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[54] OXIDIZING COMPOSITION AND PROCESS FOR ALUMINUM

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[52] **U.S. Cl.** **148/6.1,** 148/6.27
[51] **Int. Cl.** **C23f 7/06**
[58] **Field of Search** 252/387; 148/6.27, 148/6.1

[56] **References Cited**

UNITED STATES PATENTS

2,796,371	6/1957	Ostrander et al.	148/6.27 X
2,796,370	6/1957	Ostrander et al.	148/6.27 X

OTHER PUBLICATIONS

Chem. Abstracts 72:27579u Feb. 9, 1970.

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[57] ABSTRACT

The invention is for a process for providing an oxide coating on aluminum which process uses chemical means only while avoiding the use of an electric current as is required in an anodizing process. Absent conventional steps such as water rinses and the like, the process comprises cleaning, including desmutting of an aluminum part to the extent necessary, and treating with an aqueous alkaline solution of a ferricyanide compound for a time sufficient to oxidize the aluminum part. The treatment with the ferricyanide solution is considered to be a chemical oxidizing step similar to the formation of an oxide film electrically in an anodizing process, but lower in cost and having other advantages. The oxidized aluminum surface is corrosion and heat resistant, acts as a base for various coating and is readily dyed to produce brilliant colors.

24 Claims, No Drawings

OXIDIZING COMPOSITION AND PROCESS FOR ALUMINUM

BACKGROUND OF THE INVENTION

1. Introduction

This invention relates to the formation of oxide coatings on aluminum and, more particularly, to a process and composition for oxidizing aluminum using chemical means only avoiding the use of an electric current.

2. Description of the Prior Art

Methods for providing an integral oxide coating on aluminum are well known in the art. These coatings are corrosion resistant, may be dyed, and act as bases for various finishes such as paint. The most common method for forming such a coating is an electrochemical method called "anodizing" which method involves the formation of an oxide coating by passing a current through an electrolyte such as a sulphuric acid or a chromic acid solution where the aluminum part to be oxidized is the anode and the tank containing the electrolyte is the cathode. Following formation of the oxide coating, the aluminum part may be immersed in a dye bath to impart the desired coloration to the aluminum. A process for anodizing aluminum is disclosed in the Metal Finishing Guidebook Directory for 1967, Metals and Plastics Publications, Inc., Westwood, New Jersey, pages 515 to 525.

Though anodizing is one of the most widely used methods for oxidizing aluminum, it has drawbacks, one of which being the high cost of the process. This is due to the requirement for special equipment associated with passing a current through a solution. Thus, electrodes, a rectifier and special lead lined or stainless steel tanks are required. In addition, the anodizing process requires low temperatures i.e., from about 70° to 75°F for soft anodizing and from 20° to 25°F for hard anodizing. Since formation of the oxide coating is an exothermic reaction, special refrigeration equipment is required to operate the process. Further, it is necessary to air oxidize the solution during the anodizing process.

In addition to the disadvantages noted above, there are additional disadvantages to the anodizing procedure in that it is primarily useful for large parts as each part treated must have an electrical connection. Thus, small parts such as pins, bolts, and the like cannot be economically anodized.

There are also chemical methods for coloring aluminum, the most widely used chemical method being illustrated in U.S. Pat. No. 2,976,371. In the process of this patent, there is disclosed an acidic treatment solution comprising a mixture of a chromic compound selected from the group of chromic acid and water soluble salts thereof and a ferricyanide acid and water soluble salts thereof. It is believed that a complex between the aluminum and chromic acid is formed which is color receptive. The process is essentially a room temperature operation with pH adjusted to a maximum of 3. A part is treated by immersion in the above solution for a brief time, typically 5 minutes, and then colored using an organic finish such as a paint, lacquer or dye.

The above procedure avoids many of the disadvantages noted above in connection with anodizing. However, colors produced by dyeing are not uniform nor are they good decorative colors in that they have a tendency to be iridescent. Further, the chromic acid is a difficult material to dump after the treatment solution is spent. Finally, the coating is soft and does not possess good heat resistance properties.

SUMMARY OF THE INVENTION

The subject invention provides materials and a process for oxidizing aluminum to provide corrosion and heat resistant coatings which are readily dyed and receptive to various finishes. The process comprises cleaning and desmutting an aluminum part to the extent required and contacting the aluminum part with an aqueous alkaline oxidizing solution of a ferricyanide compound for a time sufficient to oxidize the surface of the aluminum part. If desired, the oxidized aluminum part may then be dyed with a suitable dye to effect a desired colored coating or coated with any other suitable finish such as paint, a lacquer or the like.

The critical step is considered to be the treatment with the aqueous alkaline ferricyanide solution which is considered to be a chemical oxidizing step similar to the formation of the oxide film electrically in an anodizing process.

The process of the subject invention overcomes the disadvantages noted above with respect both to anodizing and to chemical treatment in accordance with U.S. Pat. No. 2,796,371. With respect first to anodizing, expensive electrical equipment and special tanks are not required as the treatment process is completely chemical in nature. As a result, not only may large parts be treated, but small aluminum parts may be colored using barrel plating techniques since electrical connections are not required. With respect to the chemical process noted above, the process of this invention is an improvement thereover in that the oxide coatings are harder and possess better corrosion and heat resistant properties. In addition, when dyed, the color imparted is more uniform, brighter and substantially more desirable than those of the aforesaid chemical process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Prior to treating an aluminum part with the oxidizing formulation of this invention, the part is preferably cleaned to the extent necessary. Cleaning can be a combination of steps comprising solvent degreasing, preferably with a hydrocarbon solvent such as benzene to remove grease and oil or by soak cleaning. Thereafter, the part may be etched with a mild acid or alkaline cleaner to remove dirt, oxides and other contamination but not so as to form visible surface irregularities. Finally, if necessary, the part may be treated with a conventional desmutter to remove any residues that may be left on the surface of the part. Such a desmutter could comprise a mixture of dilute nitric and hydrofluoric acid. Intermediate between each of the aforesaid steps would be a water rinse. The entire process of cleaning is conventional in the art and not considered to be a part of this invention.

The next step in the process comprises formation of an oxide film chemically, which film is considered to be similar in function to the oxide film formed electrochemically in the conventional anodizing process. The chemical oxidant used is an aqueous, alkaline solution of a ferricyanide compound, preferably an alkali or alkaline earth ferricyanide, though ferricyanide compounds having cations other than alkali and alkaline earth metal cations are suitable provided such cations do not deposit on the aluminum part being treated. The concentration of the ferricyanide compound in solution is not critical, from 0.01 moles per liter to saturation being a satisfactory range. However, at the low concentration of 0.01 moles per liter, the process is impractical because of the long treatment time required. A preferred range for the ferricyanide compound is from about 0.1 to 0.5 moles per liter and most preferably, from about 0.20 to 0.30 moles per liter.

The oxidizing solution is an aqueous, alkaline solution with pH adjusted to between about 10 and 13, preferably between 11.2 and 12.0 and more preferably between 11.5 and 11.8. To obtain the desired pH, a pH adjustor is preferably used such as a hydroxide, a carbonate or a tribasic phosphate. The alkali and alkaline earth metal hydroxides and carbonates are suitable, potassium carbonate, sodium hydroxide and trisodium phsophate being the most preferred materials. The amount of pH adjustor used is that amount that gives the desired pH. Using potassium carbonate as an example, from about 0.1 to about 0.5 moles per liter of solution provides the desired pH.

It is also desirable to include an inhibitor for aluminum in the oxidizing solution to prevent darkening of the oxide coating and to produce brighter color if the aluminum part is subsequently contacted with a dye during the processing sequence. A suitable inhibitor is a tribasic phosphate such as tribasic sodium phsophate and tribasic potassium phosphate. The amount of the tribasic phosphate is not critical, small amounts providing some benefit with larger amounts providing greater benefit. In general, the concentration may be as low as 0.01 moles per liter to sautration or even in excess of saturation. A preferred range for the tribasic phosphate is from 0.04 to 0.50 moles per liter.

A preferred formulation in accordance with the invention is as follows:

Potassium ferricyanide	0.1 to 0.5 moles per liter
Potassium carbonate	0.1 to 0.5 moles per liter
Trisodium phosphate	0.1 to 0.5 moles per liter
Water	to 1 liter

The oxidizing solution of this invention may be used over a wide temperature range, but preferably is used below its boiling point within a temperature range of from about 70° to 100°F and preferably from about 75° to 90°F. The time of contact of an aluminum part with the oxidizing solution is likewise not critical, periods of time ranging from 1 to 60 minutes being suitable and from 5 to 20 minutes being typical.

In general, those aluminum alloys containing a high copper content require a shorter treatment than those with a low copper content. It should be understood that there is a relationship between concentration of ingredients in the oxidizing solution, temperature and time; more concentrated solutions or higher temperatures or a combination of the two resulting in shorter treatment time.

Following treatment with the oxidizing solution of this invention, the aluminum part is rinsed and may be coated with a finish such as those disclosed in U.S. Pat. No. 2,796,371 incorporated herein by reference, or a solution of a colorant which may be either an organic dye or even an inorganic pigment. Many of the colorants that may be used are those conventionally usd in anodizing. Typical of such dyes are the following, set forth for purposes of example only:

Aluminum Orange 3A	
Anthraquinone Green GNN	C.I. 61570
Alizarin Orange 2GN	C.I. 14030
Aluminum Fiery Red ML	
Wool East Orange GA	C.I. 26520
Fast Mordant Yellow GD	C.I. 25100
Chromoxane Pure Blue BA	C.I. 43830
Chlorantine Fast Red 5 BRL	C.I. 35780

The parts treated with the alkaline solution of the ferricyanide may be colored in accordance with prior art anodizing treatment procedures. Thus, dye concentration, treatment temperature and time are conventional, temperatures of from 130° to 150°F being appropriate with treatment time ranging from about ½ to 30 minutes.

Following dyeing and a water rinse, the part may be sealed if desired, using the conventional sealing step of immersion of the colored part in a solution such as nickel acetate or sodium dichromate or any other conventional material in accordance with art-recognized procedures.

The following examples are given for the purpose of illustrating the invention. It will be understood that the invention is not limited to these examples.

EXAMPLE 1

An aluminum panel of No. 6061 alloy measuring 2 × 4 × 0.016 inch is degreased by soaking for five minutes in a conventional non-etching aluminum soak cleaner made up at 60 grams per liter and maintained at 150°F. The panel is then removed, water rinsed, and next immersed in a conventional mild alkaline etching cleaner consisting of 55 grams of cleaner (Clepo No. 30R) dissolved in one liter of water. The cleaning bath is maintained at about 150°F. The panel is removed after about one minute treatment in the bath and rinsed in cold water. The clean panel is then immersed in a 10 percent nitric acid solution to desmut the same and provide a clean surface. A treatment time of one-half minute is used. The clean panel is rinsed with cold water and immersed in a solution comprising of 80 grams of potassium ferricyanide, 40 grams of potassium carbonate, 40 grams of trisodium phosphate and water to one liter. The pH of the solution is maintained at about 12.0, the temperature of the solution is held at about 75°F and immersion time is about 20 minutes. Thereafter the panel is removed and rinsed with water. The panel, having an oxide coating, is then dyed by immersion for two minutes in a dye bath maintained at about 135°F consisting of 4 grams of Chromoxane Pure Blue BA (C.I. 43830) in one liter of water. The pH of the dye is adjusted to between 6.0 and 7.0. The dyed panel is rinsed with water and sealed in a solution containing 50 grams of sodium dichromate dissolved in one liter of water with the pH maintained at about 5.9. The time of sealing is 15 minutes and the temperature of the sealing bath is maintained at about 210°F. The panel is then rinsed with water, dried in the air, and buffed by hand. It has a uniform dark blue coloration and has good wear and corrosion resisting properties.

EXAMPLE 2

Following the procedure of example 1, the following dyes are substituted for the dye used in example 1:

DYE STUFF

Fast Mordant Yellow GD, ext. conc.	C.I. 25100
Orcochrome Red 64	
Omegachrome Brilliant Blue B	C.I. 43830
Chlorantine Fast Red 5BRL	C.I. 35780

In every case, the panel is uniformly colored to the shade indicated and the colored oxide coating has good wear and corrosion resistance.

EXAMPLE 3

Foll'wing the procedure of example 1, the following aluminum alloys were dyed: 7075, 1100, 6061, 6063, 3003, 5052, 2024, 2021, 2017 and 2014 and cast alloys E40 and 356. In all cases, the panel is uniformly colored and has good wear and corrosion resistance.

EXAMPLE 4

The procedure of example 1 is repeated, but the trisodium phosphate is omitted from the oxidizing formulation. The results are similar to those of example 1 except that the colored surface is dark and not as brilliant.

It will be noted that the present invention provides a process for oxidizing aluminum and for coloring aluminum which is low in cost; does not require electrical equipment; and can be applied to small parts such as pins, bolts and the like. The colorant appears to be uniformly distributed throughout the oxide coating and is adherent to the aluminum part. The resulting colored aluminum and aluminum alloys have a deep shade and are more attractive than coatings that have heretofore been obtainable on chemically-treated aluminum or aluminum alloy surfaces.

We claim:

1. A process for forming an oxide coating on aluminum and its alloys which coating is corrosion and heat resistant, is receptive to coating and readily dyed, said process comprising the steps of cleaning the aluminum to the extent necessary and formation of said oxide coating using chemical means consisting of contacting the surface of said aluminum with an aqueous, alkaline solution of a ferricyanide salt, said solution having a pH between about 10 and 13 and said ferricyanide salt being present in solution in an amount of at least 0.01 moles per liter of solution.

2. The process of claim **1** where the ferricyanide salt is present in an amount of from 0.1 to 0.5 moles per liter of solution.

3. The process of claim **2** where the pH of the ferricyanide solution varies between 11.2 and 12.0.

4. The process of claim **2** where the pH of the ferricyanide solution varies between 11.5 and 11.8.

5. The process of claim **2** including the step of contacting the oxidized aluminum part with a colorant solution.

6. The process of claim **5** where the pH of the ferricyanide solution varies between about 11.2 and 12.0, the contact time of the aluminum with the ferricyanide solution varies from about 1 to 60 minutes, the temperature of said solution is below its boiling point and the colorant solution is a dye.

7. The process of claim **6** where the temperature varies between about 70° and 100°F and the contact time of the aluminum with the ferricyanide solution is from about 5 to 20 minutes.

8. The process of claim **6** where the ferricyanide solution contains a pH adjustor in an amount sufficient to provide the required pH and is selected from the group consisting of alkali and alkaline earth metal carbonates, hydroxides and tri-basic phsophates.

9. The process of claim **6** where the ferricyanide solution contains an inhibitor for aluminum that prevents darkening of the oxide coating.

10. The process of claim **9** where the inhibitor is a tribasic phosphate contained in solution in an amount from 0.01 moles per liter to sautration.

11. The process of claim **9** where the inhibitor is trisodium phosphate contained in solution in an amount from 0.04 to 0.50 moles per liter of solution.

12. The process of claim **2** where the ferricyanide salt is present in an amount of from 0.2 to 0.3 moles per liter of solution.

13. In a process for coloring aluminum and its alloys including the steps of cleaning the aluminum to the extent necessary, oxidizing the aluminum and contacting the aluminum with a colorant, the improvement comprising formation of said oxide coating by chemical means consisting of contacting the surface of said aluminum with an aqueous, alkaline solution of a ferricyanide salt, said solution consisting of at least 0.01 moles per liter of a ferricyanide, a pH adjustor in an amount sufficient to provide required pH and an inhibitor for aluminum to prevent darkening of the oxide coating, said aqueous, alkaline solution of the ferricyanide salt having a pH varying between about 10 and 13.

14. The process of claim **13** where said ferricyanide salt is an alkali or alkaline earth metal ferricyanide.

15. The process of claim **14** where the pH varies from about 11.2 and 12.0.

16. The process of claim **15** where the inhibitor is a tribasic phosphate contained in solution in an amount of at least 0.01 mole per liter.

17. The process of claim **14** where the aqueous, alkaline solution of the ferricyanide comprises potassium ferricyanide in an amount from 0.1 to **moles** moles per liter, potassium carbonate in an amount from 0.1 to 0.5 moles per liter, trisodium phosphate in an amount from 0.04 to 0.50 moles per liter and water to 1 liter.

18. The process of claim **17** where temperature of said ferricyanide solution is below the boiling point of said solution.

19. The process of claim **17** where the the temperature of said ferricyanide solution varies from about 70° to 100°F.

20. The process of claim **17** where the temperature of said ferricyanide solution varies from between 70° to 100°F and treatment time varies between 5 and 20 minutes.

21. An aqueous solution for oxidizing aluminum and its alloys in a process for coloring aluminum, said solution comprising a ferricyanide salt in an amount of at least 0.01 moles per liter, a pH adjustor in an amount sufficient to provide an alkaline solution having a pH varying between about 10 and 13, and an inhibitor to prevent darkening of the oxide coating, said inhibitor being present in an amount of at least 0.01 moles per liter of solution.

22. The solution of claim **21** having a pH varying between about 11.2 and 12.0.

23. The solution of claim **21** where the inhibitor is a tribasic phosphate.

24. The solution of claim 21 having the following composition:

alkali or alkaline earth metal ferricyanide	0.1 – 0.5 moles per liter
alkali metal carbonate	0.1 – 0.5 moles per liter
tribasic phosphate	0.1 – 0.5 moles per liter
water	to 1 liter

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,765,952
DATED : October 16, 1973
INVENTOR(S) : Bertha S. Tuttle and Jekabs Ozolins

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 41 after "to" replace "moles" with - 0.5 -.

Signed and Sealed this

sixteenth **Day of** *September 1975*

[SEAL]

Attest:

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Attesting Officer

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Commissioner of Patents and Trademarks