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[54] **OXIDIZING PROCESS AND COMPOSITION FOR ALUMINUM**

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[*] Notice: The portion of the term of this patent subsequent to Oct. 16, 1990, has been disclaimed.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 170,668, Aug. 10, 1971, Pat. No. 3,765,952.

[52] **U.S. Cl.** **148/6.1;** 148/6.27

[51] **Int. Cl.** **C23f 5/04**

[58] **Field of Search** 148/6.1, 6.27; 252/387

[56] **References Cited**

UNITED STATES PATENTS

2,796,370	6/1957	Ostrander et al.	148/6.27 X
2,796,371	6/1957	Ostrander et al.	148/6.27 X
3,765,952	10/1973	Tuttle et al.	148/6.1

OTHER PUBLICATIONS

Chem. Abstracts, 72:27579y, 2-9-70.

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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.

18 Claims, No Drawings

OXIDIZING PROCESS AND COMPOSITION FOR ALUMINUM

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 170,668 filed Aug. 10, 1971, now U.S. Pat. No. 3,765,952.

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. Further, after prolonged usage, the solution must be discarded due to build-up of aluminum.

In copending U.S. Pat. applications Ser. No. 170,668 a process for oxidizing aluminum to provide corrosion and heat resistant coatings which are readily dyed and receptive to various finishes is disclosed. According to the process of said application, an aluminum part is cleaned and desmutted to the extent required and contacted with an aqueous alkaline oxidizing solution of a ferricyanide compound for a time sufficient to oxidize the surface of the part. If desired, the oxidized aluminum part is then 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 in said application 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 ferricyanide salt is used in said solution in a concentration of at least 0.01 moles per liter and the solution has a pH ranging between about 10 and 13.

The process of said application overcomes the disadvantage with respect both to electrical anodizing and to chemical treatment in accordance with the aforesaid 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 said application is an improvement thereover, in that the oxide coatings are harder and possess better corrosion and heat resistance properties. In addition, when dyed, the color imparted is more uniform, brighter and substantially more desirable than those colors obtained with the aforesaid chemical process. Further, with suitable treatment and replenishment, the treatment baths of said application have an extremely long life, typically in excess of two years.

SUMMARY OF THE INVENTION

The subject invention is an improvement over that of the aforesaid U.S. Pat. application Ser. No. 170,668 in that with the use of the same ferricyanide oxidizing solutions, it has been found that the pH range of the composition can be extended below 10 and above 13 by careful temperature regulation. Thus, by use of temperatures elevated up to close to the boiling point of the solution, the pH of the composition can be reduced below 10, typically down to about 7.5. By use of temperatures below room temperature, typically down to close to the freezing point of the solution, the pH of the solution can be increased above 13, typically up to about 14.0.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention described herein relates to treatment of aluminum parts. An aluminum part is defined herein as not only a part formed from aluminum, but articles coated with aluminum such as plastic substrates coated with aluminum. The thickness of the aluminum coating is not critical, though it should be understood that with extremely thin coatings, e.g. 2000 angstroms, or less, the treating solution might attack the aluminum metal to the extent that a chemically oxidized coating may not be formed.

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 by 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 contaminants, but not so as to form visible surface irregularities. Finally, if necessary, the part may be treated with a conventional desmutter to remove any residue 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 and desmutting 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 and 0.30 moles per liter.

The oxidizing solution is an aqueous, alkaline solution with pH adjusted to between about 7.5 to 10 or 13 to 14.0. To obtain desired pH, a pH adjustor is preferably used such as an acid such as phosphoric acid as necessary, hydroxide, a carbonate or a tri-basic phosphate. The alkali and alkaline earth metal hydroxides and alkali carbonates and tri-basic phosphates are suitable, sodium and potassium carbonates, sodium and potassium hydroxides and trisodium and tripotassium phosphates being the most preferred materials. The carbonate and tri-basic phosphate act as a buffer and are preferably used in combination, especially where the tri-basic phosphate also acts as an inhibitor as will be explained in more detail below. The amount of pH adjustor used is that amount that gives the desired pH. Using potassium carbonate as an example, from about 0.01 to 0.1 moles per liter of solution provides the desired pH below **10** and from about 0.5 to about 0.75 moles per liter of solution of a combination of potassium carbonate and sodium hydroxide, the sodium hydroxide being used in the minimum amount necessary relative to the potassium carbonate to reach the desired pH provides desired pH above 13. It should be noted that potassium carbonate alone cannot be used to obtain these high pH values.

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 the aforesaid tri-basic phosphate such as tri-basic sodium phosphate and tri-basic potassium phosphate. Thus, the tri-basic phosphate is both an inhibitor and a pH adjustor. The amount of the tri-basic phosphate is not critical, small amounts providing some benefit with larger amounts providing greater benefit. In general, the concentration may be as low as 0.001 moles per liter to saturation or even in excess of saturation. A preferred range for the tri-basic 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	sufficient to provide desired pH
Water	to 1 liter

The oxidizing solution of this invention is used at a temperature commensurate with the pH of the solution. Thus, if the pH of the solution is between 7.5 and 10, the temperature is maintained between about 100°F and the boiling point of the solution. If the pH of the solution is between 13 and 14.0, the temperature of the solution is maintained within a range of about 2°F above the freezing point of the solution to about 50° to 60°F though temperatures up to about 70°F can be used if treatment precautions are exercised. It should be understood that the temperature is inversely related to pH. In other words, as the pH is increased from 13 to 14.0, the temperature is correspondingly decreased and as the pH is decreased from 10 down to about 7.5, the temperature is correspondingly increased.

The time of contact of an aluminum part with the oxidizing solution is not critical, periods of time ranging from 1 to 60 minutes being suitable and from 5 to 25 minutes being typical.

In general, those aluminum alloys containing a high copper content require a shorter treatment thant 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 temperature 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 used 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 Fast Orange GA	C.I. 26520
Fast Mordant Yellow GD	C.I. 25100
Chromoxane Pure Blue BA	C.I. 43830
Chlorontine 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 room to 150°F being appropriate with treatment time ranging from about ½ to 20 minutes dependent on temperature, lower temperatures requiring longer times.

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. Example 1 below is set forth to illustrate the procedure as set forth in the above noted copending application and the examples that follow example 1 illustrate the process of this subject invention.

EXAMPLE 1

An aluminum panel of No. 5056 alloy measuring 2 inches × 4 inches × 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 ½ minute is used. The clean panel is rinsed with cold water treated with a brightening solution desmutted, rinsed again and immersed in a solution comprising 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 65°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 5 minutes in a dye bath maintained at about 90°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 7.0 and 8.0. The dyed panel is rinsed with water and sealed in a solution containing 0.5 grams of sodium dichromate dissolved in one liter of water with the pH maintained at about 5.6. The time of sealing is 25 minutes and the temperature of the sealing bath is maintained at about 80°–90°F. The panel is then rinsed with water, dried in air, and buffed by hand. It has a uniform bright blue coloration and has good wear and corrosion resistance properties.

EXAMPLE 2

The procedure of example 1 is repeated except that the pH of the solution is reduced to about 9.5 and the concentration of the potassium carbonate and trisodium phosphate is reduced in an amount sufficient to reduce the pH to 9.5. The temperature of the oxidizing solution is maintained at about 190°F and the immersion time is about 20 minutes. All of the steps are the same. The aluminum part so treated has a uniform bright blue coloration and good wear and corrosion resistance properties.

EXAMPLE 3

The procedure of example 1 is repeated except that the pH of the ferricyanide solution is increased to about 13.5 by adding the necessary amount of potassium hydroxide while the temperature of the oxidizing solution is reduced to about 33°F. Similar results are obtained.

The colored surface such as those formed in Examples 1–3 may be bleached with concentrated, cold sulfuric acid and then re-dyed, such as if the color is not correct. This procedure establishes that the coating formed by the process herein is an oxide coating rather than a phosphate coating.

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 as well as large parts as in the prior art anodizing methods. The colorant appears to be uniformly distributed throughout the oxide coating and is adherent to the aluminum part. The resulting colored aluminum and the aluminum alloys have a deep shade and are more attractive than are those 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 part with an aqueous alkaline solution of a ferricyanide salt having a pH selected from between about 7.5 and 10 or 13 and 14.0, said ferricyanide salt being present 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 about 7.5 and 10.

4. The process of claim **2** where the pH of the ferricyanide solution varies between about 13 and 14.0.

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 7.5 and 10 and the temperature of said solution varies between about 100°F and the boiling point of the solution.

7. The process of claim **5** where the pH of the ferricyanide solution varies between about 13 and 14.0 and the temperature of the solution varies between room temperature and a temperature of about 2°F above the freezing point of the solution.

8. 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.

9. The process of claim **2** where the ferricyanide solution contains a pH adjustor in an amount sufficient to provide the required pH which pH adjustor is selected from the group consisting of alkali carbonates, alkali or alkaline earth metal hydroxides, alkali tri-basic phosphates and mixtures thereof.

10. The process of claim **2** where the ferricyanide solution contains an inhibitor for aluminum that prevents darkening of the oxide coating and enhances dyeability.

11. The process of claim **10** where the inhibitor is a tri-basic phosphate contained in solution in an amount at from 0.01 moles per liter of solution to saturation.

12. The process of claim **10** where the inhibitor is a tri-basic phosphate contained in solution in an amount of from 0.04 to 0.50 moles per liter of solution.

13. In a process for coloring a substrate coated either with aluminum or an aluminum alloy including the step 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 coating 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 ferricyanide having a pH varying between about 7.5 and 13.5.

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

15. The process of claim **13** where the inhibitor is a tri-basic phosphate contained in solution in an amount of at least 0.01 moles per liter of solution.

16. The process of claim **15** where the aqueous alkaline solution of the ferricyanide comprises potassium ferricyanide in an amount of from 0.1 to 0.5 moles per liter, trisodium phosphate in an amount of from 0.04 to 0.50 per liter of solution, potassium carbonate in an amount sufficient to provide required pH and water to 1 liter.

17. An aqueous solution for oxidizing aluminum and its alloys in a process for coloring aluminum, said solu-

tion comprising a ferricyanide salt in an amount of at least 0.01 moles per liter of solution, a pH adjustor in an amouunt sufficient to provide an alkaline solution having a pH varying between 7.5 and 10 or 13 and 14.0., and an inhibitor to prevent darkening and enhance dyeability of the oxide coating, said inhibitor being present in an amount of at least 0.001 moles per liter.

18. The solution of claim **17** where the inhibitor is a tri-basic phosphate.

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