

UNITED STATES PATENT OFFICE

2,620,265

COMPOSITION FOR TREATING ALUMINUM
AND ALUMINUM ALLOYS

Frederick Harold Hesch, Spokane, Wash., assignor
to Kaiser Aluminum & Chemical Corporation,
Oakland, Calif., a corporation of Delaware

No Drawing. Application September 28, 1950,
Serial No. 187,345

42 Claims. (Cl. 41—42)

1

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

This application is a continuation-in-part of my co-pending applications Serial No. 101,694, filed June 27, 1949, now Patent No. 2,593,447, and Serial No. 106,742, filed July 25, 1949, now Patent No. 2,593,448.

Although aluminum is ordinarily considered a bright metal, in most cases it 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 desirable lustrous finishes. However, these methods are both slow and expensive.

Chemical brightening compositions and processes have been developed for metals which produce surfaces of satisfactorily high specular reflectivity. One particular composition consisting of nitric, phosphoric and acetic acid has attracted attention in the art. However, such a chemical brightening bath requires the use of all components in a concentrated state, that is, only very minor amounts of water are permissible, as otherwise etching rather than polishing results. Accordingly, the bath has the significant practical disadvantage of high drag out losses and replenishing cost as well as high first cost. In addition, since the bath operates at elevated temperatures even small amounts of concentrated acetic acid cause obnoxious fumes and necessitates ventilation.

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 characterized by its high state of dilution, consequent low drag out and freedom from fumes. A further object is to provide a chemical solution or bright dip composition for aluminum and alu-

2

minum alloys which is characterized by the production of surfaces of high specular reflectivity due to a surface smoothing effect, 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 highly desirable 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 luster of relatively high specular reflectivity.

The invention further provides for modification of the basic bright dip composition to include as an additional constituent a metallic salt in very small amounts, which, in general, improves the specular reflectivity and effectively prevents the deposition of a certain film impairing the brightness of the surface, particularly when treating aluminum or aluminum alloys of low copper content.

Chemical brightening of aluminum has also previously been accomplished using a combination of nitric and hydrofluoric acids. The hydrofluoric acid readily dissolves any oxide film and attacks the metal. The nitric acid, which is essentially inactive toward aluminum, serves to keep the metal surface clean and substantially free from smut which might be deposited thereon during treatment. However, the etching or pitting action of the HF proved extremely difficult to control regardless of the concentration or temperature employed and uniform results could not be consistently obtained at a favorable rate of reaction.

It has been discovered according to the present invention that uniform and superior chemical brightening of aluminum and aluminum alloys to produce a relatively high specular reflectivity and significant surface smoothing effect is obtained with a bright dip composition comprising an aqueous acid solution containing as the preferred essential constituents hydrogen, fluoride, ammonium and trivalent chromium ions. Nitrate ions are also normally present since the preferred source of hydrogen ion is nitric acid. It is to be understood that certain of the ions may be present in the form of complexes, such as ammonium complexes, but that the essential constituents of the composition are defined in terms of the ions present in their simplest form.

The presence of the trivalent chromium and ammonium ions appears to exert a definite modifying effect on the action of the acid bath con-

5

the monosaccharides, for example, the hexoses, fructose, glucose, levulose, etc. and di-saccharides such as maltose, sucrose, lactose, etc. and higher carbohydrates such as starch, dextrin, etc.

It is recommended that in all cases a slight excess of reducing agent over stoichiometric amount be maintained in the bath to offset any evaporative loss and to insure that the chromium content of the solution will remain in reduced trivalent form. Even when trivalent chromium is introduced into the solution as such, it is advantageous that a reducing agent be present to prevent possible oxidation of the chromium to the hexavalent state. Any reasonable excess of polyhydric alcohol or other reducing agent will not be harmful.

In treating magnesium-containing aluminum alloys with the bright dip composition it was noted that in certain instances, a whitish film, which impaired specular reflectivity was deposited on the metal surfaces. This film, which was adherent to the surface, may presumably have been an oxide of magnesium. However, further investigation indicated that impairment of brightening and/or the formation of the film was not peculiar to magnesium-containing alloys and that commercially pure aluminum was susceptible. It was then significantly observed that less than optimum brightening occurred on those specimens of aluminum and aluminum alloys having a low copper content regardless of the presence or absence of magnesium. By "low copper content" is meant not substantially more than that amount of copper which is ordinarily present as a residual in commercial aluminum of 99+ % purity, for example, on the order of about 0.05%. Aluminum and its alloys containing higher amounts of copper exhibited optimum brightness.

It was discovered that the incorporation in the bright dip solution of the cations of a metal more electropositive than aluminum, that is, in addition to the trivalent chromium ions, eliminated the film and increased the brilliance of the metal. 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 Ed., Eighth Impression (1941) (McGraw-Hill Book Company), pages 2746 to 2748, inclusive.

In regard to the selection of the metal, it is recommended that it be one which has an electrode potential sufficiently more positive than aluminum that the galvanic couple resulting has a relatively high E. M. F., as compared, for example, to the Al-Zn couple; otherwise as the potential of the selected metal approaches that of aluminum, the advantageous results of increased brightness and film elimination are diminished to a large extent. Certain metals of these electropositive metals produce better results than others, for example, copper gives optimum results in regard to film elimination and increased specular reflectivity, and is therefore the preferred species. On the other hand, silver although increasing brightness on mill finished stock appears to promote pitting and accordingly is much less desirable. By way of further illustration, other metals which may be recommended as producing satisfactory results are iron, nickel, cobalt, gold and platinum. The metal cation may advantageously be introduced in the form of a soluble metal salt.

6

The anion of the metal salt may be any anion compatible with the other constituents of the solution and which forms a salt with the selected electropositive metal soluble in the acid solution. It is preferred where convenient to utilize the nitrates in order to avoid solutions of undue complexity. Copper nitrate is accordingly the preferred species.

The amount of the more electropositive metal may be relatively very small while completely eliminating film formation, and increasing the brightness of the surface. In fact, no such metal cations are necessary where the copper content of the aluminum or alloy is higher than above indicated, which includes the majority of aluminum alloys. The concentration of metal cation may be expressed as that produced by a solution containing the metal salt in an amount as low as 0.001% by weight of solution.

Larger amounts may advantageously be used where the brilliance of the metal is the primary consideration and the formation of metallic smut and its removal is not objectionable as an example, amounts substantially exceeding about 0.0015% by weight produced a thin non-adherent coating of copper on the brightened aluminum or aluminum alloy surface and avoidance of such deposition may be deemed desirable. This may be accomplished merely by not exceeding the amount of electropositive metal in solution which results in such smut formation. However, should the deposition occur, it is readily removed when the brightened article is subjected to the usual anodic oxidation to produce a protective coating thereon. The deposit of the selected metal, if any, may also be wiped off or dissolved by rinsing in an appropriate solution, for example, a dilute nitric acid solution after bright dipping.

It is not intended to limit the addition to the bath of the selected electropositive metal to the treatment only of those aluminum base metals containing .05% Cu or less, since improved results in degree of brightness are noted with substantially all aluminum base metals with the possible exception of those containing appreciable amounts of copper, for example 0.1% or more. For these higher copper alloys, the copper is dissolved and functions to increase specular brightness as though the copper were directly added to the bath.

The composition described in detail above produces the desired effects when the various essential ions, namely hydrogen, fluoride, and trivalent chromium with or without ammonium ion are present in the proper range of concentrations. It is to be understood that such ions may be supplied in the form of various compounds as long as their concentrations are maintained within the required range.

The proper hydrogen ion concentration for the acid solution is preferably maintained by the use of nitric acid in an amount of from about .5 to 5% by weight of the solution. When using 70% HNO₃, this amount corresponds to a volume concentration of from about 5 to 50 cc. per liter.

The fluoride ion may be introduced in the form of hydrofluoric acid, although 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 is preferred to avoid handling of the highly corrosive acid. Ammonium fluoride and ammonium bifluoride may advantageously be used, in which case the ammonium ion may be supplied in whole or in part therewith.

It has been found that the fluoride ion concentration should be maintained at a value corresponding to that produced by hydrofluoric acid within the range of from about .01 to about 0.5% by weight of solution. When using 48% HF, this corresponds to a volume concentration of from about .2 to 9 cc. per liter. Where supplied as ammonium fluoride between about 0.2 and 10 grams per liter or about 0.02 to 1% by weight of solution represent the stoichiometric equivalent to the above stated amount of HF in regard to F⁻ ion concentration. The amount of NH₄HF₂, when used to supply the fluoride ion, must also be stoichiometrically equivalent to the above range of amounts of HF, namely about 0.1 to about 8 grams per liter or .01 to 0.8% by weight.

The trivalent chromium ion in the solution is provided by adding hexavalent chromium or it may be introduced directly, as above indicated. Amounts of from about 0.005 to about 0.5% trivalent chromium may be employed. Optimum Cr⁺⁺⁺ concentration is about three (3) grams per liter or 0.3% by weight of solution. In terms of hexavalent chromium calculated as CrO₃, these amounts are about .01 to about 1%, and about 6 grams per liter or 0.6% by weight of solution, respectively. In terms of chromic nitrate calculated as Cr(NO₃)₃·9H₂O, these amounts are from about 0.04 to 4%, and 24 grams per liter or 2.4% by weight of solution. The preferred range of Cr⁺⁺⁺ is from about 1 to 4 grams per liter or 0.1 to 0.4% by weight of solution.

A part or all of the preferred ammonium ion content of the solution, as above indicated, may be supplied in conjunction with the chromium constituent or the fluoride ion. However, where these ions are present in the lower range of the recommended concentrations, it may be advisable to add additional ammonium ion. Where the ammonium ion is introduced with the fluoride ion as NH₄F or NH₄HF₂, the amount supplied thereby as a rule suffices, although with the acid salt, it may be advantageous to increase the amount of ammonium ion particularly when brightening buffed surfaces. Thus, all of the NH₄⁺ ion or the balance required may be introduced in the form of another ammonium compound, such as the hydroxide or nitrate. Ammonium hydroxide is preferably employed. The preferred amount of the ammonium constituent of the solution is equivalent to about .01 to about 0.5% ammonia by weight of the solution.

Thus, the bright dip composition of the present invention essentially comprises an aqueous acid solution containing hydrogen, fluoride, and trivalent chromium, preferably together with ammonium ions in amount stoichiometrically equivalent to from about 0.5 to 5% nitric acid, .01 to .5% hydrofluoric acid, about 0.005 to 0.5% of trivalent chromium (Cr⁺⁺⁺) and from about .01 to 0.5% ammonia, all percentages being by weight of solution. In addition, very small amounts of the cations of a metal more electro-positive than aluminum corresponding to that produced by a solution containing as low as 0.001% by weight may be incorporated to increase brightness of the surface and eliminate film formation with aluminum and aluminum alloys containing low amounts of copper.

Where the chromium is added in hexavalent form, an organic reducing agent such as those disclosed is added in amount stoichiometrically equivalent to from about .05 to about 1.5% by weight of glycerol. In addition, the amount of

the reducing agent should be slightly in excess of the stoichiometric amount required for complete reduction of the hexavalent chromium.

Excellent brightening results are obtained when the hydrogen, fluoride, Cr⁺⁺⁺, ammonium ion concentrations are maintained at any combination of values corresponding to that produced in a solution prepared from nitric acid, hydrofluoric acid, chromic salt (or hexavalent chromium compound and reducing agent) and ammonia in any combination of 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 specular reflectivity 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. A more desirable 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, specular brightness was obtained with aluminum and aluminum alloys treated by a five minute immersion in a solution (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	Percent Weight of Solution
HNO ₃	25 (70% HNO ₃)..		2.5
HF.....	5 (48% HF).....		.3
NH ₄ OH.....	13 (28% NH ₃).....		1.3
Glycerol.....	5.....		.6
CrO ₃		6	.6
Water.....		Balance	

¹ Calculated as NH₃.

Example II

The following solution gave excellent results on aluminum and its alloys when immersed for about three and one-half minutes at a bath temperature of about 200–208° F.:

Constituent	Volume Concentration cc./liter	Weight Concentration g./liter	Percent Weight of Solution
HNO ₃	25 (70% HNO ₃)..		2.5
CrO ₃		6	0.6
NH ₄ HF ₂		6	0.6
Glycerol.....	5.....		0.6
Water.....		Balance	

Example III

To illustrate the direct addition of trivalent chromium the following solution was prepared and samples brightened by a 5 minute immersion at a bath temperature of 190–200° F.

Constituent	Volume Concentration cc./liter	Weight Concentration g./liter	Percent Weight of Solution
HNO ₃	30 (70% HNO ₃)	-----	3.0
NH ₄ F.....	-----	6	0.6
Cr(NO ₃) ₃ ·9H ₂ O.....	-----	24	2.4
Water.....	-----	Balance	-----

No glycerine or other reducing agent was added and the samples were of optimum brightness having high specular reflectivity and exhibiting a surface smoothing effect.

Example IV

An aluminum alloy containing less than .05% Cu was treated with the composition of Example I for five minutes at a temperature of about 200° F. The specular reflectivity was impaired by a whitish film adhering to the surface. To the solution was added 0.0148 gram per liter or 0.0015% by weight Cu(NO₃)₂·3H₂O. A sample of the same metal was then immersed for five minutes at a temperature of about 200° F. The surface had a bright finish of high specular reflectivity and no indications of a white film were evident.

The procedure followed in treating the aluminum or alloy articles with the bright dip is merely to immerse the article in the heated solution for the required time. The article is thoroughly water rinsed and dried. However, it is advantageous that prior to immersion the metal be cleaned or degreased by the use of a mild, inhibited alkaline cleaner. 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.

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.

It has been found that the bath requires only the addition of nitric acid at first to renew the supply of hydrogen ions depleted. However, fluoride ions are also depleted and when replenished vastly increase the life of the bath before a new bath is required. Replacing only nitric, the bath life is about 17 square feet of aluminum per gallon, but with addition of fluoride 190 square feet of aluminum per gallon may be processed with excellent results. Where hexavalent chromium is added, glycerine or other reducing agent is depleted and should be added in amount necessary to stabilize the bath against oxidation of trivalent chromium.

The chemical 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. Stainless

steel of certain specifications is also suitable for containers for the solution.

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 produce a definite surface smoothing effect but not as marked as that produced by the expensive electropolishing methods requiring high current densities. However, the surface luster or brightness is of relatively high specularity and compares well 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. A further advantage over previous chemical baths resides in the high dilution of the aqueous solution lowering drag out losses, and the comparative freedom from fumes.

I claim:

1. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing trivalent chromium ions in amount from about .005 to about 0.5%, and hydrogen and fluoride ions in amount stoichiometrically equivalent to from about 0.5 to about 5% nitric acid, and about .01 to about 0.5% hydrofluoric acid by weight of solution.

2. A composition according to claim 1 containing also cations of a metal more electropositive than aluminum.

3. A composition for chemically brightening aluminum and aluminum alloys comprising an acid aqueous solution containing trivalent chromium ions in amount from about .005 to about 0.5% and hydrogen, fluoride, and ammonium ions in amount stoichiometrically equivalent to from about 0.5% to 5% nitric acid, about .01 to about 0.5% HF, and about .01 to about 0.5% ammonia by weight of solution.

4. A composition according to claim 3 containing also cations of a metal more electropositive than aluminum.

5. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing as essential constituents hydrogen, fluoride, and trivalent chromium ions in concentration stoichiometrically equivalent to from about 0.5 to about 5% nitric acid, about .01 to about 0.5% hydrofluoric acid, about .04 to about 4% chromic nitrate calculated as Cr(NO₃)₃·9H₂O by weight of solution.

6. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing as essential constituents hydrogen, fluoride and trivalent chromium ions in concentration stoichiometrically equivalent to from about 0.5 to about 5% nitric acid, about .01 to about 0.5% hydrofluoric acid, and about .01 to about 1% of a hexavalent chromium compound calculated as CrO₃ together with an organic compound containing carbon, oxygen and hydrogen and oxidizable by hexavalent chromium present in amount stoichiometrically equivalent to from about .05 to about 1.5% glycerol by weight of solution.

7. A composition according to claim 6 containing also the cations of a metal more electropositive than aluminum.

8. A composition according to claim 6 in which the organic compound is a carbohydrate.

9. A composition according to claim 6 in which the organic compound is a water miscible monohydric alcohol.

10. A composition according to claim 6 in which the organic compound is a water miscible polyhydric alcohol.

11. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing hydrogen, fluoride, ammonium and trivalent chromium ions in amount stoichiometrically equivalent to that produced by a solution containing from about 0.5 to 5% nitric acid, about .02 to 1% ammonium fluoride and about 0.1 to 0.4% trivalent chromium by weight of solution.

12. A composition according to claim 11 in which the trivalent chromium is supplied by the introduction of a hexavalent chromium compound in amount of from about .01 to about 1% calculated as CrO_3 and an organic compound containing carbon, oxygen and hydrogen and oxidizable by hexavalent chromium in amount slightly in excess of stoichiometric with respect to the chromium.

13. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing as essential constituents hydrogen, fluoride, ammonium and trivalent chromium ions in concentration stoichiometrically equivalent to from about 0.5 to 5% nitric acid, about .01 to 0.5% hydrofluoric acid, about .01 to 0.5% ammonia, and about .01 to 1% of a hexavalent chromium compound calculated as CrO_3 by weight of solution together with an organic compound containing carbon, hydrogen and oxygen and oxidizable by hexavalent chromium present in an amount stoichiometrically equivalent to from about .05 to 1.5% glycerol by weight of solution.

14. A composition according to claim 13 in which the organic compound is a carbohydrate.

15. A composition according to claim 13 in which the organic compound is a water miscible monohydric alcohol.

16. A composition according to claim 13 in which the organic compound is a water miscible polyhydric alcohol.

17. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing hydrogen, fluoride, ammonium and trivalent chromium ions in amount stoichiometrically equivalent to that produced by a solution containing from about 0.5 to 5% nitric acid, about .01 to 0.8% ammonium bifluoride, and about 0.1 to 0.4% trivalent chromium by weight of solution.

18. A composition according to claim 17 in which the trivalent chromium is supplied by the introduction of a hexavalent chromium compound in amount of from about .01 to 1% calculated as CrO_3 and an organic compound containing carbon, hydrogen and oxygen and oxidizable by hexavalent chromium in amount slightly in excess of stoichiometric with respect to the chromium.

19. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing hydrogen, fluoride, and trivalent chromium ions and cations of a metal more electropositive than aluminum in amount stoichiometrically equivalent to that produced by a solution containing from about 0.5 to 5% nitric acid, about .01 to 0.5% hydrofluoric acid, about 0.1 to 0.4% trivalent chromium by weight of solution, and very small amounts but

not less than about .001% by weight copper nitrate calculated as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

20. A composition according to claim 19 containing also ammonium ions in amount stoichiometrically equivalent to from about .01 to 0.5% ammonia by weight of solution.

21. A composition for the chemical brightening of aluminum and aluminum alloys comprising an acid aqueous solution containing hydrogen, fluoride, and trivalent chromium ions in amount stoichiometrically equivalent to from about 0.5 to 5% nitric acid, about .01 to 0.5% hydrofluoric acid, the trivalent chromium ions being supplied by reduction in situ of hexavalent chromium present in amount stoichiometrically equivalent to from about .01 to 1% calculated as CrO_3 .

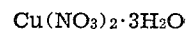
22. A composition according to claim 21 containing also ammonium ions in amount stoichiometrically equivalent to from about .01 to 0.5% ammonia by weight of solution.

23. A composition for chemically brightening aluminum and aluminum alloys essentially comprising an aqueous solution of about 2.5% HNO_3 , about 0.3% HF , about 0.3% NH_4OH , about 0.6% chromic acid and about 0.6% glycerol by weight of solution.

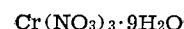
24. A composition for chemically brightening aluminum and aluminum alloys essentially comprising an aqueous solution of about 2.5% HNO_3 , about 0.6% NH_4HF_2 , about 0.6% chromic acid and about 0.6% glycerol by weight of solution.

25. A composition for chemically brightening aluminum and aluminum alloys essentially comprising an aqueous solution of about 3.0% HNO_3 , about 0.6% NH_4F and about 2.4% chromic nitrate calculated as $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ by weight of solution.

26. A composition according to claim 23 containing also about .0015% by weight of



27. A chemical bath for brightening aluminum and aluminum alloys comprising a dilute acid aqueous solution containing from about 0.5 to 5% HNO_3 , about .01 to 0.5% HF , and about 0.04 to about 4% chromic nitrate calculated as



by weight of solution.

28. A chemical bath according to claim 27 containing also about .01 to 0.5% by weight ammonium hydroxide calculated as NH_3 .

29. A chemical bath according to claim 27 containing from about .001 to .01% copper nitrate calculated as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

30. A chemical bath for brightening aluminum and aluminum alloys comprising a dilute acid aqueous solution containing from about 0.5 to 5% HNO_3 , about .01 to 0.5% HF , about .01 to 1% chromic acid calculated as CrO_3 , and about .05 to 1.5% of a water miscible polyhydric alcohol by weight of solution.

31. A bath according to claim 30 containing also about .01 to 0.5% by weight ammonium hydroxide calculated as NH_3 .

32. A chemical bath for brightening aluminum and aluminum alloys comprising a dilute acid aqueous solution containing from about 0.5 to 5% HNO_3 , about .02 to 1% NH_4F , about .01 to 1% chromic acid calculated as CrO_3 and about .05 to 1.5% of a water miscible polyhydric alcohol by weight of solution.

33. A chemical bath for brightening aluminum and aluminum alloys comprising a dilute acid aqueous solution containing from about 0.5 to 5%

HNO₃, about .01 to 0.8% NH₄HF₂ about .01 to 1% chromic acid calculated as CrO₃ and about .05 to 1.5% of a water miscible polyhydric alcohol by weight of solution.

34. A process for the chemical brightening of aluminum and aluminum alloys which comprises treating the metal in an aqueous acid bath containing from about .005 to 0.5% by weight trivalent chromium ions, and hydrogen and fluoride ions in amount corresponding to that produced in a solution containing from about 0.5 to 5% HNO₃, and about .01 to 0.5% HF by weight of solution, and maintaining the solution at a temperature of about 100° F. to the boiling point.

35. A process according to claim 34 in which the bath also contains ammonium ions in amount stoichiometrically equivalent to from about .01 to 0.5% by weight ammonia.

36. A process according to claim 34 in which the bath also contains cations of a metal more electropositive than aluminum.

37. A process according to claim 34 in which the bath also contains ammonium ions in amount stoichiometrically equivalent to from about .01 to 0.5% ammonia by weight and cations of a metal more electropositive than aluminum.

38. A process according to claim 34 in which the trivalent chromium ions are supplied by reduction in situ of hexavalent chromium present in amount of from about .01 to from about 1% by weight calculated as CrO₃.

39. A process for the chemical brightening of aluminum and aluminum alloys which comprises treating the metal in an aqueous acid solution containing hydrogen, fluoride, ammonium and trivalent chromium ions in amount corresponding to that produced in a solution containing from about 0.5 to 5% nitric acid, about .01 to 0.5% HF, about .01 to 0.5% ammonia by weight, the trivalent chromium being supplied by reduction in situ of hexavalent chromium in amount from about .01 to 1% by weight calculated as CrO₃ with an organic compound containing carbon, hydrogen and oxygen and oxidizable by hexavalent chromium in amount slightly in excess of stoichiometric with respect to said chromium, maintaining the bath in contact with the metal at a temperature of from about 190° F. to the boiling point for a time sufficient to brighten said metal, and thereafter removing adhering solution from the metal.

40. A process according to claim 39 in which the cations of a metal more electropositive than

aluminum are introduced in amount not less than that stoichiometrically equivalent to about .001% copper nitrate calculated as Cu(NO₃)₂·3H₂O to increase specular reflectivity and to eliminate film formation on the metal surface.

41. A process for the chemical brightening of aluminum and aluminum alloys which comprises immersing the metal in a heated aqueous bath containing from about 0.5 to 5% nitric acid, about .01 to 0.8% ammonium bifluoride, about .01 to 1% chromic acid, and about .05 to 1% glycerol by weight of solution, and maintaining the bath in contact with the metal at a temperature of from about 190° F. to the boiling point for a time sufficient to brighten the same.

42. A process for the chemical brightening of aluminum and aluminum alloys which comprises subjecting the metal surface to the action of an acid aqueous solution containing hydrogen, nitrate, fluoride, ammonium and trivalent chromium ions in amount corresponding to that produced by a solution containing by weight from about 0.5 to 5% HNO₃, about .01 to 0.5% HF, about .01 to 0.5% ammonia, about .01 to 1% chromic acid (calculated as CrO₃), and as an organic reducing agent for converting the hexavalent chromium to trivalent chromium in situ, an amount of a carbohydrate stoichiometrically equivalent to from about .05 to 1% glycerol by weight of solution, and maintaining the metal in contact with the solution for a time sufficient to brighten the surfaces thereof.

FREDERICK HAROLD HESCH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
590,966	Cornwall	Oct. 5, 1897
2,168,909	Mason	Aug. 8, 1939
2,245,219	Murray	June 10, 1941
2,266,430	Matthews	Dec. 16, 1941
2,285,468	Slunder	June 9, 1942
2,428,464	Lum et al.	Oct. 7, 1947
2,428,749	De Long	Oct. 7, 1947
2,522,474	Waitkins et al.	Sept. 12, 1950
2,535,794	Hempel	Dec. 26, 1950
2,547,536	Pollard	Apr. 3, 1951
2,593,448	Hesch	Apr. 22, 1952
2,593,449	Hesch	Apr. 22, 1952