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PROCESS FOR ETCHING ALUMINUM AND ALUMINUM ALLOY SURFACES

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This invention relates to the production of etched aluminum and aluminum alloy surfaces, and is especially concerned with novel procedure for increasing the etching rate on these surfaces and for producing brightened etched surfaces of this type.

It is well known to etch alkali soluble metals, such as aluminum and its alloys, with a solution having a solvent action on the aluminum or aluminum alloy surface, such as a hot aqueous solution, e.g., one containing sodium hydroxide. One method of carrying out such etching treatment is by immersion of the metal surface to be etched in the alkali solution. The etched article is then further treated to remove "smut," e.g., by immersion in nitric acid, washed, and dried.

Generally a matte surface is obtained by the foregoing procedure. However, many applications of etched aluminum or aluminum alloys require that the etched surface be brighter than is normally obtained by conventional etching procedures. This is true especially of zinc and copper alloys of aluminum.

One object of this invention is to provide etched surfaces of aluminum and its alloys having improved appearance.

Another object is to provide procedure for producing bright, etched aluminum and aluminum alloy surfaces.

Yet another aim of the invention is to increase the etching rate of aluminum and aluminum alloy surfaces in alkali solutions.

It is known to treat an aluminum or aluminum alloy surface preparatory to applying an adherent metallic or non-metallic coating thereon, with an aqueous alkaline solution of an alkali metal carbonate containing a chromate to produce an oxide coating on said surface, followed by removal of the oxide coating with an aqueous solution of chromic or nitric acid. In this process, relatively dilute alkaline solutions of the alkali metal carbonate, e.g., sodium carbonate, are employed, but a relatively large proportion of chromate, e.g., potassium dichromate, to alkali metal carbonate is employed. Thus, a proportion of about one part of the chromate to three parts of the alkali metal carbonate is generally employed in this process.

We have now discovered that when an aluminum or aluminum alloy surface is treated or etched in stronger alkali solutions than those employed in the above process and having dissolved therein a minor amount of a compound of chromium, titanium, vanadium, or manganese, said compound being present in substantially smaller proportion to the alkali than in the case of the chromate in the aforementioned prior art process, the dissolution or etching rate of the aluminum is accelerated and an etched substantially bare metal surface is obtained of generally enhanced brightness as compared to the conventional prior art procedure for etching aluminum.

In accordance with the foregoing, and contrary to the prior art, we have discovered that chromate and dichromate-containing alkaline solutions of concentrations sufficient to dissolve aluminum metal will cause such a solu-

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tion with substantially no formation of an oxide coat on the metal if the chromate or dichromate is employed in ratios of from about .1 to about 10% calculated upon the weight of NaOH which will produce in the alkaline solution the OH ion concentration produced by the weight of alkaline material actually employed. The weight of alkaline material employed is such that it will produce an alkaline solution having an OH ion concentration equivalent to that produced by employing about 0.1 to 10 mols NaOH for every liter of such alkaline solution. This result is unexpected since as is taught by the prior art, such chromate or dichromate ion in alkaline solutions produce, instead of a corrosion of the metal to form a metallic surface, a substantial coating of oxide on the metal.

The results obtained by us as distinguished from the results obtained by the prior art are in our view due to the fact that we employ the chromates and dichromates in amounts in which their inhibiting action on the corrosion is insufficient to produce any substantial oxide formation, whereas in the prior art the much greater ratio of chromate or dichromate to the alkali is such that these materials inhibit the solution of the metal and aid in the production of an oxide coat.

In its broader aspects, the invention comprises the use of a chromium, titanium, vanadium or manganese compound in the same weight ratio as for the chromates, as noted above.

The chromium, titanium, vanadium, and manganese compounds employed as additives in the aqueous alkali etching bath according to the invention are soluble in the alkali, preferably alkali metal hydroxide, etching solution, particularly in the relatively small amounts of such compounds used and at the relatively high temperatures of solution normally employed for etching aluminum or its alloys in alkali solutions. Illustrative compounds which can be used are alkali metal chromates and dichromates such as potassium chromate and potassium dichromate, chromium sulfate, chromium oxide, titanium oxide, titanium oxalate, vanadium pentoxide, vanadium trioxide, manganese sulfate, and manganese dioxide. In the alkaline solutions employed, the dichromate generally reverts to the chromate. The preferred additive materials are the chromium compounds, particularly the alkali metal chromates and dichromates. The above compounds can be employed separately, or mixtures of two or more of the compounds may be used.

In practicing the invention, the article having an aluminum or aluminum alloy surface can be immersed in a hot aqueous solution containing an alkali such as sodium or potassium hydroxide, trisodium phosphate, sodium carbonate, or the like, or mixtures thereof. The strong alkali etchant materials, most desirably caustic soda, produce best results according to the invention. Temperature of the solution may range say from room temperature to about 212° F. Generally, temperature is maintained in a range from about 100° F. to about 210° F. during treatment.

According to the invention, the alkali concentration of the etching solution should be such that the solution has an alkalinity and OH ion concentration equivalent to that produced by the above noted 0.1 to 10 mols NaOH per liter of solution, with best results realized at the higher OH ion concentrations equivalent to 1 mol of sodium hydroxide or above. The preferred amount of brightening and accelerating compound added to the alkali etching solution is in the range of about 2 to 6% calculated on the same basis as previously given. The brightening and accelerating compound in the solution can be replenished from time to time where the bath is in continuous use.

A dark highly adherent film called "smut" is generally present on the surface of aluminum or aluminum alloys following treatment in the alkali etching solution. These

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smuts are insoluble in water and most acids and generally require treatment in nitric acid, mixtures of HNO_3 and H_2SO_4 , or mixtures of chromic and sulfuric acids for their removal. Following such smut removal and subsequent washing and drying of the aluminum surface treated according to the invention, such surface is found to possess high luster or brightness. This characteristic can be detected visually or by any other method. The specular reflectance of the etched aluminum and aluminum alloy surfaces produced according to the invention is materially greater than for etched surfaces of this type obtained by etching in conventional alkali solutions not containing our additive compounds. Thus, the specular reflectance of the metal surfaces obtained according to the invention may be as much as 50% or more greater than that realized by use of conventional alkali solutions.

The bright etched surface of the aluminum base material produced according to the invention process has no substantial oxide coating thereon as produced in the aforementioned prior art carbonate-chromate treating bath, but may have a thin oxide surface film formed when said surface is exposed to contact with the air. However, this thin oxide film does not materially reduce the brightness or specular reflectance of the aluminum surface produced according to our process.

The following are examples of practice of the invention, all quantities where not otherwise specified, being in terms of parts by weight.

Example 1

An aqueous etching solution is prepared by dissolving an etchant composition in water to produce a solution concentration of 10%. The etchant composition is composed of about 96 parts of caustic soda and about 4 parts of chromium sulfate intimately mixed therewith. An aluminum alloy article containing about 91% aluminum and about 4.5% copper is etched in the solution while maintained at a temperature of about 190° F. The article is then withdrawn from the bath, the smut removed in an acid bath, and the article washed and dried.

The etched surface of the alloy is found to be substantially brighter than the surface of an article of the same alloy which is treated in an etching bath of the same composition and under the same conditions as described above, except that the chromium sulfate is omitted. This is shown from the comparative specular reflectances of the respective articles, the article treated in the bath containing chromium sulfate having a specular reflectance 25 to 40% greater than the article which is treated in the conventional bath without the chromium sulfate. Further, the rate of etching in the bath containing chromium sulfate is improved or accelerated about 8% over the rate of etching of the same alloy in the same bath under the same conditions, but omitting the chromium compound.

Example 2

Results similar to those of Example 1 may be obtained employing the same procedure and conditions, but using chromium oxide in place of chromium sulfate.

Example 3

An etching solution may be prepared composed of about 8% by weight of a mixture of NaOH and potassium dichromate (4 parts of the dichromate to 96 parts NaOH). An article having an aluminum alloy surface containing about 91% aluminum and about 4.5% copper is immersed in the solution and etched therein while the solution is maintained at a temperature of about 180°–190° F. The etched surface obtainable after washing and drying is found to be very bright and the rate of the etching reaction in the solution is increased by the addition of the dichromate over that of the same solution in its absence.

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Example 4

An etching solution may be prepared in the manner described in Example 3 except that titanium oxide is substituted for the potassium dichromate. Results similar to those noted in Example 3 may be obtained otherwise employing the same procedure and conditions noted therein.

Example 5

Results similar to those of Example 3 are obtainable employing the procedure and conditions described therein but replacing the potassium dichromate with vanadium pentoxide.

Example 6

An aqueous etching solution is prepared by dissolving an etchant composition in water to produce a solution concentration of 10%. The etchant composition is composed of 98 parts of caustic soda and 2 parts of manganese dioxide intimately mixed therewith. A 24S aluminum alloy article is etched in the solution while maintained at a temperature of about 190° F. The article is then withdrawn from the bath, the smut removed, and the article washed and dried. The rate of etching in this solution is about 8.5% greater than in the same bath under the same conditions but in the absence of the manganese dioxide.

The term "aluminum" as used herein and in the appended claims is intended to denote and to include aluminum and aluminum base alloys including the usual impurities present in aluminum ingots of commercial grade or such impurities as are picked up in the course of the usual handling operations incident to ordinary smelting practice.

While we have described a particular embodiment of our invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

We claim:

1. A method of etching an article having an aluminum surface, which comprises treating said surface with an etching solution containing an alkaline material and a compound of a metal of the group consisting of chromium, titanium, vanadium, and manganese, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said compound present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

2. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein a chromium compound, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said compound present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

3. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein an alkali metal chromate, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said chromate present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

4. A method of etching an article having an aluminum

surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein an alkali metal dichromate, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said dichromate present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

5. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein chromium sulfate, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said chromium sulfate present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

6. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein a titanium compound, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said compound present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

7. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein titanium oxide, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said titanium oxide present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

8. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein a vanadium compound, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said compound present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

9. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein vanadium pentoxide, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said vanadium pentoxide present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration, and producing an aluminum surface free of any substantial oxide coating.

10. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution having dissolved therein chromium oxide, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter of solution, and the amount of said chromium oxide present being from about 0.1 to 10% calculated on the equivalent weight of NaOH to produce said alkalinity and hydroxyl ion concentration,

and producing an aluminum surface free of any substantial coating.

11. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and a compound of a metal of the group consisting of chromium, titanium, vanadium, and manganese, the concentration of caustic soda in said solution ranging from about 0.1 to 10 mols per liter of solution, said compound being present in an amount of from about 0.1 to about 10% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

12. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and an alkali metal chromate, the concentration of caustic soda in said solution ranging from about 0.1 to 10 mols per liter of solution, and said chromate being present in an amount from about 0.1 to about 10% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

13. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and having dissolved therein an alkali metal dichromate, the concentration of caustic soda in said solution ranging from about 0.1 to 10 mols per liter of solution, and said dichromate being present in an amount from about 0.1 to about 10% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

14. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and chromium sulfate, the concentration of caustic soda in said solution ranging from about 0.1 to 10 mols per liter of solution, and said chromium sulfate being present in an amount from about 0.1 to about 10% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

15. A method of etching an article having an aluminum surface, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and chromium oxide, the concentration of caustic soda in said solution ranging from about 0.1 to 10 mols per liter of solution, and said chromium oxide being present in an amount from about 0.1 to about 10% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

16. A method of etching and brightening the surface of an aluminum article, which comprises treating said surface with a hot aqueous alkaline etching solution containing caustic soda and a chromium compound, the concentration of caustic soda in said solution being at least 1 mol per liter of solution, and said compound being present in an amount of from about 2 to about 6% by weight of said caustic soda, and producing an aluminum surface free of any substantial oxide coating.

17. A method of etching an article having an aluminum surface, which comprises treating said surface with an etching solution containing an alkaline material and a minor amount of a member of the group consisting of chromium, titanium, vanadium and manganese in ionic form, said solution having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter, the amount of said member employed being such as to form a bright etched aluminum surface, and producing an aluminum surface free of any substantial oxide coating.

18. A method of etching an article having an aluminum surface, which comprises treating said surface with an etching solution containing an alkaline material and a minor amount of chromium in ionic form, said solution

having an alkalinity and OH ion concentration equivalent to that produced by about 0.1 to 10 mols NaOH per liter, the amount of chromium employed being such as to form a bright etched aluminum surface, and producing an aluminum surface free of any substantial oxide coating.

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