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ELECTROPLATING SILVER ON ALUMINUM AND ITS ALLOYS

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This inventaion relates to methods of electroplating. More particularly it relates to methods of forming adherent coatings of silver, capable of being polished to a high lustre, on a base of aluminum or aluminum alloys.

It is well known that metal coatings formed directly on aluminum or aluminum alloys by electroplating possess poor adherence. It has been proposed to increase this adherence by first forming an oxide coating on the aluminum base by means of anodic treatment in an acid bath and then dissolving a portion of the oxide film in an acid or alkaline bath, prior to electroplating (W. J. Travers, Transactions of the Electrochemical Society, vol. LXXV, 1939, p. 201; U. S. Patent 1,971,761). It has also been proposed to electroplate directly over an oxide film produced by anodizing aluminum or aluminum alloys in chromic acid or phosphoric acid solution without intermediate treatment of the oxide film (J. Fischer U. S. Patents 1,947,981, 2,036,962 and 2,095,519).

It has been found that, when plating with silver, a far superior adherence is obtained by the method of the present invention than by any of the previously proposed methods. The method of the present invention involves preliminary cleaning of the predominantly aluminum base, anodizing of this metal base at moderate temperatures in a dilute aqueous phosphoric acid solution and electroplating the anodized aluminum in an aqueous solution of silver alkali cyanide containing an excess of free alkali cyanide considerably greater than that commonly present in silver plating baths. No alteration of the anodic coating prior to electroplating is necessary or desirable.

Any suitable preliminary cleaning operations may be employed provided that they do not unduly roughen the smooth surface of the aluminum base. A preferred cleaning procedure involves immersion successively in carbon tetrachloride (or other suitable chlorinated solvent) an aqueous sodium hydroxide solution, concentrated nitric acid and an aqueous sodium cyanide solution, with appropriate rinsing in water between each step.

The anodizing is ordinarily carried on with alternating current in order to prevent the formation of a current blocking film before the desired degree of anodizing has been achieved. The length of time during which the anodizing operation is permitted to continue is dependent upon the composition of the aluminum alloy. Pure aluminum, in general, tends to form an

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oxide film less slowly than those alloys containing small amounts of magnesium or other alloying metals.

When too thick an oxide film is formed during the anodizing operation, this condition may be remedied by the initial application of a relatively high current density in the silver plating bath for several seconds, followed by the use of the normal plating current density.

The following specific examples will illustrate procedures by which the present invention may be practiced.

Example 1

A smooth surfaced body of an aluminum alloy, composed of 2.5 per cent magnesium, 0.25 per cent chromium and the balance aluminum together with small amounts of iron and silicon as impurities, was subjected to a cleaning procedure consisting of immersion in carbon tetrachloride, followed in succession by immersion in a sodium hydroxide solution (one pound per gallon) for five to ten seconds, rinsing in hot water, immersion in concentrated nitric acid for several seconds, rinsing in cold running water, immersion in sodium cyanide solution (four to six ounces per gallon) for from five to ten seconds and rinsing thoroughly in cold running water. The clean aluminum body was then suspended in a three per cent aqueous phosphoric acid anodizing solution (66 cubic centimeters phosphoric acid per gallon). In this anodizing procedure an initial alternating current voltage of five volts was applied and this potential was gradually increased to fifty volts. The anodizing operation was allowed to proceed for ten minutes from the time at which the applied potential reached forty volts. The current density was not permitted to exceed 3.5 amperes per square foot throughout the anodizing procedure. The temperature of the anodizing solution was maintained at between 70° F. and 75° F. by means of cooling coils immersed in the solution. The anodized body was then removed from the anodizing bath and washed thoroughly in cold running water. The anodized body was then suspended as the cathode in a silver plating solution consisting of an aqueous solution of 1.5 ounces per gallon of silver sodium cyanide and 6 ounces per gallon of sodium cyanide. The aluminum body in the plating solution was subjected to an initial current density of sixteen amperes per square foot for two to three seconds. The current density was then reduced to 1.50 to 2 amperes per square foot and the plating was continued for forty-five minutes. A smooth,

firmly adherent, continuous and impervious coating of silver was produced. This coating was polished to a brilliant lustre.

Example 2

The procedure described in Example 1 was carried out using a body of substantially pure aluminum (99 per cent aluminum containing iron and silicon as impurities), except that in the plating operation a current density of between 1.50 and 2 amperes per square foot was applied initially, omitting the high current density used initially in Example 1. Similar results were obtained.

The concentration of the phosphoric acid solution used for anodizing may vary somewhat but is preferably between about 0.5 per cent and about 10 per cent by weight. In general the most satisfactory results are obtained with a concentration of about three per cent by weight. The optimum time for which the anodizing is allowed to continue is dependent upon the composition of the alloy as indicated above. Ordinarily the anodizing time will not exceed 10 minutes. The temperature of the anodizing bath is preferably maintained in the range of 70° F. to 75° F. In general it is difficult to insure satisfactory results if the temperature exceeds about 85° F. or goes below about 60° F. The current density ordinarily should not exceed about 6 amperes per square foot during the anodizing procedure.

With substantially pure aluminum as used in Example 2, it is ordinarily satisfactory merely to place the anodized body in the plating bath and subject it to a low plating current density, as for instance 1.50 amperes to 2 amperes per square foot. With certain aluminum alloys, if the anodizing time used is as long as that used for substantially pure aluminum, as in Example 1, it is necessary to subject the anodized body, after it is placed in the plating bath to an initially high current density. This current density will ordinarily vary between about 16 amperes per square foot and about 30 amperes per square foot and will be applied for between about 2 and about 5 seconds, depending upon the thickness of the oxide film, as determined by the composition of the alloy and the anodizing time. If the anodizing time is restricted for those alloys which form oxide films more rapidly, this initial high current density may be eliminated in most instances.

In the plating solution the best results are obtained when the ratio of free sodium cyanide to silver sodium cyanide is maintained at about 4:1. This ratio may vary however between about 5:1 or 6:1 and about 3:1 or 2:1, or even slightly beyond these limits. The total concentration of the cyanide may vary between about fifteen ounces per gallon and about five ounces per gallon and even somewhat beyond these limits but is preferably maintained at the value set forth in the specific examples above. The other plating conditions may vary as in common silver plating practice. Although sodium cyanide and silver sodium cyanide were used in the specific examples above any suitable alkali cyanide or silver alkali cyanide, particularly potassium cyanide and silver potassium cyanide may be used.

Although the invention has been described in terms of its specific embodiments, certain modifications and equivalents will be apparent to those skilled in the art and are intended to be included within the scope of the invention, which is to be

limited only by the reasonable scope of the appended claims.

What is claimed is:

1. The method of silver plating a predominantly aluminum body which comprises anodizing said body by utilizing said body as an electrode, immersing the electrode in an electrolyte consisting essentially of an approximately three per cent aqueous solution of phosphoric acid, subjecting the electrode to an alternating current for a time sufficient to form an adherent anodic coating on the surface of said body while maintaining said electrolyte at a temperature between about 70 degrees F. and about 75 degrees F. and while maintaining the current density at a value not exceeding about six amperes per square foot, and subsequently electro-depositing silver on said body by utilizing said body as a cathode in a silver plating bath consisting of an aqueous solution containing about 1.5 ounces of a silver alkali cyanide per gallon and about 6 ounces of a free alkali cyanide per gallon, without substantial alteration of said anodic coating prior to immersion in said bath.

2. The method of silver plating a predominantly aluminum body which comprises anodizing said body by utilizing said body as an electrode, immersing the electrode in an electrolyte consisting essentially of an aqueous solution of phosphoric acid at a concentration between about 0.5 per cent and 10 per cent by weight, subjecting the electrode to an alternating current for a time sufficient to form an adherent anodic coating on the surface of said body while maintaining said electrolyte at a temperature between about 60 degrees F. to about 85 degrees F., and while maintaining the current density at a value not exceeding about six amperes per square foot, and subsequently electro-depositing silver on said body by utilizing said body as a cathode in a silver plating bath consisting of an aqueous solution containing between about five ounces per gallon and about fifteen ounces per gallon of a cyanide mixture consisting of an alkali cyanide and a silver alkali cyanide in the ratio of between about 6:1 and about 3:1, without substantial alteration of said anodic coating prior to immersion in the plating bath.

3. The method of plating a predominantly aluminum body with silver which comprises anodizing said body by utilizing said body as an electrode, immersing the electrode in an electrolyte consisting essentially of an aqueous solution of phosphoric acid at a concentration between about 0.5 per cent and 10 per cent by weight, and subjecting the electrode to an alternating current for a time sufficient to form an adherent anodic coating on the surface of said body, while maintaining the current density at a value not exceeding six amperes per square foot, and subsequently electro-depositing silver on said body by utilizing said body as a cathode in a silver plating bath consisting of an aqueous solution of an alkali cyanide and a silver alkali cyanide in the ratio of between about 6:1 and about 2:1, without substantial alteration of the oxide film formed by anodizing prior to immersion in the plating bath.

4. The method of plating a predominantly aluminum body with silver which comprises anodizing said body by utilizing said body as an electrode, immersing the electrode in an electrolyte consisting essentially of an aqueous solution of phosphoric acid at a concentration between about 0.5 per cent and 10 per cent by weight,

and subjecting the electrode to an alternating current for a time sufficient to form an adherent anodic coating on the surface of said body, while maintaining the current density at a value not exceeding about six amperes per square foot, and subsequently electro-depositing silver on said body by utilizing said body as a cathode in a silver plating bath consisting of an aqueous solution of an alkali cyanide and a silver alkali cyanide in the ratio of about 4:1.

5. The method of plating a predominantly aluminum body with silver which comprises anodizing said body by utilizing said body as an electrode, immersing the electrode in an electrolyte consisting essentially of an aqueous solution of phosphoric acid at a concentration between about 0.5 per cent and 10 per cent by weight, and subjecting the electrode to an alternating current for a time sufficient to form an adherent anodic coating on the surface of said body, while maintaining the current density at a value not exceeding six amperes per square foot, and subsequently electro-depositing silver on said body by utilizing said body as a cathode in a silver plating bath consisting of an aqueous solution containing between about five ounces per gallon and about fifteen ounces per gallon of a cyanide mixture consisting of an alkali cyanide and a silver alkali cyanide in the ratio of between about 6:1 and about 3:1.

6. The method described in claim 1 wherein the alkali cyanide is sodium cyanide and the silver alkali cyanide is silver sodium cyanide.

7. The method described in claim 2 wherein the alkali cyanide is sodium cyanide and the silver alkali cyanide is silver sodium cyanide.

8. The process described in claim 4 wherein the silver plating bath contains about 1.5 ounces of silver sodium cyanide per gallon and about six ounces of sodium cyanide per gallon.

9. The method of silver plating a predominantly aluminum body comprising subjecting said body to an alternating current potential while immersed in a 3 per cent aqueous solution of phosphoric acid maintained at a temperature between about 70° F. and about 75° F., maintaining the current density at between about 3.5 and about 6 amperes per square foot by applying an initial voltage of 5 volts and gradually increasing the voltage to about 50 volts as an anodic coating is formed on the body, removing the anodized body from the phosphoric acid solution and washing thoroughly with water, immersing said body, before any substantial alteration of the anodic coating, as the cathode in a silver plating bath consisting of an aqueous solution of about 1.5 ounces per gallon of silver sodium cyanide and about 6 ounces per gallon of sodium cyanide, and electro-depositing silver on said cathode by subjecting said cathode to a current density of about 1.5 to 2 amperes per square foot for a time sufficient to form a silver coating on said cathode of the desired thickness.

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