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ANODIC TREATMENT OF ALUMINUM SURFACES

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This invention relates to an electrolyte and method for anodically oxidizing the surfaces of aluminum and aluminum alloys. More particularly, the invention relates to an improved electrolyte annd method for producing a clear or transparent, substantially non-iridescent anodic oxide film on the surfaces of aluminum and aluminum alloys.

Aluminum products are often required to have highly polished surfaces and in many cases a surface of high specular reflectivity must be provided. Several processes may be employed to impart to aluminum and aluminum alloy surfaces a high lustre of optimum specular reflectivity among which may be mentioned buffing, chemical brightening and/or electrobrightening. The latter technique is illustrated in regard to the electrolytes, current density, temperature and time employed by reference to U. S. Patents Nos. 2,040,617 and 2,040,618 to R. B. Mason et al. and U. S. Patent 2,108,693 to R. B. Mason. The reflecting surface of the aluminum or aluminum alloys subjected to the treatments disclosed in these patents is stated to have a reflectivity of from as high as 80 to over 87%. However, these are total reflectivity figures including scattered or diffusely reflected light as well as specularly reflected light. More recently chemical baths for brightening aluminum annd aluminum alloys have been developed whereby a relatively high specular reflectivity may be imparted, as opposed to a lustrous appearance wherein the surface causes predominantly diffuse reflection of light usually characteristic of the ordinary chemical bright dips.

Regardless of the manner in which the metal surface is rendered specularly reflective, it is usually desirable and often necessary, to further process the polished or brightened metal surface in order to preserve the lustrous finish. Lacquering has been employed in certain instances, but the lacquer coating on the polished metal does not provide optimum protection for the manifold conditions presented by the wide variety of applications for such reflective surfaces, and, moreover, it is difficult to obtain permanent adherence of such coatings especially during subsequent fabrication. Accordingly, the more generally employed method of protecting annd preserving the polished condition of the metal is to form a clear, transparent, anodic film on the metal surface.

It has been known for a number of years that an artificial oxide film can be formed on aluminum or aluminum alloy surfaces by an electrolytic process, known as anodizing, in a suitable electrolyte. There are a number of well-known anodizing processes; but the fundamental principle underlying all is that the article to be treated is made the anode (instead of the cathode as in electroplating) in an electrolyte capable of yielding oxygen. When current is passed, an initial oxide film forms on the metal surface, and progressive oxidation takes place beneath the film thus formed. After passage of the current through the bath for a predetermined time, an inert, durable aluminum oxide coating is obtained. Although the principles of the various anodizing processes are the same, the properties of anodic coatings will vary, depending upon a number of factors among which is the composition of the electrolyte. In the past, the principal electrolytes used for anodizing aluminum and aluminum alloys have been sulfuric acid (U. S. Patents 1,869,041, 1,869,042, 1,869,058 and 1,900,472 cover the concentration of the

sulfuric acid electrolyte from 5 to 77%) and chromic acid. Other electrolytes, such as oxalic acid, boric acid, and phosphoric acid, have been used, although not as extensively as the former two.

The anodizing process most commonly in use which produces a substantially clear anodic film is that wherein sulfuric acid is the electrolyte. Of course, in anodizing a highly polished aluminum surface, such as those obtained by buffing and/or electrobrightening, or chemical brightening, it is imperative that the anodic film be non-iridescent and that such oxide film will not markedly impair or decrease the specular reflectivity of the surface. The disadvantage of the films produced by the sulfuric acid electrolyte is that when formed of sufficient thickness to eliminate iridescence, a clouding of the polished metal surface takes place during anodizing to give the appearance of a cloudy grey film which impairs specular reflectivity.

Phosphoric acid, as above-mentioned, has been used as an anodizing electrolyte, and produces a clear oxide film. However, such films are always relatively thin, and consequently iridescent. Prolonged periods of anodizing with phosphoric acid fail to eliminate iridescence, but do, however cause cloudiness in the film and/or on the metal thereby seriously reducing specular reflectivity. Thus, it may be seen that with such electrolytes it is possible to produce anodic coatings that are non-iridescent or substantially so, but in so doing the specular reflectivity of the metal surface is considerably decreased (sulfuric acid). Conversely, coatings that do not markedly impair specular reflectivity may be produced, but these show a decided iridescence (phosphoric acid).

It is, therefore, a primary object and purpose of this invention to provide an improved electrolyte and method for the anodic production of an oxide film on aluminum and aluminum alloys which is substantially clear or transparent and non-iridescent.

A more specific object is to provide an anodizing electrolyte and method to produce on aluminum and aluminum alloys, having a polished surface of high specular reflectivity, a clear protective anodic film of sufficient thickness to substantially eliminate iridescence, while maintaining the high specular reflectivity of the metal surface at a maximum, that is, with a minimum reduction in gloss reflectivity.

These and other objects and advantages of the invention will be apparent from the following detailed description of the invention.

It has been discovered according to the invention that an anodic film which is clear or substantially transparent and non-iridescent may be produced on aluminum and aluminum alloy surfaces by an electrolytic treatment in which the metal is the anode, that is, by anodizing, in an electrolyte comprising essentially sulfuric and phosphoric acids in certain suitable proportions. Moreover, it has been discovered that the sulfuric-phosphoric acid electrolyte is particularly suitable in providing a protective anodic film on aluminum and aluminum alloy surfaces upon which a lustrous finish of high specular reflectivity has been previously been produced by any of the known brightening or polishing methods. The anodic film thus formed preserves the lustrous finish from deterioration and is of sufficient thickness to eliminate or substantially eliminate iridescence while producing only a relatively slight loss in the specular reflectivity of the surface.

No attempt is here made to explain the improved result flowing from the fact that the combined phosphoric and sulfuric acids in the electrolyte act to modify the effect of either constitutent when used alone.

The anodizing electrolyte and method of the invention may be applied to any aluminum or aluminum alloy surface whether previously polished or not to produce a clear, transparent substantially non-iridescent protective film. However, it is particularly useful where the metal surface has been polished to a high specular reflectivity by mechanical polishing (buffing), electrobrightening, electropolishing or chemical brightening.

The concentrations of the sulfuric acid and phosphoric

acid electrolytes may be varied throughout a relatively wide range of percentages by weight. The phosphoric acid constituent predominates in the electrolyte, being present in amounts of from about 15 to about 40% by weight of total solution. It is, of course, necessary that the aqueous electrolyte solution contain at least effective amounts of sulfuric acid and generally at least about 2% sulfuric acid is required, while it may advantageously be as high as 10%. Expressed in terms of concentration, beneficial results are obtained with phosphoric acid concentrations varying from about 175 to about 500 grams per liter and with sulfuric acid concentrations of from about 30 to slightly over 100 grams per liter.

Optimum coatings of oxide film affording very good protection and causing a minimum of reduction in specular or gloss reflectivity have been produced with a concentration of about 45 grams per liter of sulfuric acid and about 408 grams per liter of phosphoric acid, that is, about 3.7% H_2SO_4 and about 33.6% H_3PO_4 by weight of total solution.

The voltage suitably impressed on the electrolytic cell electrodes may vary from about 5 to 50 volts e. m. f. to produce a current density of from about 5 to about 30 amperes per square foot. (The current density is here computed by dividing the total current applied by the total area of conductive anode material immersed in the electrolyte.)

Although direct current is preferably employed in the anodizing process, alternating current may satisfactorily be used in lieu of direct current.

The anodizing time may be widely varied and depends to a large extent on other factors such as electrolyte concentrations, temperature, and current density. In general, the time for anodic treatment of a brightened aluminum or aluminum alloy surface is from about one-half minute to fifty minutes to produce a clear non-iridescent film of sufficient thickness to afford adequate protection, for example, 0.00005 to .0001 inch.

A temperature of from about 60 to about 90° F. is recommended (about 15 to 35° C.), higher temperatures being suitably employed with shorter times of treatment and lower temperatures with longer times. Optimum results have been produced in about ten minutes with a current density of 10 amperes per square foot at an e. m. f. of 25 volts and a temperature of from 75 to 80° F.

In general, all other conditions being held constant, if the processing time, the current density or the temperature is increased there is a tendency for a dull cloudy film to be produced. Conversely decrease of time, current density or temperature, other factors remaining fixed, tends to produce a thin film having a characteristic iridescence. As a rule, it is desirable to subject the brightened anodized metal to any of the conventional sealing treatments, for example, immersing in water at 80 to 100° C., to reduce the porosity and absorptivity of the oxide film.

The invention is further illustrated by the following example which includes the preliminary brightening, and which is not intended to constitute a limitation thereof, it being understood, as set forth above, that the several factors involved may be varied within a wide range with beneficial results.

Samples of a common aluminum alloy were prepared by first mechanically buffing, after which they were cleaned free of any adhering buffing compound, grease or other adhering foreign material by immersion in a mild inhibited alkaline cleaner. The samples were then electrobrightened by being connected as anodes in an aqueous electrolytic bath of 2.5% by weight fluoboric acid (HBF_4) for two minutes at a current density of 70 amperes per square foot and a bath temperature of 75 to 85° F.

The brightened samples contained a thin film or smut on the surface which was removed by a six minute immersion in a smut removal bath consisting of an aqueous solution containing about 5% ortho-phosphoric acid and about 2% chromic acid calculated as CrO_3 at a temperature of about 180 to 212° F. The solution was agitated during immersion.

The cleaned smut-free samples which had a specular reflectivity of 78% were then connected as anodes in an aqueous electrolyte containing 3.7% by weight sulfuric acid and 33.6% by weight phosphoric acid, the balance being water. A D. C. voltage of 25 volts was impressed on the cell, the current density being 10 amperes per square foot, with the bath at 75–80° F. for a period of ten minutes. The anodized samples were then removed and examined. The oxide film was clear and essentially non-iridescent and the specular reflectivity as measured by a Henry Gardner 60° glossmeter was 65%, as compared with 78% given above for the samples prior to anodizing and subsequent to smut removal after electrobrightening. The reduction in reflectivity was smaller than samples anodized by the conventional sulfuric acid electrolyte according to the procedures disclosed in U. S. Patents 1,869,041, 1,869,042, 1,869,058 and 1,900,472, above mentioned. The actual absolute value of the specular reflectivity of the treated samples was in most cases at least 65%, while those anodized with sulfuric acid alone were no higher than 50%.

It is, of course, essential that all materials to be anodized be clean. Where polishing is accomplished by buffing, a mild alkaline cleaner is recommended to insure a clean surface. In addition, where the article is not to be electrobrightened, it is advisable in order to secure maximum specular reflectivity to deoxidize the metal by the use of a deoxidizing bath such as the phosphoric acid-chromic acid smut removal solution, above-mentioned. When the anodizing is preceded by an electrobrightening process which includes a deoxidizing step, only a thorough water rinse is recommended prior to anodizing.

The apparatus employed for the process may be constructed of any material resistant to the acid electrolyte under the conditions employed. Thus, the tanks, cooling or heating equipment and agitators may be lined suitably with rubber, glass, lead, or lead alloy, or carbon.

The apparatus preferably is equipped with heating and cooling coils or jackets, such as steam and water coils, so that close control of operating temperatures can be maintained. Agitation is recommended to maintain uniform temperature in the bath and consequently of the work and to remove any gas which might form and passivate the work. Air or mechanical agitation may be used.

The process and electrolyte of the invention are equally or more economical than the phosphoric acid process and only moderately more expensive than the sulfuric acid electrolyte while productive of results superior to both. In the foregoing specification and in the claims percentages by weight are based on total solution weight.

What is claimed is:

1. In a process of producing and preserving bright surfaces of high specular reflectivity on aluminum and aluminum base alloys, the step which comprises anodically coating the brightened metal surface with a clear non-iridescent protective oxide film in an electrolyte consisting essentially of from about 15 to about 40% by weight phosphoric acid and from about 2 to about 10% by weight sulfuric acid, balance substantially water.

2. A process according to claim 1 in which the electrolyte comprises an aqueous solution consisting essentially of about 33.6% by weight ortho-phosphoric acid and about 3.7% by weight sulfuric acid.

3. A process according to claim 1 in which the metal is subjected to the action of the electrolyte at a current density of about 10 amperes per square foot and a temperature of about 75° F.

4. A process according to claim 1 in which the metal is anodized for from one-half minute to about fifty minutes.

5. A process for producing a clear, non-iridescent oxide film on aluminum and aluminum base alloys having bright surfaces of high specular reflectivity which comprises cleaning the metal, electrobrightening the cleaned metal, subjecting the electrobrightened metal to an acid solution to remove the smut film, and thereafter anodically coating the brightened metal in an electrolyte consisting essentially of from about 15 to about 40% by weight phosphoric and from about 2 to about 10% by weight sulfuric acid, balance substantially water, at a current density of from about 5 to about 30 amperes per square foot and a temperature of from about 60 to about 90° F.

6. A process according to claim 5 in which the metal is anodized for from about one-half minute to about fifty minutes.

7. A process for anodically coating aluminum and aluminum base alloys with a clear non-iridescent protective oxide film which comprises subjecting the cleaned metal as anode to the action of an electrolyte consisting essentially of from about 15 to about 40% by weight phosphoric acid and from about 2 to about 10% by weight sulfuric acid, balance substantially water, in an electrolytic cell for from about one-half minute to about fifty minutes at a current density of from about 5 to 30 amperes per square foot and a temperature of about 60 to about 90° F.

8. A process for the formation of a clear non-iridescent protective oxide coating on aluminum and aluminum base alloys comprising anodically coating the metal surface in an electrolyte consisting essentially of from about 15 to about 40% by weight phosphoric acid and from about 2 to about 10% by weight sulfuric acid, balance substantially water.

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