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2,795,490

PROCESS FOR ETCHING ALUMINUM ALLOY SURFACES

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This invention relates to the production of etched aluminum alloy surfaces, and especially concerns novel procedure for producing etched surfaces of this type having a smoother and substantially less nodular finish than is conventionally obtained.

It is well known to etch alkali soluble metals such as aluminum alloys with a solution having a solvent action on the aluminum alloy surface, such as a hot aqueous alkali solution, e. g., one containing sodium hydroxide. One method of carrying out the 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.

When aluminum alloys are etched in alkali solutions, e. g., containing sodium hydroxide, potassium hydroxide, or equivalent agents as alkali, under some conditions of treatment such as temperature and concentration of the etching solution, and with some alloys, e. g., zinc and copper alloys of aluminum, a relatively pebbly or nodular etched surface is obtained. This may occur when such alkali etching solutions contain the alkali material as the sole ingredient, or when the solution also contains additives such as citric acid or salts thereof, as described and claimed in application Serial No. 445,197, filed July 22, 1954, by Kenneth W. Newman, now Patent No. 2,739,883; or other agents such as, for example, gluconic acid, or salts thereof, sorbitol, and the like. An etching bath producing a nodular etched surface as aforementioned is termed herein a "nodulizing" etching solution. The theory of why this occurs is not known to applicants.

However, many applications of etched aluminum alloys require that the etched surface be smoother and less nodular than is obtained under the above conditions.

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

Another object is to provide procedure for producing etched aluminum alloy surfaces which are smooth and substantially free of bumps and nodules.

Yet another object is the provision of relatively simple and inexpensive procedure for obtaining improved etched surfaces on aluminum alloys, particularly copper and zinc alloys of aluminum.

We have discovered that when the etched surface of an aluminum alloy treated in an alkali etching solution is bumpy and nodular, i. e., the solution is a nodulizing etching solution, if a sulfur-containing material is added to the nodulizing etching solution and a piece of said alloy is treated in the resulting solution, the etched surface so obtained is substantially free of bumps or nodules, and is smoother and more uniform than that produced in the nodulizing etching solution in the absence of such material.

The sulfur-containing material employed as an additive in the aqueous alkali etching bath according to the invention is of the class consisting of those having a reactive sulfur and those having a reactive SH— group. These materials include normal sulfides and polysulfides,

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thio and polythio compounds, and such materials may be inorganic or organic in nature. Illustrative examples of these materials are elemental sulfur, alkali metal sulfides and polysulfides, such as sodium sulfide and sodium polysulfide, sodium thiosulfate, thiuram sulfides and disulfides such as tetramethyl-thiuram sulfide and tetra-methyl-thiuram disulfide, thioureas, thiono and thio carbamates, e. g., thiourea and alkyl and aryl substituted thioureas such as diethyl and diphenyl thiourea, ethyl thio carbamate ($C_2H_5SSCNH_2$) and ethyl thiono carbamate ($C_2H_5OSCNH_2$), and alkyl and aryl mercaptans such as ethyl mercaptan and phenyl mercaptan. The preferred materials are the alkali metal sulfides and polysulfides, sulfur, thioureas, and mercaptans in the order named. These materials may be employed separately, or mixtures of two or more of these materials can be used.

The etching treatment is carried out in an aqueous solution containing an alkali such as sodium or potassium hydroxide, trisodium phosphate, sodium carbonate or the like, or mixtures thereof. Temperature of the solution may range say from room temperature, for example, 60° to 70° F., to about 212° F. Generally, a hot solution is employed, with temperature maintained in a range from about 140° F. to about 210° F. during treatment.

The alkali concentration of the etching solution is not critical, and such concentration may range say from 0.1 to 10 normal, preferably in the range of 1 to 3 normal. The amount of sulfur-containing material added to the nodulizing etching solution may likewise vary but is usually substantially less than the amount of alkali employed. Generally, from about 0.1 to about 10% of the sulfur-containing material based on the weight of the alkali can be used, with amounts in the range of about 2 to 6% preferred. The sulfur-containing material in the solution can be replenished from time to time where the bath is in continuous use.

In practicing the invention, a test piece of the aluminum alloy to be etched is immersed in the alkali etching solution and etched for a period sufficient to dissolve a substantial amount of surface metal, e. g., $\frac{1}{32}$ to $\frac{1}{16}$ inch, under the conditions, e. g., concentration of solution and temperature, at which a part composed of the same alloy is to be etched. For example, the alkali etchant solution concentration may be 5% or 10%, and the solution temperature may be 190° F. The test piece is then withdrawn, the smut removed, e. g., by a nitric acid solution, and the sample washed and dried. If the etched surface so obtained is bumpy or nodular, the solution is a nodulizing etching solution. A sulfur-containing additive according to the invention is then incorporated in the aforementioned amounts in the nodulizing etching solution. The part to be etched is then immersed in the resulting solution for the period required to produce the desired depth of etch on the surface of the part.

The additive employed in the process of our invention, as set forth in the specification and claims, and which has a reactive sulfur or sulfhydryl group, is one capable of precipitating metallic ions in the alkali solution employed in the etching reaction, such as the ions of the metallic alloying constituents of the aluminum alloy processed.

A convenient method of selecting a sulfur-containing material for the process of the invention is to choose an alkali solution in the range of 0.1 to 10 normal and corresponding preferably to the concentration to be employed in the etching process in which such material is to be used, e. g., 2 normal. The solution is then heated to the operating temperature at which etching is to take place, e. g., 190° F., and the sulfur-containing material added to the solution, preferably in an amount in the range of 0.1 to 10% by weight of the alkali, e. g., about 3%. A one molal solution of any of the following salts, the metallic elements of which are generally present as alloying

constituents of the aluminum alloy to be etched, is then added to the solution: a soluble cuprous, cupric, zinc, or iron salt. If a precipitate is formed with any one of these salts, which precipitate contains a metal atom and a sulfur atom, for example, the sulfide of the metal, this indicates the sulfur-containing material is suitable for use in the invention process, i. e., it has a reactive sulfur or sulfhydryl group. In practice, if one of the above salts does not form a precipitate, then another is employed until they have all been tried or until at least one of these salts produces a precipitate, to show suitability of the particular sulfur-bearing material in our process.

However, if a precipitate is not formed under the above conditions, i. e., at the elevated temperatures of the bath normally employed in aluminum etching operations, this does not necessarily mean that the particular sulfur-containing material being tested is unsuitable. Under these circumstances the solution containing such material and one or more of the above soluble salts is cooled, for example, to room temperature to determine whether a precipitate will form at the lower temperatures. If such precipitate does form, the sulfur-containing material is suitable for use in our process.

By the term "precipitate" is meant the formation of any observable solid material in the solution, whether in suspension or colloidal dispersion in the solution, or in the form of a relatively dense mass which may drop to the bottom of the solution which contains a sulfur-bearing material. Since under some circumstances and with certain metals or salts thereof, e. g., a soluble zinc salt, a precipitate may form which contains compounds other than sulfur compounds, it is desirable to test the precipitate for the presence of such sulfur compounds. If such sulfur compounds, e. g., zinc sulfide, are present as a solid constituent of said precipitate then the sulfur-bearing additive material is deemed suitable for purposes of the invention, that is, it has a reactive sulfur or SH— group.

The dark highly adherent film called "smut" generally present on the surface of aluminum alloys following treatment in the alkali etching solution may be more easily removed when our sulfur-containing additives are used according to the invention procedure than is usually the case when such additives are not employed. These smuts are insoluble in water and most acids, and generally require treatment in nitric acid, mixtures of HNO₃ and H₂SO₄, or mixtures of chromic and sulfuric acids for their removal. Examples of smut removing compositions which can be used are a 5 to 10% solution of nitric acid, and a solution of the composition disclosed in application Serial No. 448,775, filed August 9, 1954, of Kenneth W. Newman, comprising 77.1% sodium acid sulfate, 1% ammonium bifluoride, 0.1% of a wetting agent, for example, Nacconol Z, which is an alkyl aryl sulfonate sold by National Aniline Division, Allied Chemical & Dye Corp., N. Y. C., and 21.8% potassium dichromate. Following such smut removal, and subsequent washing and drying of the aluminum alloy surface of the part etched according to the invention, such surface is found to be very smooth and uniform, and substantially free of nodules.

When using a nodulizing caustic soda etching solution or a nodulizing etching solution containing an equivalent alkaline etching agent, free however of our sulfur-bearing materials, the result is a rough pebbly etched surface as aforementioned. Such surface appears full of small bumps easily discernible with the naked eye. The bumps are distributed over the surface in a heterogeneous irregular pattern with valleys between the bumps. It is believed these bumps are the result of an uneven rate of etch across the entire surface, the etch rate being least at the apices of the bumps and increasing along the surfaces, moving from the top of the bumps into the valleys. The surface is shiny under strong reflected sunlight, and appears visually as illuminated across the surface with no interference or refraction phenomenon since no color is discernible.

However, if as little as 1% of the sulfur-containing material of the invention is added to the nodulizing etching solution, the etched surface obtained is smooth and while a surface etch pattern is visible in the form of barely discernible striations, no discrete hillocks are observable even with a magnifying 2 power lens. The surface appears crystalline but smooth under strong reflective sunlight and iridescent and colored, indicating either interference or refraction phenomenon. This surface may be termed jewel-like for this reason.

The difference in surface, i. e., bumpy, large grained and irregular in the case of the nodulizing alkali etchant solution free of sulfur-containing material, and the smooth, fine grained, non-bumpy surface when employing such additive material in said solution is readily discernible in any form of illumination or even by feel. The etched surface obtained when using the nodulizing etchant solution free of the sulfur-bearing material of the invention will be termed irregular or coarse grained, as well as nodular, and when such sulfur-containing material is used in said solution, smooth or fine grained.

It is to be understood that comparisons of the coarse grained nodular surface obtained on an aluminum alloy under nodulizing conditions, with the substantially nodule-free fine grained surface produced by use of our sulfur-bearing materials, e. g., sodium sulfide, according to the invention, is based on the use of the same etching conditions, i. e., the same alkali etchant such as caustic soda, the same solution concentration, and the same temperature, and also on the use of the same aluminum alloy, except that the etching solution in one case wherein the smooth fine grained surface is obtained also contains the sulfur bearing material. Thus, for example, the etched surfaces of two aluminum alloy parts of the same alloy composition can be compared for the invention purposes by etching each for the same period of time in the same 5% caustic soda etching solution and at the same temperature of 190° F. except that in one case the solution contains our sulfur-bearing material.

Examples of aluminum alloys which can be treated to from a smooth etched surface according to the invention are as follows:

Designation	Approximate Composition
14S-----	0.50-1.2% Si, 1.0% Fe, 3.9-5.0% Cu, 0.40-1.2% Mn, 0.20-0.8% Mg, 0.10% Cr, 0.25% Zn, 0.15% Ti, Rem. Al.
17S-----	0.8% Si, 1.0% Fe, 3.5-4.5% Cu, 0.40-1.0% Mn, 0.20-0.8% Mg, 0.10% Cr, 0.25% Zn, Rem. Al.
24S-----	0.50% Si, 0.50% Fe, 3.8-4.9% Cu, 0.30-0.9% Mn, 1.2-1.8% Mg, 0.10% Cr, 0.25% Zn, Rem. Al.
61S-----	0.40-0.8% Si, 0.7% Fe, 0.15-0.40% Cu, 0.15% Mn, 0.8-1.2% Mg, 0.15-0.35% Cr, 0.25% Zn, 0.15% Ti, Rem. Al.
75S-----	0.50% Si, 0.7% Fe, 1.2-2.0% Cu, 0.30% Mn, 2.1-2.9% Mg, 0.18-0.40% Cr, 5.1-6.1% Zn, 0.20% Ti, Rem. Al.

Other aluminum alloys may also be etched employing the invention principles, to obtain the invention results.

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 was prepared by dissolving an etchant composition in water to produce a solution concentration of 10%. The etchant composition was composed of 96 parts of caustic soda and 4 parts of sodium sulfide. An article having a 24S aluminum alloy surface was etched in this solution while maintained at a temperature of about 190° F. The article was then withdrawn from the bath, the smut removed from the etched surface of the article by treatment with a solution of the smut removing composition of application Serial No. 448,775, described above, and the article washed and dried. The etched aluminum alloy surface of the article was fine grained, smooth, and substantially free of nodules.

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Example 2

An aqueous etching solution was prepared by dissolving an etchant composition in water to produce a solution concentration of 10%. The etchant composition was composed of 96 parts of caustic soda and 4 parts of sulfur in the form of flowers of sulfur. A 24S aluminum alloy was etched in the solution while maintained at about 190° F. Following smut removal, as previously described, and washing, the etched surface of the alloy was observed to be smooth, nodule-free, and uniform.

Example 3

An etching solution was prepared composed of about 8% by weight of a mixture of NaOH and thiourea (2 parts thiourea to 98 parts NaOH). A 24S aluminum alloy was immersed in the solution and etched therein while the solution was maintained at a temperature of about 180°–190° F. The etched surface of the alloy obtained after smut removal, washing, and drying was fine grained, smooth, and substantially nodule-free.

Example 4

Results similar to Example 1 were obtained by employing the procedure and conditions set forth therein, but substituting for the etchant composition of Example 1 an etchant composition composed of 95 parts of caustic soda and 5 parts of phenyl mercaptan.

Example 5

Results along the lines of Example 1 may be obtained employing the procedure and conditions of Example 1, but replacing the sodium sulfide with tetramethyl thiuram sulfide.

Example 6

A test piece of 24S aluminum alloy was immersed in a 5% caustic soda etching solution and etched therein at a solution temperature of 190° F. until the exposed surface was etched to a depth of about 1/8 inch. The article was then withdrawn from the bath, the smut removed from the etched surface by treatment with a solution of the smut removing composition of application Serial No. 448,775, described above, and the article washed and dried. The etched surface so obtained was observed to be coarse grained and nodular, and composed of bumps or hillocks of relatively large size. This indicated the above solution was a nodulizing etching solution.

Another aqueous etching solution was prepared by dissolving an etchant composition in water to produce a solution concentration of 5%. The etchant composition was composed of 97 parts of caustic soda and 3 parts of sodium sulfide. An article having a 24S aluminum alloy surface was etched in this solution while maintained at a temperature of 190° F. The article was then withdrawn from the bath, the smut removed from the etched surface by treatment with a solution of the smut removing composition of application Serial No. 448,775, described above, and the article washed and dried. The etched aluminum alloy surface so obtained was fine grained and in the form of striations with no discernible nodules or hillocks.

Example 7

The same procedure was carried out as in Example 6, except that the etchant composition of the second etching solution was composed of 99 parts of NaOH and 1 part of sodium sulfide. The results obtained were similar to those obtained in Example 6.

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

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alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a sulfur-containing material of the class consisting of those having a reactive sulfur and those having a reactive SH— group, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material.

2. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution containing caustic soda and having dissolved therein a sulfur-containing material of the class consisting of those having a reactive sulfur and those having a reactive SH— group, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material.

3. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution having dissolved therein a sulfur-containing material of the class consisting of those having a reactive sulfur and those having a reactive SH— group, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material, said sulfur-containing material being present in an amount of from about 0.1% to about 10% by weight of said alkali.

4. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a mercaptan.

5. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution containing caustic soda and having dissolved therein from about 0.1 to about 10% by weight of said caustic soda, of a mercaptan.

6. A method as defined in claim 5, wherein said mercaptan is phenyl mercaptan.

7. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution having dissolved therein a thiourea.

8. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution containing caustic soda and having dissolved therein from about 0.1 to about 10% by weight of said caustic soda, of thiourea.

9. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution having dissolved therein a thiuram sulfide.

10. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution having dissolved therein a thiuram disulfide.

11. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution containing

caustic soda and having dissolved therein tetramethyl thiuram sulfide.

12. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with a hot alkali etching solution containing caustic soda and having dissolved therein tetramethyl thiuram disulfide.

13. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a sulfur-containing material having a reactive sulfur, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material.

14. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a sulfur-containing material having a reactive SH— group, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material.

15. A method of etching an article having an aluminum alloy surface, which comprises adding a sulfur-containing material of the class consisting of those having a reactive sulfur and those having a reactive SH— group, to a nodulizing alkali etching solution, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material, and treating said alloy surface in the resulting solution to obtain a smooth substantially nodule-free etched surface.

16. A method of etching an article having an aluminum alloy surface, which comprises adding a sulfur-containing material of the class consisting of those having a reactive sulfur and those having a reactive SH— group, to a nodulizing hot alkali etching solution containing caustic soda, said sulfur-containing material being capable of forming a precipitate with an ion taken from the group

consisting of copper, zinc and iron ions when a solution containing such ion is added to an alkali solution of said sulfur-containing material, and treating said alloy surface in the resulting solution to obtain a smooth substantially nodule-free etched surface.

17. A method of etching an article having an aluminum alloy surface, which comprises adding a thiourea to a nodulizing hot alkali etching solution containing caustic soda, and treating said alloy surface in the resulting solution to obtain a smooth substantially nodule-free etched surface.

18. A method of etching an article having an aluminum alloy surface, which comprises adding a mercaptan to a nodulizing hot alkali etching solution containing caustic soda, and treating said alloy surface in the resulting solution to obtain a smooth substantially nodule-free etched surface.

19. A method of etching an article having an aluminum alloy surface, which comprises adding a thiuram sulfide compound to a nodulizing hot alkali etching solution containing caustic soda, and treating said alloy surface in the resulting solution to obtain a smooth substantially nodule-free etched surface.

20. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a thio carbamate.

21. A method of etching an article having an aluminum alloy surface to produce a smooth substantially nodule-free etched surface, which comprises treating said alloy surface with an alkali etching solution having dissolved therein a thiono carbamate.

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