, containing alkali chromate, in order to remove the smudge film, or preferably an acid smut removing solution, such as phosphoric and chromic acids.

It is a primary object and purpose of this invention to provide an improved electrolyte and electrolytic method by which surfaces of high specular reflectivity are imparted to aluminum and aluminum base alloys.

A further advantage and object of the invention is the provision of an electrolyte and method for rapidly electrobrightening aluminum surfaces which overcome the difficulties abovementioned by eliminating the formation of a film which causes smudges, and therefore obviating the necessary additional operation of the prior art for removal of such smudge-forming superficial film. These and other objects and advantages will become apparent from the following detailed description of the invention.

It has been discovered that aluminum articles may be rapidly electrolytically brightened to a high specular reflectivity without the occurrence of a superficial smudge-forming film by anodic treatment in a particular electrolyte and that such electrobrightened surfaces may have a protective anodic oxide coating subsequently applied without intermediate smudge removal treatment and without significant loss in specular reflectivity. Other forms of protective coatings may be applied to the specularly reflecting surfaces produced by the electrobrightening electrolyte and method of the invention, such as clear transparent lacquer coatings.

The essential active constituents of the improved electrolyte are chromic, hydrofluoric and sulfamic acids. Salts of hydrofluoric and sulfamic acids may be substituted at least in part for the free acids up to the extent they will yield such acids in the presence of the quantity or concentration of chromic acid employed in the elec-

trolyte. The salts must be those containing cations which will not adversely affect the results of the process, for example, ammonium salts.

In practicing the invention, the reflecting surface or other aluminum article is made the anode in an electrolytic cell in which the electrolyte is a solution, predominantly aqueous, of chromic acid, hydrofluoric acid and sulfamic acid. A suitable organic etching inhibitor, for example, lower molecular weight aliphatic alcohols, such as, glycerol, ethylene glycol, diethylene glycol, mannitol and sorbitol may be added to the electrolyte to modify the rate of action of the active constituents. Monoethers of such polyhydric alcohols are also suitable for this purpose, such as Cellosolve and Carbitol.

Depending upon the surface conditions of the metal, the electrobrightening procedure may be preceded by a cleaning process to remove any dirt or grease or other foreign particles adhering to the surface. Any non-etching cleaning solvent or chemical free from objectionable attack on the metal is suitable, for example, a mild inhibited alkaline solution. Mechanical cleaning by frictional contact with the surface may be employed, but is not recommended, particularly where the surface of the work has been given a high polish of a specular nature, since any abrasive action may impair the polish thereon. For optimum specular reflectivity, the work is usually buffed before electrobrightening where the shape of the article permits.

The electrobrightening process, above outlined, imparts to the surface a bright finish of high specular reflectivity, and apparently also forms a thin transparent film which affords some protection to the bright surface against loss of reflection factor due to handling, corrosion, and the like, and which is substantially free from smudge-forming tendencies. This may suffice in certain applications where the reflecting surface is not subjected to excessive handling or considerable exposure to atmospheric influences.

However, where conditions of use are more adverse to preservation of the high degree of specular reflectivity of the surface, it is recommended that the electrobrightened surface be subjected to another electrolytic treatment under conditions to form thereon by anodic oxidation a hard, transparent oxide coating of sufficient thickness to protect the bright surface from staining, marking, corrosion or other deterioration caused by exposure to weather, handling, washing, etc. Such anodic oxide coatings of the colorless transparent type are well known in the art and are those which consist mainly of aluminum oxide formed integral with the reflecting surface by anodic oxidation in a suitable electrolyte, such as sulfuric acid or oxalic acid. A particularly suitable electrolyte for this purpose comprising essentially sulfuric and phosphoric acids in appropriate concentrations and the anodizing method employed is disclosed and claimed in my copending application Serial No. 164,304 filed May 25, 1950, which provides a clear transparent non-iridescent oxide coating causing a minimum reduction in reflection factor.

After deposition of the oxide coating, the surface may be subjected to a sealing treatment, such as the conventional hot water process, usually at a temperature of from 160 to 212° F., to render the initially porous oxide film impervious.

However, it is to be understood that such sealing procedure is not necessary to satisfactory

attainment of the objects of the invention, and that bright aluminum surfaces of high specular reflectivity may be produced without such treatment. Furthermore, although it is the preferred embodiment of the invention to first preliminarily clean the surface to free the same of grease and dirt, then electrobrighten in the improved electrolyte, then anodically coat with oxide, and finally seal the coating, the electrolytic brightening in the solution of chromic, sulfamic and hydrofluoric acids may be conducted without such preliminary or subsequent steps.

Either alternating or direct current may be utilized in the operation of the electrolytic cell containing the aqueous solution of chromic, hydrofluoric and sulfamic acids and wherein the aluminum article is made the anode. Direct current is preferred, however, due to the facility of control of the process afforded thereby. A current density of from about 10 to 80 amperes per square foot may be employed with good results, depending upon the particular alloy being treated. Somewhat lower values may be used when the concentrations of the active electrolyte constituents, particularly HF, and the temperature are relatively low without any adverse chemical attack on the metal. A potential of about 5 to 50 volts has been found most suitable for maintaining the current densities given above, although this will vary depending upon the conductivity of the electrolyte which in turn is dependent on composition, concentration and temperature of the bath. Higher voltages are required for a low conductivity electrolyte and lower voltages suffice for those of higher conductivity.

The operating temperature is suitably from about 100 to about the boiling point, while the optimum or preferred temperature is from about 170 to about 180° F.

A further advantage of the invention is the rapidity with which the metal surface is brightened. The time of treatment will vary, of course, with the current density temperature, electrolyte concentrations, and the degree of brightening desired. However, aluminum surfaces of equally high specular reflectivity are produced in an electrolytic treatment time of only from about one and one-half to three minutes compared to a recommended five to fifteen minutes for the process involving a hydrofluoboric acid electrolyte, other conditions being equal. Moreover, no subsequent time-consuming smudge removal step is required in the present process.

Thus, the invention produces results equal to or better than previous processes, while greatly reducing cost due to economy in process steps, equipment, time and power consumption.

The chromic acid constituent of the electrolyte when combined with the hydrofluoric and sulfamic acids appears to aid in the production of a bright reflective surface and a thin clear film free of smudge forming propensities. In addition, the sulfamic acid either directly or by modification of the action of the other constituents advantageously functions to improve the results. However, it is not intended to limit the invention to any proposed theory or mechanism, it being sufficient to state that the electrolyte and process provide a rapid and superior means of imparting to aluminum and aluminum base alloy surfaces a high specular reflectivity.

In general, it has been determined that an electrolyte comprising an aqueous solution having the following ranges of constituent concen-

trations, in terms of percentages by weight of solution, in any combination is highly suitable for production of bright surfaces free from smudge-forming tendencies:

Constituent	Concentration Weight or Volume	Percent by Wt. of Solution
Sulfamic Acid (HSO_3NH_2).....	$\frac{1}{2}$ -4 g./l.....	0.05-0.4
Chromic Acid Anhydride (CrO_3)..	3-22 g./l.....	0.3-2.1
Hydrofluoric Acid (HF).....	3-12.5 cc./l. (48% HF).	0.1-0.8
Glycerol.....	$\frac{1}{2}$ -4 cc./l. (95% $\text{C}_3\text{H}_8\text{O}_3$).	0.05-0.5

The optimum concentrations or percentages by weight of the electrolyte constituents are as follows:

Constituent	Concentrations	Percent by Wt. of Solution
HSO_3NH_2	2.25 g./l.....	0.23
CrO_3	7.5 g./l.....	0.75
HF.....	5 cc./l. (48% HF).....	0.29
Glycerol.....	2.5 cc./l. (95% $\text{C}_3\text{H}_8\text{O}_3$).....	0.31

The invention is not absolutely limited to the foregoing specific constituents, but includes such equivalent substances as will produce an electrolyte of substantially the same chemical composition among which may be mentioned the following:

Ammonium salts of sulfamic and hydrofluoric acids and alkali metal salts of these acids, although the presence of alkali metal ions is preferably to be avoided. Where salts of certain components are used the requisite hydrogen ion concentration must be supplied by one or more of the other constituents.

The invention is more fully illustrated with reference to the following example, which is not to be construed as a limitation thereof:

A high purity aluminum sample, previously buffed to impart an initial specularly reflective surface was connected in an electrolytic cell as the anode. The specular or gloss reflectivity as measured by a Henry Gardner 60° Glossmeter was 70%.

The electrolyte in the cell was prepared by adding to a liter of water, 5 cubic centimeters of 48% hydrofluoric acid, 2.25 grams of sulfamic acid, 7.5 grams of chromic acid and 2.5 cc. of glycerol (95% $\text{C}_3\text{H}_8\text{O}_3$). The electrolyte had the following composition by weight of solution:

	Per cent
HSO_3NH_2	0.23
CrO_3	0.75
HF	0.29
Glycerol	0.31
Water	98.42

A direct current at current density of 20 amperes per square foot was used at a voltage of about 35 volts for three minutes with an electrolyte temperature of 170-180° F. The brightened surface had a specular or gloss reflectivity of about 85 percent.

The brightened article was then subjected to anodic oxidation in a combined sulfuric acid-phosphoric acid electrolyte containing 3.7% and 33.6% by weight of the acids, respectively. A direct current voltage of twenty-five volts was

impressed on the cell at a current density of ten amperes per square foot with the electrolyte at a temperature of 75-80° F. for a period of ten minutes. The clear, transparent oxide film was sealed by immersion in boiling water for about ten minutes. The specular reflectivity was only slightly reduced from the value for the brightened surface before deposition of the oxide film.

Although several of the aluminum base alloys when brightened by the present process do not exhibit specular reflectivity to the same degree as pure aluminum, nevertheless the electrolyte and method of the invention are fully applicable to aluminum base alloys in general.

At comparable current densities the process of the invention imparts a slightly higher gloss (mirror) reflectivity more rapidly than the process employing fluoboric acid, while eliminating the smudge removal step.

What is claimed is:

1. A method of brightening aluminum surfaces comprising subjecting the surface as anode to an electrolytic treatment in an electrolyte consisting essentially of from about 0.1% to 0.8% HF, from about 0.05 to 0.4% HSO_3NH_2 and from about 0.3 to 2.1% CrO_3 , balance substantially all water, said percentages being by weight of the total solution.

2. As an electrolyte for electrolytically brightening aluminum surfaces, an aqueous solution consisting essentially of from about 0.1 to 0.8% hydrofluoric acid, from about 0.05 to 0.4% sulfamic acid and from about 0.3 to 2.1% chromic acid, all percentages being by weight of total solution.

3. An electrolyte according to claim 2 which contains from about 0.05 to 0.5% of an organic inhibitor selected from the group consisting of lower molecular weight aliphatic polyhydric alcohols and their monoethers.

4. A method of producing on aluminum and aluminum alloys surfaces of high specular reflectivity having integral therewith a durable protective oxide coating, which is clear, transparent and impermeable comprising anodically treating said aluminum surface in an electrolyte consisting of 0.29% hydrofluoric acid, 0.23% sulfamic acid and 0.75% chromic acid, balance substantially all water, at a temperature of from about 100 degrees F. to about the boiling point at a current density of from about 10 to 80 amperes per square foot, thereafter anodically producing thereon a transparent oxide coating, and treating said coating with hot water at a temperature of from about 160 degrees F. to about the boiling point to render it impervious.

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