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METHOD OF ELECTROPLATING ALUMINUM

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This application is a continuation-in-part of our earlier filed application, Serial No. 381,733, filed September 22, 1953, now abandoned, and assigned to the same assignee as the present invention which application in turn is a continuation-in-part of our application, Serial No. 295,352, filed June 24, 1952, now abandoned.

The present invention relates to a method of electroplating aluminum. More particularly it is concerned with a method of providing an aluminum article with an adherent coating of another metal such as silver.

More specifically, the invention relates to an improved method of providing an aluminum article with a non-porous, intermediate zinc coating whereby good adherence between a subsequently applied metal plate and the surface of the aluminum article is obtained. While the invention is particularly concerned with the application of electro-deposited silver coatings, it is not necessarily restricted thereto and can be employed for the application of plates of copper, cadmium, tin, or multiple plates of copper and silver, cadmium and tin, etc.

Several plating processes are known for the deposition of a metal plate, such as silver plate, upon aluminum. In one of these the aluminum is first anodically cleaned in a solution of phosphoric acid after which a coating of silver is applied or electroplated thereon. While the oxide coating on the aluminum base resulting from the anodic treatment in the acid bath results in an improved adherence of the silver plate, the resultant product is not particularly useful for electrical applications due to the high electrical resistance of the intermediate oxide film. Another known method for applying silver to an aluminum article comprises the preplating of the aluminum with a layer of zinc from a suitable zincate plating bath. The zinc coating, as a base for the ultimate silver plate, has been found to be a necessity if proper adhesion is to be obtained. However, the known zincate pretreatments have not been completely satisfactory in being both cumbersome and in many cases quite unreliable. In many of the known zincate pretreatments, as many as 8 or 10 individual steps are involved before actually depositing the silver coating. These processes include one or more pickling steps employing strong hot acid solutions. Furthermore, the zinc coatings applied by the previously known zincate methods are inherently porous and spongy, making it difficult, if not impossible, to completely rinse away all traces of the alkaline zincate solution. The residual alkali along with the natural galvanic action between silver, zinc and aluminum cause the silver plate to blister, particularly when the plated articles are subjected to elevated temperatures or used in electrical applications where a current flows between the aluminum base and the silver coating.

In accordance with the present invention, there has been provided an improved and effective method of pretreating the aluminum article in a modified zincate type bath whereby there is obtained a non-porous coating of zinc of such a character that a subsequently applied silver plate is of high quality and adheres to the underlying surface without blistering at all temperatures up to the melting point of the aluminum base. In addition, the bond between the silver plate and the aluminum base is characterized by an electrical resistance substantially lower

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than the electrical resistance of bonds obtained by previously known zincate pretreatments.

These and other advantageous results are obtained in accordance with present invention by employing a novel zincate pretreatment essentially comprising the steps of first anodically polishing the aluminum article in a bath comprising zinc cyanide, an alkali cyanide and an alkali hydroxide and thereafter while the article is still immersed in this treating solution, depositing on the article a non-porous coating of zinc. The zinc coated article is then rinsed free of all traces of the zincate bath and is silver plated in a suitable plating bath. Preferably the silver plate is of the dense or hard type.

In general, the zincate pretreating bath is a comparatively low viscosity bath containing the equivalent of from 13 to 20 ounces per gallon of sodium hydroxide, 4 to 20 ounces per gallon of sodium cyanide and 4 to 30 ounces per gallon of zinc cyanide. Various additional agents may also be present as will become apparent from the various examples given hereinafter. It is essential that the zincate bath be held at an elevated temperature of about 90° F. to 180° F. and preferably about 120° F. to 180° F. although the anodic film temperature may be somewhat higher and approaching 200–210° F. during the anodic treatment. It is also essential that the current density and treating times be carefully controlled to raise the temperature of at least the surface of the aluminum article above the bath temperature during the anodic treatment, and, in this respect, it has been found that the current density should range from 2 to 60 amperes per square inch and the processing range from 60 to 2000 ampere seconds. The time is lengthened for low current density and conversely shortened for high current density. The preferred conditions are 7 to 15 amperes per square inch of surface within a processing range of 400 to 2000 ampere seconds.

Pure and relatively pure aluminum can be processed within the extreme ranges given. Some alloys respond more satisfactorily when treated at the maximum solution temperatures. After the anodic treatment and while the aluminum article is still immersed in the zincate bath and at the elevated temperature resulting from the anodic treatment zinc is immediately deposited upon the aluminum surface. The time allowed for this zinc plating step is at least one second and may range up to about ninety seconds or even longer in certain cases. The zinc may be deposited either galvanically merely by opening the electric circuit, or alternatively, by reversing the direct current flow and reducing the current density so that during the plating period, the aluminum article is a cathode at a current density preferably not exceeding about 1.0 ampere per square inch.

For a better understanding of how the present invention may be carried into effect, the following illustrative examples are given:

Example 1

An aluminum article was preliminarily cleaned for the removal of all grease and oil from the surface. One cleaning procedure found to be effective involved the immersion of the article in petroleum spirits or other suitable solvent. The article was then immersed in a zinc electrolyte bath of the following composition:

	Optimum Concentration (Ounces per gallon)	Preferred Range (Ounces per gallon)
Zinc Cyanide	20	4–30
Sodium Cyanide	9	4–20
Sodium Hydroxide	18	13–20
Sodium Carbonate	2	0.1–6
Potassium Fluoride	1.5	1–2
Silver Cyanide	0.06	0.04–0.1
Sodium Sulphide	0.05	0.01–0.07

The bath was operated at a temperature between 130 and 140° F. The aluminum article was made the anode in this bath while employing any suitable cathode material such as mild steel or zinc. The anodic pretreatment of the aluminum article at a current density of from 7 to 10 amperes per square inch for a period of time between 20 and 30 seconds resulted in a further cleaning and electropolishing of the aluminum. During this step the article became heated well above the temperature of the bath. At the end of this time, the circuit was opened and zinc immediately deposited upon the aluminum by galvanic displacement. The time allowed for this reaction was about fifty seconds although times ranging from one to ninety seconds are suitable depending on how thick a zinc plate is desired. Thereafter the zinc-coated aluminum article was removed from the electrolyte and washed under clean running water in preparation for silver plating. A silver strike is recommended if the aluminum is to be plated in a still tank although the strike is not required when the work is plated by the use of a high speed plating machine. A suitable typical silver plating solution for depositing a hard, dense silver plate by the tank method comprises 15 ounces silver cyanide, 12 ounces potassium cyanide and from 0.05 to 0.1 ounce sodium thiosulfate per gallon of solution with the solution operated at a temperature in the neighborhood of 100° F. Proper physical characteristics of the silver are best obtained at current densities of 0.50 to 0.80 amp. per square inch. Adequate solution agitation and filtration should be supplied. If a high speed plating method is employed, the silver plating solution employed may typically be one containing about 10 ounces of silver cyanide, 8 ounces potassium cyanide and about 20 ounces potassium nitrate per gallon of solution with an operating temperature of the solution from 80° F. to 120° F. and a current density range of from 0.1 to 4.5 amps. per square inch. The silver-plated products were characterized by a hard dense bright silver plate which was relatively non-pourous and which adhered to the aluminum article at all temperatures up to the melting point of aluminum. No blistering was noted in the plate at elevated temperatures. The silver plate applied over the above-described zinc coating withstood the passage of electric currents of high amperage. For example, two ¼" x 4" aluminum bus bars having their ends zinc coated and silver-plated in accordance with the present invention were bolted in overlapping relationship with an overlapping area of about eight square inches. A current in excess of 200,000 amps. was passed through the bars for one-half second with no apparent effect on the silver plate or the electrical resistance of the joint.

Example 2

An aluminum article was preliminarily cleaned for the removal of all grease and oil from the surface. One cleaning procedure found to be effective involved the immersion of the article in petroleum spirits or other suitable solvents. The article was then immersed in a zinc electrolyte bath of the following composition:

	Optimum Concentration (Ounces per gallon)	Preferred Range (Ounces per gallon)
Zinc Cyanide	20	4–30
Sodium Cyanide	9	4–20
Sodium Hydroxide	18	13–20
Sodium Carbonate	2	0.1–6
Potassium Fluoride	1.5	1–2
Silver Cyanide	0.06	0.04–0.1
Sodium Sulphide	0.05	0.01–0.07

The bath was operated at a temperature of between 130 and 140° F. The aluminum article was made the anode in this bath while employing any suitable cathode material such as mild steel or zinc. The anodic pretreatment of the aluminum article at a current density of from 7 to 10 amperes per square inch for a period of time between 20 and 30 seconds resulted in a further cleaning and electropolishing of the aluminum. During this step the article became heated well above the temperature of the bath. At the end of this time, the circuit was opened and zinc immediately deposited upon the aluminum by displacement. The time allowed for this reaction was about ninety seconds although times ranging from one to ninety seconds are suitable depending on how thick a zinc plate is desired. Thereafter the zinc-coated aluminum article was removed from the electrolyte and washed under clean running water in preparation for silver plating. A silver strike is recommended if the aluminum is to be plated in a still tank although the strike is not required when the work is plated by the use of a high speed plating machine. A suitable silver plating solution for depositing a hard, dense silver plate by the tank method comprises typically 15 ounces silver cyanide, 12 ounces potassium cyanide and from 0.05 to 0.1 ounce sodium thiosulfate per gallon of solution with the solution operated at a temperature in the neighborhood of 100° F. Proper physical characteristics of the silver are best obtained at current densities of 0.50 to 0.80 amp. per square inch. Adequate solution agitation and filtration should be supplied. If a high speed plating method is employed, the silver plating solution employed may typically be one containing about 10 ounces of silver cyanide, 8 ounces potassium cyanide and about 20 ounces potassium nitrate per gallon solution with an operating temperature of the solution from 80° F. to 120° F. and a current density range of from 0.1 to 4.5 amps. per square inch. The silver-plated products were characterized by a hard dense bright silver plate which was relatively non-porous and which adhered to the aluminum article at all temperatures up to the melting point of aluminum. No blistering was noted in the plate at elevated temperatures. The silver plate applied over the above-described zinc coating withstood the passage of electric currents of high amperage. For example, two ¼" x 4" aluminum bus bars having their ends zinc coated and silver plated in accordance with the present invention were bolted in overlapping relationship with an overlapping area of about eight square inches. A current in excess of 200,000 amps. was passed through the bars for one-half second with no apparent effect on the silver plate or the electrical resistance of the joint.

Example 3

In this example the article was pre-cleaned as above and the zinc electrolyte employed in processing the aluminum article had the following composition:

	Optimum Concentration (Ounces per gallon)	Preferred Range (Ounces per gallon)
Zinc Cyanide	20	4–30
Sodium Cyanide	9	4–20
Sodium Hydroxide	18	13–20
Sodium Thiosulfate	2	0.1–8
Silver Cyanide	0.03	0.01–0.07
Sodium Sulfide	0.05	0.01–0.07
Sodium Carbonate	2	0.1–6

In the anodic cleaning step, the aluminum piece was made the anode at a current density of between 7 and 10 amperes per square inch for about 25 seconds. At this point, the circuit was instantly reversed so that the aluminum article became the cathode and the current density was reduced to between 0.2 and 0.5 ampere per square inch. These conditions were maintained for a period of about 3 seconds during which time a non-porous deposit of zinc was electroplated on the aluminum article although times ranging from one to ninety seconds and longer were found to be suitable. After rinsing, the zinc coated article was coated with an electrodeposited silver plate.

While various illustrative examples have been given of baths which can be employed for the anode treatment of the aluminum, it is to be understood that the invention is not limited to these specific baths. Baths having the same effective compositions can be prepared by other means. For example, a suitable aqueous bath can be prepared from sodium cyanide, 28 ounces per gallon, sodium hydroxide, 9 ounces per gallon and metallic zinc, 14 ounces per gallon.

The term "aluminum" as used herein and in the appended claims is intended to cover not only pure or commercially pure aluminum but also various aluminum alloys. Examples of aluminum alloys which have been successfully processed in accordance with the present invention include alloy 3S containing 1.2% manganese; and alloy 61S containing about 1% magnesium, 0.6% silicon, 0.25% copper and 0.25% chromium.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of preparing an aluminum base article for the application of an electroplated coating which comprises immersing said aluminum base article in a hot electrolyte bath comprising an aqueous solution of zinc cyanide, an alkali cyanide and an alkali hydroxide, anodically treating the immersed article by passing a direct current through said article as the anode at a current density of about 2–60 amperes per square inch, thereafter discontinuing the anodic treatment and while said article is still immersed in said bath, depositing on said article a non-porous coating of zinc from said bath for at least one second and subsequently electrodepositing a metal coating on the zinc-coated article.

2. The method of claim 1 in which the anodic treatment is continued for a time such that the total ampere-seconds is from 60 to 2000.

3. The method of claim 2 wherein the electrolytic bath contains from 4 to 30 ounces zinc cyanide, from 4 to 20 ounces sodium cyanide and from 13 to 20 ounces sodium hydroxide per gallon electrolyte.

4. The method of claim 3 wherein the zinc coating is galvanically deposited on said aluminum article for from one second to about ninety seconds.

5. The method of claim 3 in which the electrolyte also contains from 1 to 2 ounces per gallon potassium fluoride.

6. The method of claim 3 in which the electrolyte also contains from 0.1 to 8 ounces sodium thiosulfate.

7. The method of claim 4 in which the electrolyte also contains from 1 to 2 ounces per gallon potassium fluoride.

8. The method of claim 4 in which the electrolyte also contains from 0.1 to 8 ounces sodium thiosulfate.

9. The method of silver plating an aluminum article which comprises immersing said article in a hot electrolyte comprising an aqueous solution containing from 4 to 30 ounces zinc cyanide, 4 to 20 ounces sodium cyanide, 13 to 20 ounces sodium hydroxide, 0.01 to 0.07 sodium sulfide and 0.1 to 6 ounces sodium carbonate per gallon of solution, anodically treating the immersed article by passing a direct current through said article at a current density of from about 7 to 15 amperes per square inch for from 20 to 30 seconds, discontinuing the anodic treatment and, while said article is still immersed in said solution depositing a non-porous coating of zinc on said article for at least one second and subsequently electrodepositing a silver plate over said zinc coating from a silver plating bath comprising an aqueous solution of silver cyanide and sodium cyanide.

10. The method of claim 9 in which the zinc coating is galvanically deposited on said aluminum article for from one second to about ninety seconds.

11. The method of silver plating an aluminum article which comprises immersing said article in a hot electrolyte comprising an aqueous solution containing from 4 to 30 ounces zinc cyanide, 4 to 20 ounces sodium cyanide, 15 to 20 ounces sodium hydroxide, 0.01 to 0.07 ounce silver cyanide, 0.01 to 0.07 ounce sodium sulfide and 0.1 to 6 ounces sodium carbonate per gallon of electrolyte solution, anodically treating the immersed article by passing a direct current through said article at a current density of from about 7 to 15 amperes per square inch for from 20 to 30 seconds, discontinuing the anodic treatment, and, while said article is still immersed in said solution passing a direct current through said article as a cathode at a current density of from 0.2 to 0.5 ampere per square inch for at least one second to deposit a non-porous coating of zinc on said article and subsequently electrodepositing a silver plate over said zinc coating from a plating bath essentially composed of silver cyanide and sodium cyanide.

12. The method of claim 11 in which the zinc coating is galvanically deposited on said aluminum article for from one to ninety seconds.

13. The method of silver plating an aluminum article which comprises immersing said article in a hot electrolyte comprising an aqueous solution containing from 4 to 30 ounces of zinc cyanide, 4 to 20 ounces of sodium cyanide, 13 to 20 ounces sodium hydroxide, 0.1 to 6 ounces sodium carbonate, 1 to 2 ounces potassium fluoride, 0.04 to 0.1 ounce silver cyanide and 0.01 to 0.07 ounce sodium sulfide per gallon of solution and anodically treating the immersed article by passing a direct current through said article at a current density of about 7 to 15 amperes per square inch for from 20 to 30 seconds, discontinuing the anodic treatment and, while said article is still immersed in said solution depositing a non-porous coating of zinc on said article for at least one second and subsequently electrodepositing a silver plate over said zinc coating from a silver plating bath essentially composed of an aqueous solution of silver cyanide and sodium cyanide.

14. The method of claim 13, wherein the zinc coating is galvanically deposited on said aluminum article for from one to about ninety seconds.

15. The method of silver plating an aluminum article which comprises immersing said article in hot electrolyte comprising an aqueous solution containing from 4 to 30 ounces of zinc cyanide, 4 to 20 ounces of sodium cyanide, 13 to 19 ounces sodium hydroxide, 0.1 to 8 ounces sodium thiosulfate, 0.1 to 0.7 sodium sulfide and 0.1 to 6 ounces sodium carbonate per gallon of solution, anodically treating the immersed article by passing a direct current through said article at a current density of about 7 to 15 amperes per square inch for from 20 to 30 seconds, discontinuing the anodic treatment and, while said article is still immersed in said solution depositing a non-porous coating of zinc on said article for at least one second and subsequently electrodepositing a silver plate of said zinc coating from a silver plate bath essentially composed of an aqueous solution of silver cyanide and sodium cyanide.

16. The method of claim 15 wherein the zinc coating is galvanically deposited on said aluminum article for from one to about ninety seconds.

17. The method of silver plating an luminum article which comprises immersing said article in a hot electrolyte comprising an aqueous solution containing from 4 to 30 ounces of zinc cyanide, 4 to 20 ounces of sodium cyanide, 13 to 20 ounces sodium hydroxide, 0.1 to 8 ounces sodium thiosulfate, 0.01 to 0.07 ounce silver cyanide, 0.01 to 0.07 ounce sodium sulfide and 0.1 to 6 ounces sodium carbonate per gallon of solution, anodically treating the immersed article by passing a direct current through said article at a current density of about 7 to 15 amperes per square inch for from 20 to 30 seconds, discontinuing the anodic treatment, and, while said article is still immersed in said solution depositing a non-porous coating of zinc on said article for at least one second and subsequently electrodepositing a silver plate of said zinc coating from a silver plating bath essentially composed of an aqueous solution of silver cyanide and sodium cyanide.

18. The method of claim 17 wherein the zinc coating is galvanically deposited on said aluminum article for from one to about ninety seconds.

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