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METHOD OF PRODUCING OXIDE COATED
ALUMINUM AND ALUMINUM BASE ALLOYS
AND ELECTROLYTE THEREFOR

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This invention refers to a method of producing oxide coated aluminum and aluminum base alloys and an electrolyte therefor.

It is known to produce such oxide coatings on aluminum and aluminum base alloys by subjecting these materials to the action of an electric current in an acid electrolyte of definite concentration. Thus, it has been suggested to use as electrolyte sulphuric acid in concentrations of 10-20% or of 35-77%. Furthermore, instead of sulphuric acid, oxalic acid or chromic acid have been employed for this purpose. To these electrolytes there have already been added other substances, such as potassium sulfate, aluminum sulfate, sodium sulfate, sodium hyposulfite, chromic acid or its salts, nitric acid and others more. With these known electrolytes in general in the course of the oxidation process only a small decrease of the current strength takes place due to the increase of thickness of the oxide coating, when care is taken that the bath is sufficiently cooled and thoroughly stirred. If, however, the cooling as well as the stirring are insufficient or are interrupted, the heat produced during the process cannot be removed properly. Hence, the bath temperature increases and due to said increase, the strength of current likewise. This reciprocal increase of bath temperature and current strength very readily leads to destruction or heavy corrosion of the aluminum article to be coated.

Now, it has been found that these undesirable phenomena are prevented by adding to the electrolytic oxidising bath compounds of heavy metals and/or complex acids derived from said metals.

Especially suitable are compounds of such metals that are capable of occurring in more than one state of valency such as compounds of manganese, cobalt, nickel and the like. Of course, the heavy metal compounds used are added to the bath preferably in a state that is the most stable under the operating conditions of said bath.

Not suitable are such heavy metal compounds, the anions or cations of which prevent the formation of a uniform protective coating; thus, larger amounts of chlorides or of such metals that during the oxidation process are precipitated by the action of the current or by reaction with the electrode material, such as the compounds of silver, mercury and the like, cannot be used.

Likewise, potassium permanganate or bichromates or also chromic acid anhydride have the disadvantage that, on account of possible reduction during the electrolysis, it is rather dif-

ficult to keep the composition of the bath constant. Hence, uniform operation of the bath cannot be assured when using these simple acids of heavy metals. In contrast hereto the above mentioned advantages are achieved when adding the salts of manganese or chromium or the like, for instance, the sulfates and others, to the electrolyte.

Especially suitable are the so-called complex acids derived from heavy metals, such as phosphotungstic acid, molybdic-sulphuric acid and the like whereby the heavy metal is present as anion in these compounds. Of course, under certain circumstances it is possible and even advantageous to use these complex acids in combination with other heavy metal compounds such as the sulfates, nitrates, and the like of said metals.

Furthermore there may be used as electrolytes the so-called permolybdic acid or per-tungstic acid as they are obtained by treating the insoluble simple molybdic or tungstic acids with strong hydrogen peroxide solutions. Said acids, in contrast to the simple acids they are derived from, are water soluble and correspond in their constitution to the complex acids mentioned above; for, the oxygen atoms therein are attached to the molecule in a more complex manner than, for instance, in the simple metal acids, as chromic acid or permanganic acid.

The favorable action of these per-molybdic or per-tungstic acids on electrolysis may be increased by the addition of polybasic hydroxy acids, such as citric acid and the like. Likewise the addition of small amounts of phosphoric acid or phosphates to said per-acids increases the effectiveness and stability of the same.

The amount of phosphoric acid used, for this purpose, preferably should not exceed that amount being equivalent to the per-tungstic acid present in the electrolyte and may be between $\frac{1}{10}$ and $\frac{1}{20}$ of said equivalent. As phosphates there may also be used insoluble phosphates provided they are capable of forming soluble compounds with the acids present in the electrolyte. The addition of said phosphates or phosphoric acid has the further advantage that such baths may be used with high current density even at an increased temperature in continuous operation.

The amounts of the metal compounds used according to this invention are dependent on the properties of said compounds and must be adjusted to the requirements of the bath, the type of current used, the material to be coated and the like.

It is very surprising that the additions according to the present invention have the remarkable effects observed; for, hitherto, one avoided always to add heavy metal salts to the acid electrolytes due to the general assumption that such an addition would cause corrosion and non-uniform formation of the oxide coating.

Besides, the use of the above mentioned heavy metal compounds has the further advantage that the protective coatings obtained are usually of better appearance than the coatings produced hitherto. Thus, it is almost impossible to produce uniform transparent coatings on cast aluminum articles because with such layers the grain structure of the superficially etched metal surface below said layer will always be visible. Now, when producing cast articles, the size of grain is not always the same all over the visible surface. The thin-walled places of the casting usually show a finer grain than the thick-walled places due to the quicker cooling of the former. This different grain structure in turn becomes conspicuously manifest on the transparent coating produced by means of the known oxidation electrolytes and the surface of said coating appears unpleasant and non-uniform. Furthermore, the rough grain structure of the castings produces an undesirable ice-fern-like appearance of the oxidized aluminum article. All these disadvantageous phenomena are to a large extent overcome by the present invention.

The oxidation may be carried out by means of alternating or direct current alone or in known combinations with each other.

The following examples serve to illustrate the invention without, however, limiting the same to them:

Example 1

A suitable electrolyte is produced by dissolving 20 grams of tungstic acid in 30 ccs. of concentrated hydrogen peroxide solution and adding said solution to a solution of 300 grams of sodium sulfate and 20 grams of citric acid in 1 liter of water. The oxidation of aluminum articles and the like in said electrolyte is carried out at a bath temperature of 20-30° C. with alternating current and a voltage of 15 to 25 volts. After 30 minutes a transparent oxide coating is obtained that imparts to the aluminum article a silver-like appearance.

Example 2

A suitable electrolyte is produced by dissolving 20 grams of freshly precipitated tungstic acid in 30 ccs. of concentrated hydrogen peroxide solution and adding said solution to a solution of 50 grams of concentrated sulfuric acid and 20 grams of citric acid in 1 liter of water. The oxidation of aluminum articles is carried out with direct current of 15 to 20 volts at room temperature. After 60 minutes a transparent oxide coating of the same appearance as described in Example 1 but of higher hardness is obtained.

Example 3

An electrolyte containing 25 grams of permolybdic acid, 20 grams of citric acid, 80 grams of concentrated sulfuric acid and 200 grams of crystalline sodium sulfate in 1 liter of water is used for the oxidation of aluminum articles and the like. The oxidation is effected by means of alternating current superposed on direct current with a voltage of 13 to 20 volts and at a bath temperature of 15-25° C. After 30 minutes a

uniform, dense and transparent oxide coating of remarkable brightness is obtained.

Example 4

In the place of the electrolytes of the preceding examples an electrolyte is used consisting of 25 grams of per-tungstic acid, 300 grams of sodium sulfate, 20 grams of citric acid and 1.5-2 grams of phosphoric acid in 1 liter of water.

Example 5

In the place of the electrolytes of the preceding examples an electrolyte is used consisting of 25 grams of per-tungstic acid, 5-8 grams of potassium phosphate, 200 grams of sodium sulfate, 50 grams of concentrated sulfuric acid and 20 grams of citric acid in 1 liter of water.

Example 6

An electrolyte containing 120 grams of concentrated sulfuric acid and 50 grams of phosphotungstic acid in 1 liter of water is used for the oxidation of cast aluminum articles and the like. The oxidation is carried out with direct current at 20-22 volts and at a bath temperature of 18-22° C. Thereby within about 45 minutes a uniform oxide-coating of excellent anti-corrosive properties is produced.

Example 7

The oxidation of aluminum articles is carried out with alternating current of 21 volts in an electrolyte containing 100 grams of concentrated sulfuric acid and 100 grams of crystalline manganese sulfate. The bath temperature at the beginning of the electrolysis is 19° C. Without cooling it increases within 45 minutes to 27° C. The strength of current on the other hand remains practically constant throughout the oxidation. In contrast hereto on working with an electrolyte that contains merely 100 grams of sulfuric acid in 1 liter of water and no manganese sulfate the strength of current increases from 1.42 amperes to 2.40 amperes during electrolysis while the temperature increase is about the same as with the manganese containing electrolyte. Hence, when using the manganese containing electrolyte the aluminum articles show a clear and bright oxide coating while the coating with a sulfuric acid electrolyte is dull and of a lower hardness. Thus, the addition of a heavy metal compound, such as manganese sulfate has the effect that the baths are less sensitive toward mistakes in operating the same and give better results.

Also when keeping the bath temperature constant during electrolysis, the heavy metal salts have the same regulating influence upon the strength of current as described above. Thus, for instance, with the electrolyte without manganese sulfate the current strength decreases from 1.40 amperes at the beginning of the experiment to 1.30 amp., while with addition of manganese sulfate the decrease is much greater, i. e. from 1.62 amp. at the beginning to 1.15 amp. at the end of the electrolysis. In spite of the greater decrease in current strength the oxide-coatings obtained in the presence of manganese sulfate are at least 20% thicker than in the absence of said salt.

Example 8

Instead of the electrolyte employed in Example 7 an electrolyte is used consisting of 60 grams of concentrated sulfuric acid, 100 grams of manganese sulfate and 25 grams of phospho-

tungstic acid in 1 liter of water. The result is about the same as achieved with the electrolyte of Example 7.

Example 9

Instead of the electrolyte employed in Example 7 an electrolyte is used with about the same result that consists of 50 grams of concentrated sulfuric acid and 20 grams of crystalline cobalt sulfate in 1 liter of water.

Example 10

Instead of the electrolyte employed in Example 7 an electrolyte is used with about the same result that consists of 60 grams of oxalic acid and 40 grams of molybdo-oxalic acid in 1 liter of water.

Of course, articles coated according to this invention with a protective oxide layer can be colored in any known manner. The coating may further be worked up so as to improve its properties; thus, for instance, it may be subjected to a treatment with boiling water, steam or boiling chromate solutions or it may be immersed into varnishes, molten wax and the like.

Instead of the metal salts mentioned in the examples, there may be used likewise other salts of heavy metals, such as ferrous sulfate, ferrous citrate, nickel acetate, manganese phosphate, chrome alum, chromium sulfate, etc.

Furthermore many other changes and variations in the reaction conditions, the chemicals employed, their concentration and the like may be made by those skilled in the art in accordance with the principles set forth herein and in the claims annexed hereto.

It is understood that the expression "aluminum" in the claims is intended to cover both aluminum itself and alloys of aluminum.

What we claim is:

1. An acid bath for anodic treatment of aluminum, containing manganous sulfate.
2. An aqueous acid bath for the anodic treatment of aluminum, containing cobalt sulfate.
3. An aqueous acid bath for the anodic treatment of aluminum, containing a soluble complex acid having the heavy metal having more than one stage of oxidation in the anion and having also a negative element other than oxygen in the anion, that does not undergo decomposition under the influence of the electric current and that does not react with the electrode material.
4. An aqueous acid bath for the anodic treatment of aluminum, containing phosphotungstic acid.
5. An aqueous acid bath for the anodic treatment of aluminum, containing a soluble complex acid having the heavy metal having more than one stage of oxidation in the anion and having also a negative element other than oxygen in the anion, and a soluble heavy metal salt, said complex acid and heavy metal salt being incapable of undergoing decomposition under the influence of the electric current and of reacting with the electrode material.
6. An aqueous acid bath for the anodic treatment of aluminum, containing a compound selected from the group of compounds consisting of per-tungstic acid and per-molybdic acid, and a phosphoric acid compound.
7. An aqueous acid bath for the anodic treatment of aluminum, containing a compound selected from the group of compounds consisting

of per-tungstic acid and per-molybdic acid, and an organic polybasic acid.

8. In a method of producing oxide-coated aluminum, the step of passing an electric current through an aluminum material as an anode in an acid electrolyte containing a compound of a heavy metal having more than one stage of oxidation with simple acids, said compound being soluble and stable in said acid electrolyte and not being decomposed under the influence of the electric current.

9. In a method of producing oxide-coated aluminum, the step of passing an electric current through an aluminum material as an anode in an acid electrolyte containing a soluble complex acid having the heavy metal having more than one stage of oxidation in the anion and having also a negative element other than oxygen in the anion, that does not undergo decomposition under the influence of the electric current and that does not react with the electrode material.

10. In a method of producing oxide-coated aluminum, the step of passing an electric current through an aluminum material as an anode in an acid electrolyte containing a soluble complex acid having the heavy metal having more than one stage of oxidation in the anion and having also a negative element other than oxygen in the anion, and a soluble heavy metal salt, said complex acid and heavy metal salt being incapable of undergoing decomposition under the influence of the electric current and of reacting with the electrode material.

11. In a method of producing oxide-coated aluminum, the step of passing an electric current through an aluminum material as an anode in an acid electrolyte containing a compound selected from the group of compounds consisting of per-tungstic acid and per-molybdic acid.

12. A method according to claim 8 wherein sulfuric acid is used as acid constituent.

13. An aqueous acid bath for the anodic treatment of aluminum, containing a soluble heavy metal compound that does not undergo decomposition under the influence of the electric current and that does not react with the electrode material, said heavy metal having more than one stage of oxidation, said compound being taken from the class consisting of metal salts having the heavy metal in the cation and complex acids and per-acids having the heavy metal in the anion.

14. An aqueous acid bath for the anodic treatment of aluminum, containing a soluble heavy metal compound that does not undergo decomposition under the influence of the electric current and that does not react with the electrode material, said heavy metal having more than one stage of oxidation, said compound being taken from the class consisting of phosphotungstic acid, molybdic-sulphuric acid, molybdo-oxalic acid, permolybdic acid, pertungstic acid.

15. An aqueous acid bath for the anodic treatment of aluminum and its alloys containing compounds of heavy metals having more than one stage of oxidation with simple acids, said compounds being soluble and stable in said acid bath and not being decomposed under the influence of the electric current.

16. An aqueous acid bath for the anodic treatment of aluminum and its alloys containing compounds of heavy metals having more than one stage of oxidation with simple acids, said compounds being soluble and stable in said acid bath and not being decomposed under the influence of the electric current.

ence of the electric current, said compounds being taken from the class wherein said metal is in the cation forming salts with said acids, and is in the anion forming complex acids with said acids.

- 5 17. An aqueous acid bath for the anodic treatment of aluminum and its alloys containing compounds of heavy metals having more than one stage of oxidation with simple acids, said
10 compounds being soluble and stable in said acid

bath and not being decomposed under the influence of the electric current, said heavy metals being taken from the class consisting of manganese, cobalt, nickel, molybdenum, chromium, and tungsten, and the acids from the group consisting of sulphuric, phosphoric, oxalic, and hydrogen peroxide. 5

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