United States Patent Office 2,756,131 Patented July 24, 1956

2,756,131

METHOD FOR GLOSSING ARTICLES MADE OF ALUMINUM AND PARTICULARLY PURE ALUMINUM AND ITS ALLOYS

Heinrich Neunzig, Gindorf, near Grevenbroich, Germany, assignor to Vereinigte Aluminium-Werke Aktiengesellschaft, Bonn (Rhine), Germany, a corporation of Germany

No Drawing. Application August 18, 1953, Serial No. 375,060

Claims priority, application Germany August 22, 1952

2 Claims. (Cl. 41—42)

This invention relates to the glossing of aluminum and aluminum alloys as well as of articles made thereof or being coated with aluminum or aluminum alloys.

Many processes have been developed to serve this purpose, which are either based on a purely chemical basis or on the use of electric current.

In the chemical processes of this type, which have the advantage of a smaller apparatus expenditure and of a simpler manipulation over the electrical or electrolytical procedures, alkaline or acid solutions are used, which remove a portion of the metal surface and level the same; the glossing capacity of these methods is based upon this removal and upon the leveling action.

By using for this purpose solutions containing nitrate, hydrogen, ammonium, fluorine and advantageously also lead ions it was discovered, by the inventor, that the gloss and the brilliancy of the treated surfaces may be improved in a surprisingly effective manner if, together with the glossing agents, substances are used which inhibit the glossing action of the said substances. These substances exert an inhibiting influence upon the gloss producing agents and solutions; in the following they will be denoted as "inhibitors." Moreover, it was found that by the use of these inhibitors, in spite of the surprising surface leveling action, the surface removal of the treated aluminum or alloy is reduced and that therefore a saving results of metal and glossing solution. Moreover by the application of the inhibitors a reflective capacity of 82 per cent may be obtained of the treated surfaces. The weight reduction of the treated articles amounts only to 24 grams per square meter, corresponding to a thickness reduction of $^{9}/_{1000}$ of a millimeter; in the same bath and without an inhibitor, a weight reduction is produced of 54 grams per square meter corresponding to a reduction of the thickness of $^{20}/_{1000}$ of a millimeter. The highest reflective capacity obtainable without the inhibitors amounts to 79.8%.

Consequently, by the surface treatment according to the invention the dimensional stability of the worked articles may be satisfactorily preserved; this is particularly true in view of the following protective oxidation of the glossed articles whereby a thickness reduction of, for instance, $^{9}/_{1000}$ of a millimeter can be fully compensated.

Substances are preferably used as inhibitors which reduce or slow-down the surface attacking action of the gloss producing baths without, however, creating protective layers. Good results are obtained by the admixture to the gloss or brilliancy creating solutions of arabic gum, dextrin, gelatin, glue, lignin sulfo acid and salts thereof, artificial tanning substances, nicotine, nicotine sulfate, amines such as amyl amine and also dibenzyl sulfide.

It is advisable to add these inhibitors to the gloss creating solutions at a rate of about 0.5 to 2 per cent and preferably 1 per cent. The beneficial action of these substances becomes particularly apparent if a lead ion concentration is maintained in the glossing solutions amounting to 0.05 to 0.5 gram per liter.

The gloss producing solution may, for instance, contain per one liter

1.6 to 2.7 and preferably 2.1 gram mol. nitric acid
1.8 to 3.5 and preferably 2.8 gram mol. ammonium
3.5 to 7.0 and preferably 5.6 gram mol. hydrofluoric acid
2.5 times 10^{-5} to 2.5 times 10^{-4} gram mol. lead
0.5 to 2 per cent and preferably 1.0 per cent of an inhibitor.

The treating bath may be produced by mixing a suitable quantity of pure nitric acid, pure hydrofluoric acid and preferably pure lead nitrate and adding upon admixture of the inhibitor an aqueous ammonia solution or by entering gaseous ammonia into the diluted solution.

By the use of these weak, thinly fluid and therefore cheap solutions it is possible, after a short treating time, to produce high gloss surfaces on aluminum and its alloys and particularly on magnesium containing aluminum. The displacement, preferably manually, of the articles in the treating solutions is advisable as it prevents the adherence of gas bubbles to the same.

The invention is particularly applicable to articles made of pure homogeneous aluminum and aluminum magnesium alloys having a maximum content of 2.7 per cent Mg or articles consisting of other materials and being ovated with aluminum or the said alloys.

Moreover, it has been found that colorless transparent protective layers do not reduce the gloss of the treated Al articles if the latter are anodically or chemically oxidized after the glossing treatment.

The invention has the advantage of far greater simplicity and economy over the known combined polishing and electrolytical treatments; this experience applies particularly to small mass-produced articles, for instance, casings for condensors, bottle capsulae, stamped objects and the like.

A protective layer may also be produced in conformity with the invention upon reflectors without in the least reducing their shine.

Moreover, and in conformity with the invention articles made of other materials than aluminum may be effectively glossed by covering the same entirely or partly with a thin layer or a foil of pure aluminum having preferably a purity of 99.8 to 99.95 per cent and treating them as previously described. The aluminum foils may contain up to about 2.7 and preferably 0.5 per cent Mg thereafter, the treated articles may be chemically or anodically oxidized.

The articles to be treated in the above described manner may consist of synthetic materials and may be made, for instance, by injection molding; therefore the invention may be advantageously used for the production of vehicle parts and fittings. The portions of the articles not covered with Al must be provided with a protective coating prior to their location into the glossing solution and prior to oxidation.

A plastic sealing or binding material may be inserted between the articles and the coating to be glossed which material may be hardenable by chemical action or heat, whereby a satisfactory cohesion is produced between the article and the coating.

It may be advantageous to replace the plastic sealing materials by paper or similar soft materials which are impregnated with binders. In this manner the influence of unevenness of the article surface onto the coating is eliminated.

The layers created by oxidation on aluminum or its alloys are boiled in the usual manner in water to produce a tight seal.

This procedure, however, causes, particularly with oxi-

dized articels made of very pure aluminum, an undesirable change of the surface of the oxidized layers, which are thereby softened. In this state the surface is not resistant to abrasion; moreover, upon abrasion a cloudiness is produced in the lower and harder portion of the oxidized layer because parts of the soft or upper layer are pressed into the pores of the harder layers located underneath the upper softer layers which cannot be removed.

This disadvantage is fully eliminated by a treatment of the oxidized parts with an aqueous ammonium bifluoride and alkalichromate containing solution. Solutions are successfully usable which contain by weight 0.3 to 0.9 and preferably 0.6 per cent NH_3, 0.7 to 2.1 and preferably 1.4 percent HF, 0.6 to 1.8 and preferably 1.2 percent CrO_3 and which may be produced by mixing 2 kilograms of a 70 percent hydrofluoric acid, 2.4 kilograms of a 25 percent ammonia solution and 4 kilograms sodium chromate in 100 liters water. The duration of the treatment is to be at least 12 minutes.

These solutions may be generally replaced by solutions which act as a solvent upon the hydrolised and compacted layers, whereas the less hydrolised layers remain less influenced. For instance, nitric acid preferably having a concentration of between 25 to 40 percent preferably 30 percent, by weight or a mixture of a solution of nitric acid and chromic acid may be used, the treatment being conducted at a temperature of above 20° C. and particularly 20° to 25° C. for a period of 1 to 5 minutes, preferably 3 minutes.

The invention will now be more fully described by the following examples.

Example 1

A workpiece made of a pure aluminum and containing 0.5 percent Mg is subjected for a period of 10 seconds and at a temperature of 50° C. to the action of an aqueous bath containing 13 weight percent of nitric acid, 16 weight percent of ammoniumbifluoride, 0.02 weight percent of lead nitrate and 1 weight percent of a gum arabic solution the latter acting as the glossing inhibitor. The surface of the thus treated aluminum article has a reflective capacity of 82 percent at a weight reduction of 24 grams per sq. meter and a thickness reduction of $^{9}/_{1000}$ millimeter.

By an identical treatment without the admixture of the inhibitor the values of the reflective capacity were 79.8 percent and the weight reduction 54 grams per square meter and a $^{20}/_{1000}$ millimeter thickness reduction.

Example 2

Condensator housings were exposed to the action of an aqueous solution which contained

2.1 gram/mol. nitric acid
2.8 gram/mol. ammonium
5.6 gram/mol. hydrofluoric acid
1% by weight of arabic gum per liter at a temperature of 16° C. and a time of 15 seconds.

After rinsing with water, the articles were exposed to the action of a solution containing per liter

0.47 gram/mol. sodium carbonate
0.047 gram/mol. sodium chromate
0.0008 gram/mol. sodium silicate for ten minutes at a temperature of 95 to 100° C.

An entirely colorless, pervious, bright protective surface layer resulted with increased chemical stability and grip resistance.

Example 3

Reflectors made of pure aluminum sheets having a thickness of 0.8 mm. and an Al content of 99.9 per cent were treated for the obtainment of a high reflective capacity as follows:

Removing of fat from the surface by dipping the sheets at a temperature of 25° C. in a solution consisting of

80 volume parts of concentrated nitric acid, and
20 volume parts of concentrated hydrofluoric acid.

These reflectors were dipped in a brilliancy promoting bath at a temperature of 58° C. for 10 seconds, which bath contained

2.3 gram/mol. of nitric acid
3 gram/mol. of ammonium
6 gram/mol. of hydrofluoric acid
25 times 10^{-5} gram mol. lead
10 grams arabic gum.

Hereupon an intermediary treatment was carried on for 30 seconds with a 40 per cent nitric acid. The following step was an additional shining of the reflectors in an electrolyte containing

50 grams of trisodiumphosphate and
150 grams of sodium carbonate per liter at a median current density of 4 amp./dm.^{2} for 10 minutes.

An anodic glossing of the treated reflectors followed in a sulphuric acid electrolyte at a current input of 20 amp./min. Thereupon, the anodically oxidized reflectors were boiled in distillated water and compressed in a 30 per cent nitric acid at 25° C. for 2 minutes.

The reflectors were rinsed with water between the individual treating steps.

Example 4

Tea pots made of a homogeneous pure aluminum magnesium alloy sheet having 0.5 per cent Mg and a thickness of 1.5 millimeters by drawing and having a handle attached thereto of a thickness of 10 millimeters and made of the same alloy are treated by the following steps:

Removal of fat by dipping the articles in a solution which contains

80 volume parts of concentrated nitric acid, and
20 volume parts of hydrofluoric acid at 25° C. for 10 minutes;

Heating the fat-freed pots in hot water having a temperature of 100° C. for at least 5 minutes whereby the pot and the handle are heated to an equal temperature;

Glossing the hot pots by moving the same for 15 seconds at a temperature of 60° C. through a solution, which contained per liter

2.1 gram mol. nitric acid
2.8 gram mol. ammonium
5.6 gram mol. hydrofluoric acid
25 times 10^{-4} gram mol. lead
10 grams arabic gum.

An intermediary treatment of the pots consists of a ten second dipping into a 25 per cent nitric acid at 25° C. and thereupon suspending of the pots at 20° C. in a solution containing .06 gram mol. sodium chromate for at least 10 seconds.

Electrolytic oxidation of the treated pots in a sulfuric acid electrolyte at a temperature of 20° C. and a current density of 35 amp./min.

Subsequent packing of the oxidic layer by handling the pots in distilled water at a temperature of 92° C. for 20 minutes.

After-treatment of the shined and anodically oxidized pots by boiling the same in distillated water and handling the same in a 25 weight per cent nitric acid at a temperature of 25° C. for two minutes.

Rinsing with water between the individual treating steps.

Example 5

Door handles produced by die casting and plated with a pure aluminum sheet having a thickness of 0.6 millimeters are treated by the following steps:

Removal of fat by dipping the handles for 20 seconds at a temperature of 25° C. in a solution containing

85 vol. parts of concentrated nitric acid, and
15 vol. parts of concentrated hydrofluoric acid.

Heating the handles in water at 100° C. for 3 minutes until the same have reached a temperature of 60° C.

Glossing the heated handles for 15 seconds by a to-and-fro movement through a solution at 50° C. which contained

2.1 gram mol. nitric acid
2.8 gram mol. ammonium
5.6 gram mol. hydrofluoric acid
25 times 10^{-5} gram mol. of lead, and
50 grams of dextrin.

An intermediary treatment by dipping the handles in 30 weight per cent nitric acid for 30 seconds and suspension of the same at 22° C. in a solution which contained 0.12 gram mol. per liter of sodium chromate for at least 10 minutes.

Anodic oxidation of the handles in a sulfuric acid electrolyte at 18° C. and a current supply of 50 amp./min.

Compaction of the anodic protective layer applied to the handles by suspension of the same in distilled water having a temperature of 90° to 92° for 30 minutes.

Final treatment of the handles in a 40 per cent nitric acid at a temperature of 25° C. for two minutes.

Rinsing with water between the individual treating steps.

Example 6

Decorative buttons made of a homogeneous pure aluminum alloy with 1 per cent Mg are treated by the following steps:

Glossing for 10 seconds by a to-and-fro movement at 52° in a bath containing per liter.

2.1 gram mol. nitric acid
2.8 gram mol. ammonium
5.6 gram mol. hydrofluoric acid
25 times 10^{-4} gram mol. lead, and
10 grams arabic gum.

An intermediary treatment for 10 seconds consisting in dipping the buttons in a 40 per cent nitric acid at a temperature of 22° C.

Application to the buttons of a protective layer by chemical treating consisting in dipping the same for 10 minutes at a temperature of 95° C. in a solution which contained per liter

0.47 gram mol. sodium carbonate
0.047 gram mol. sodium chromate
0.0008 gram mol. sodium silicate.

Rinsing with water between the individual treating steps.

Since certain changes in carrying out the above process could be made without departing from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific exemplifications thereof will suggest various other modifications and applications of the same.

It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific exemplifications of the invention described herein.

Having thus described the invention, what I claim as new and desire to be secured by Letters Patent, is as follows:

1. A method for brightening the surface of articles made of aluminum and of aluminum alloys and particularly magnesium containing aluminum alloys comprising applying to said articles a hot aqueous solution containing per liter between 1.6 to 2.7 gram molecules of nitric acid, between 1.8 to 3.5 gram molecules of ammonium, 3.5 to 7.0 gram molecules of hydrofluoric acid, 2.5 times 10^{-5} to 2.5 times 10^{-4} gram molecules lead nitrate and 0.5 to 2 percent of an inhibitor selected from a group consisting of gum arabic and dextrin.

2. A method for brightening the surface of articles made of aluminum and of aluminum alloys and particularly magnesium containing aluminum alloys comprising applying to said articles a hot aqueous solution containing per liter between 1.6 to 2.7 gram molecules of nitric acid, between 1.8 to 3.5 gram molecules of ammonium, 3.5 to 7.0 gram molecules of hydrofluoric acid, 2.5 times 10^{-5} to 2.5 times 10^{-4} gram molecules lead nitrate and about 1 percent of an inhibitor selected from a group consisting of gum arabic and dextrin.

References Cited in the file of this patent

UNITED STATES PATENTS

2,593,447	Hesch	Apr. 22, 1952
2,593,449	Hesch	Apr. 22, 1952
2,614,912	Rice	Oct. 21, 1952
2,614,913	Reindl et al.	Oct. 21, 1952
2,625,468	Prance et al.	Jan. 13, 1953
2,650,156	Shelton-Jones	Aug. 25, 1953
2,650,875	Dvorkovitz	Sept. 1, 1953

OTHER REFERENCES

Lange Handbook of Chemistry, fourth edition, Handbook Publishers, Sandusky, Ohio, 1941, pages 946 and 947.