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METHOD AND COMPOSITION FOR TREATING ALUMINUM AND ALUMINUM ALLOYS

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This invention relates to the brightening of aluminum and aluminum alloys. More particularly, the invention relates to a composition and method for chemical brightening of aluminum and its alloys.

Although aluminum is ordinarily considered a bright metal, it often presents a dull or matte-like finish due to the oxide films formed on its surfaces during processing. Many aluminum and aluminum alloy products are fabricated from mill finished sheet having such a characteristic dull appearance, which leads to a demand by fabricators for means to impart a bright, lustrous finish to their products. One widely used method of polishing aluminum and its alloys is by mechanical buffing with a suitable abrasive. However, this mechanical polishing is expensive and is not easily adaptable to articles having intricate shapes and inaccessible surfaces. Other methods known as electropolishing and electrobrightening involve subjecting the aluminum article to an electrolytic treatment and produce a desirable lustrous finish. However, the methods are both slow and expensive.

It is, therefore, a primary object and purpose of the invention to provide a composition and method for the chemical brightening or polishing of aluminum and aluminum alloys which eliminates the necessity for a separate smut removal treatment. A further object is to provide a chemical solution or bright dip for aluminum and aluminum alloys which is characterized by its economy in use, short immersion time required to obtain the desired effect, and ease of application. Another object is to produce on aluminum and aluminum alloy articles polished or brightened surfaces by means of a chemical bright dip composition and process which effectively removes the dulling oxide films from the metallic surfaces and imparts thereto a high luster.

Chemical brightening of aluminum has previously been accomplished using a combination of nitric and hydrofluoric acids. The hydrofluoric acid readily dissolves any oxide film and attacks the metal. However, the etching action of the HF proved difficult to control regardless of the concentration or temperature employed, and uniform results could not be consistently obtained.

Uniform and superior chemical brightening of aluminum and aluminum alloys can be obtained with a bright dip composition comprising an aqueous acid solution containing hydrogen, nitrate and fluoride ions, and cations of a metal more electropositive than aluminum, as disclosed and claimed in my copending application, S. N. 101,692 filed June 27, 1949.

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The presence of cations of a metal more electropositive than aluminum is accomplished by the addition of a soluble salt of the selected metal to the chemical bath and greatly enhances the luster or brightness of the aluminum and aluminum alloys. It is believed that this beneficial effect is due to reduction of the metal cations in solution and deposition of the metal to form a galvanic couple with the aluminum. This is evidenced by a metallic smut formed on the surface of the aluminum, the presence of which markedly improves the brightening effect. However, this smut formation necessitates a separate treatment for removal; such as, a dip in nitric acid or a mechanical wiping.

It has now been found according to the present invention that this apparently necessary smut formation is completely eliminated by the presence of chromate ions in the bright dip solution, while at the same time the increased brightening effect is retained.

The term "electropositive" as used in the specification and appended claims is based upon the definition and values of single electrode potentials on the hydrogen scale given in the "Chemical Engineers' Handbook," John H. Perry, editor-in-chief, 2nd edition, eighth impression (1941) (McGraw-Hill Book Company), pages 2746 to 2748, inclusive. It is there indicated that "In solutions containing their own ions, noble metals (e. g. with electrolytic solution pressures lower than that of hydrogen) acquire a positive potential, while base metals (e. g. with electrolytic solution pressures greater than that of hydrogen) acquire a negative potential."

The term "chromate" is used generically to designate bivalent anions containing chromium and includes the presence of the dichromate ion ($\text{Cr}_2\text{O}_7^{=}$), as well as the higher polychromates or complexes which may form from the $\text{CrO}_4^{=}$ in acid solution.

In general, the soluble salt supplying the metal cations may be that of any metal more electropositive than aluminum which will not be precipitated in the form of an insoluble salt of any of the anions present in the bright dip, namely, fluoride (F^-), nitrate (NO_3^-), and chromate ions under the conditions existing during treatment, that is, the pH or acidity, the temperature, and solution concentrations. Examples of such metals are copper, silver, platinum and gold. In the presence of the nitric acid which supplies the hydrogen ions, such metals are not precipitated by the above-named anions.

The more electropositive metal is preferably one which is electropositive to hydrogen, where

the electrode potential of $H_2=0.00$, in order that a couple of relatively high E. M. F. will be obtained. Copper is the preferred metal from the standpoint of cost while producing optimum results. Silver, which is below copper in the series produces excellent results, as do the truly noble metals, platinum and gold.

The anion of the metal salt may be any anion compatible with those existing in the bright dip solution and which forms a salt with the selected metal soluble in the acid solution. It is preferable, however, that the anion be that of the strongest or predominating acid, namely, nitric acid, whenever possible in order to avoid solutions of undue complexity. Consequently, copper and silver nitrate are the preferred species.

The amount of metal cation in the solution preferably corresponds to that produced by addition of from about .01 to 0.6% by weight of a soluble salt of the metal.

The chromate ions in the bath are preferably formed by the addition of chromic anhydride CrO_3 to the acid solution, although such ions may be introduced by addition of equivalent amounts of chromate salts, for example, ammonium chromate or dichromate. The concentration of chromate ion is suitably controlled by the addition of chromates or chromic anhydride in an amount about 0.1 to 1.5% by weight of solution, calculated as CrO_3 .

The proper hydrogen ion concentration is maintained by the use of nitric acid, in an amount of from about .5 to about 6% by weight of the solution. When using 70% HNO_3 , this amount corresponds to a volume concentration of from about 5 to 60 cc./liter.

The fluoride ion may be introduced in the form of hydrofluoric acid, or an equivalent amount of any soluble salt of the acid which forms hydrofluoric acid in situ in the solution in the presence of nitric acid, and the cation of which will not adversely affect the proper functioning of the chemical bath, for example, ammonium fluoride. It has been found that the fluoride concentration should be maintained at a value corresponding to an amount of hydrofluoric acid within the range of from about .01 to about 0.5% by weight of solution. When using 48% HF, this amount corresponds to a volume concentration of about .2 to about 9 cc./liter.

Thus, the bright dip composition of the present invention essentially comprises an aqueous solution containing from about .5 to 6% nitric acid by weight, fluoride and chromate ions in amount corresponding to that produced by about .01 to 0.5% hydrofluoric acid, and about 0.1 to 1.5% chromic anhydride, and cations of a metal more electropositive than aluminum corresponding to that produced by about .01 to 0.6% of a soluble salt of the metal.

Excellent brightening and polishing results are obtained when the hydrogen, fluoride, chromate and metal ion concentrations are maintained at any combination of values corresponding to that produced by a solution containing nitric acid, hydrofluoric acid, a soluble salt of a metal more electropositive than aluminum and chromate ion (calculated as chromic anhydride) in any combination of constituent amounts within the ranges above stated, or any combination of equivalent substances which will produce a solution of substantially the same chemical composition.

It is to be noted that a satisfactory degree of brightening is obtained when using any of the constituents in smaller or larger amounts than

indicated above. However, the desired effect is more readily obtained by operating within the stated ranges.

The chemical bath may be operated at temperatures of from about 100° F. to the boiling point. The desired brightening is accomplished with a shorter immersion time at the higher temperatures of from about 190° F. to boiling, and accordingly, this range is preferred. The time of immersion of the articles being treated in the bath should be sufficient to produce the desired brightening, yet insufficient to cause any undue etching of the metal. It is, of course, dependent primarily on solution temperatures and concentrations and may be widely varied. An immersion time of from about one-half to about ten minutes is recommended.

As specific examples, not intended to limit the invention, maximum brightness was obtained with an aluminum alloy treated by a five minute immersion in solutions at a temperature of 190° F. to boiling prepared by addition of the indicated compounds.

Example I

Constituent	Volume Concentration, cc./liter	Weight Concentration, g./liter	Per Cent Weight of Solution
HNO_3	50 (70% HNO_3)..	-----	5
HF.....	2 (48% HF).....	-----	0.1
$Cu(NO_3)_2$	-----	1	0.1
CrO_3	-----	8	0.8
Water, Balance.	-----	-----	-----

Example II

Constituent	Volume Concentration, cc./liter	Weight Concentration, g./liter	Per Cent Weight of Solution
HNO_3	50 (70% HNO_3)..	-----	5
HF.....	2 (48% HF).....	-----	0.1
$AgNO_3$	-----	1	0.1
CrO_3	-----	8	0.8
Water, Balance.	-----	-----	-----

The procedure followed in treating the metal articles with the chemical bath is merely to immerse the article in the heated solution for the required time and thereafter thoroughly water rinse and dry the treated article. However, it is advantageous that the metal to be processed be cleaned or degreased by the use of a mild, inhibited alkaline cleaner, for example, Kelite Aviation Cleaner (KDL #1). This is preferably accomplished by immersion in a heated solution of the cleaner for a few minutes, for example, two minutes in solution at 180-200° F., followed by a thorough rinsing prior to introduction into the bright dip solution. No metallic smut is formed during the brightening operation due to the presence of chromate ion. Thus, the necessity of a subsequent metallic smut removal operation is obviated.

Agitation of the bath is not essential, but is recommended since it produces more uniform results and tends to decrease the required immersion time. Mechanical or air agitation may be used, but the former is preferable since it does not cool the solution as does air agitation.

The process may be operated on a continuous or semi-continuous basis, or it may be conducted as a batch process. In case of the former, the components are gradually depleted and calculated additions of the compounds supplying

these ions are periodically added to maintain proper concentrations.

The chemical polishing treatment may be conducted in any suitable tank or other apparatus provided with a lining impervious to the corrosive action of the nitric and hydrofluoric acids at the operating temperatures. A particularly useful lining is Karbate—a treated carbon product resistant to attack by all chemicals except those which are highly oxidizing. Karbate is manufactured in molded slabs, blocks and other shapes.

The heating of the solution may be accomplished by the use of Karbate tubes or heat exchangers, or, if electrical heating is desired, Karbate shielded immersion heaters may be employed.

The results obtained with the chemical bright dip of the present invention do not produce a surface smoothing effect in comparison to mechanical buffing or electropolishing. However, the surface luster or brightness compares very favorably with that produced by electrobrightening, while the chemical bright dip requires only a short immersion time and no electric current. In short, the improved chemical bath produces the desired result much more economically.

What is claimed is:

1. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing hydrogen, nitrate, fluoride, and chromate ions and the cations of a metal more electropositive than aluminum in concentration corresponding to that produced by a solution containing by weight from about .5 to about 6% nitric acid, about .01 to about 0.5% hydrofluoric acid, about 0.1 to about 1.5% chromic acid anhydride, and from about .01 to about 0.6% of a soluble salt of the selected metal.

2. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing hydrogen, nitrate, fluoride and chromate ions and the cations of a metal electropositive to hydrogen in concentration corresponding to that produced by a solution containing by weight from about .5 to about 6% nitric acid, about .01 to about 0.5% hydrofluoric acid, about 0.1 to about 1.5% chromic acid anhydride, and from about .01 to about 0.6% of a soluble salt of the selected metal, the presence of the chromate ions effectively eliminating deposition of a metallic smut on the surface of the aluminum and aluminum alloys.

3. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing from about .5 to about 6% nitric acid by weight, fluoride and chromate ions in amount corresponding to that produced by about .01 to about 0.5% hydrofluoric acid and about 0.1 to about 1.5% chromic anhydride by weight, respectively, and about .01 to about 0.6% by weight of a soluble salt of a metal more electropositive than aluminum.

4. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing from about .5 to about 6% nitric acid by weight, fluoride and chromate ions in amount corresponding to that produced by about .01 to about 0.5% hydrofluoric acid and about 0.1 to about 1.5% chromic anhydride by weight, respectively, about .01 to

about 0.6% by weight of a soluble salt of a metal electropositive to hydrogen.

5. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing by weight from about .5 to about 6% nitric acid, about 0.01 to about 0.5% hydrofluoric acid, about .01 to about 0.6% of a water soluble salt of a metal more electropositive than aluminum, about 0.1 to about 1.5% chromic acid (calculated as CrO_3).

6. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing by weight from about .5 to about 6% nitric acid, about .01 to about 0.5% hydrofluoric acid, about .01 to about 0.6% of a water soluble salt of a metal electropositive to hydrogen, and about 0.1 to about 1.5% chromic acid (calculated as CrO_3).

7. A composition according to claim 6 in which the soluble salt is a nitrate.

8. A composition according to claim 6 in which the metal of the salt is copper.

9. A composition according to claim 6 in which the metal of the salt is silver.

10. An aqueous solution for brightening aluminum and aluminum alloys consisting essentially of about .5-6% nitric acid, about 0.01-0.5% hydrofluoric acid, about .01-0.6% cupric nitrate, and about 0.1-1.5% chromic acid by weight (calculated as CrO_3), said chromic acid preventing deposition of a metallic smut on the surface of the aluminum and aluminum alloys.

11. An aqueous solution for brightening aluminum and aluminum alloys consisting essentially of about .5-6% nitric acid, about 0.01-0.5% hydrofluoric acid, about 0.1-0.6% silver nitrate, and about 0.1-1.5% chromic acid by weight (calculated as CrO_3), said chromic acid preventing deposition of a metallic smut on the surface of the aluminum and aluminum alloys.

12. A process for the chemical brightening of aluminum and aluminum alloys which comprises immersing the metal in a heated aqueous bath containing by weight about .5 to about 6% nitric acid, about 0.01 to about 0.5% hydrofluoric acid, about 0.01 to about 0.6% of a water soluble salt of a metal more electropositive than aluminum, and about 0.1 to about 1.5% chromic acid (calculated as CrO_3) for a time sufficient to brighten the metal but insufficient to cause undue etching, maintaining the temperature of the bath at about 100° F. to the boiling point, and thereafter rinsing the thus treated metal.

13. A process for the chemical brightening of aluminum and aluminum alloys which comprises immersing the metal in a heated aqueous bath containing by weight about .5 to about 6% nitric acid, about 0.01 to about 0.5% hydrofluoric acid, about 0.1 to about 0.6% of a water soluble salt of a metal electropositive to hydrogen, and about 0.1 to about 1.5% chromic acid (calculated as CrO_3) for from about one-half to about ten minutes, maintaining the temperature of the bath at about 190° F. to the boiling point, and thereafter water rinsing the thus treated metal, the presence of chromate ion preventing deposition of metallic smut on the aluminum and aluminum alloys.

14. A process according to claim 13 in which the metal to be brightened is cleaned with a mild inhibited alkaline solution and then rinsed prior to immersion in the brightening bath.

15. A process according to claim 13 in which the salt is a nitrate.

16. A process according to claim 13 in which the metal of the salt is copper.

17. A process according to claim 13 in which the metal of the salt is silver.

18. A process for the chemical brightening of aluminum and aluminum alloys which comprises treating the metal in an aqueous acid bath containing hydrogen, nitrate, fluoride, and chromate ions and the cations of a metal more electro-positive than aluminum in concentration corresponding to that produced by a solution containing by weight from about .5 to 6% nitric acid, about .01 to 0.5% hydrofluoric acid, about 0.1 to about 1.5% chromic anhydride and from about .01 to 0.6% of a soluble salt of the selected metal,

maintaining the temperature of the bath at from about 100° F. to the boiling point, and thereafter removing from the metal the adhering solution.
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