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**METHODS OF ELECTROPLATING ALUMINUM
AND ALLOYS THEREOF****Thomas J. Connor, Penn Wynne, Pa., assignor to Gen-
eral Electric Company, a corporation of New York****No Drawing. Filed June 4, 1958, Ser. No. 739,680****15 Claims. (Cl. 204—33)**

This invention relates to methods for electroplating aluminum and alloys thereof. More particularly, it relates to improved methods for providing articles of aluminum and alloys thereof with a firm, dense, non-porous zinc coating which serves as a firmly adhering base for metal deposited on said articles. While the examples herein are directed to the electrodeposition of silver on aluminum or aluminum alloy articles prepared as described herein, it will be appreciated that the invention applies as well to the deposition of other metals including brass, copper, cadmium, tin, and combinations thereof among others.

A number of plating processes are known for the deposition of 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 final 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. This is commonly known as the zinc immersion process. The zinc coating, as a base for the ultimate silver plate, has been found to be necessary 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. 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, causes 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.

It has also been found that while particular zincate baths as developed heretofore are suitable for pure aluminum or particular aluminum alloys, they are specialized in that such factors as the type of alloy treated is generally limited and that treating parameters such as temperatures, times, current densities and solution compositions must be kept under close control.

A principal object of this invention is to provide improved means for electroplating metals on aluminum and its alloys and for preparing the basis metal for the reception of the plated metal.

Briefly, by the present invention, there are provided improved processes for electroplating aluminum and various alloys thereof in which there is provided a dense,

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firm, thin, zinc coating on the basis metal which serves as an adherent substrate for the subsequently deposited metal.

Those features of the invention which are believed to be novel are specifically pointed out in the claims appended hereto. The invention will, however, be better understood and other advantages and benefits thereof appreciated from a consideration of the following description. It will be understood that wherever the term "aluminum" is used, its alloys, such as those mentioned herein, are included.

According to one aspect of the present process, the aluminum containing article to be plated is first cleaned or etched in an alkaline bath, which is heated to about 160° F. and rinsed. It is then immersed in a modified zinc cyanide solution, preferably at a temperature of from about 70° F. to 90° F. for a short period of time, during which time, the water from the rinse is dissipated, the solution etches the article slightly and a thin, superficial displacement zinc coating is deposited thereon. Typically, a suitable displacement coating is of the order of 0.000015 mil thick and ranges from about 0.00001 to 0.001 mil. Generally, this action takes place in any time over 1 second to times up to 15 seconds or more which have been found suitable although much longer times can be used if desired. For example, times of from 6 to 10 seconds have been found suitable at a bath temperature of 75° F. At higher bath temperatures, shorter times can be used. Articles of aluminum alloy such as 2024 containing appreciable copper are advantageously treated after the first alkaline cleaning to an acid dip for several minutes.

While the article is still immersed in the modified zinc cyanide solution, direct electric current is passed there-through with the article being made the cathode, and thereby an additional thin, dense electrodeposit of zinc is applied to the article. This layer of zinc ranges typically from about 0.00008 to 0.03 mil thick with a normal coating being of the order of 0.003 mil. The current density is found to be advantageously varied from several amperes per square foot to over, or the order of, 1500 amperes per square foot. At the higher current densities, a shorter time of deposition is required to provide a dense, thin deposit, while at lower current densities a longer time is required. Generally, per square foot of article or cathode, the current time limits are from about 10 ampere seconds to about 15,000 ampere seconds, it being realized, of course, that this depends upon the particular solution composition, bath temperature, agitation and the cathode current density employed. Generally speaking, above 15,000 ampere seconds per square foot, adhesion becomes spotty with gentle agitation. Even though up to 150,000 ampere seconds may be used with high agitation, the results tend to be erratic.

The following examples will illustrate the practice of the invention, it being realized that such examples are illustrative rather than limiting of the invention.

Example 1

Aluminum articles of pure E.C. aluminum and alloys 1100 and 6061 were cleaned in a bath containing, by weight, per gallon of water solution, 10 ounces of sodium hydroxide and 10 ounces Rochelle salt or potassium sodium tartrate, the bath being maintained at 160° F. for about 30 to 120 seconds. The sodium hydroxide, of course, serves to clean and etch the surface of the article and dissolve or remove the oxide film therefrom. The Rochelle salt serves to keep in solution any alloy constituents such as magnesium and manganese which would otherwise form gel-like hydroxides which would adhere to the article and prevent adequate cleaning and satis-

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factory subsequent treating. The articles were next removed from the cleaning bath and rinsed in cold water. They were then immersed in a bath having the following composition.

	Optimum Concentration (Ounces per Gallon)	Preferred Range (Ounces per Gallon)
Zinc Cyanide.....	10	1 to 30
Sodium Cyanide.....	8.5	4 to 54
Sodium Hydroxide.....	10	5 to 20
Sodium Sulfide.....	0.05	0.01 to 0.07
Operating Temperature.....	75° F.	50 to 120° F.

The articles were allowed to remain in the bath for 10 seconds during which time a thin, adhesive, dense coating of zinc was acquired by the article. Following this, the articles were made the cathode while current was passed through the solution and an additional thin electro-deposit of zinc was applied for a period of about 6 seconds. The aluminum articles were exposed during the 6-second period in such manner as to provide a range of current density varying from about 2 amperes per square foot to about 500 amperes per square foot, it being realized that higher current densities can be used with a corresponding reduction in plating time as is well known to those skilled in the art. The articles were next rinsed in cold water. 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 12 ounces silver cyanide, 18 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 0.5 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 free 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 nonporous 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

Aluminum articles comprising E.C. aluminum and aluminum alloys 6061, 6063, 7075, 3003, 2024 and 2014 were etched in a caustic solution similar to that of Example 1, except that the Rochelle salt was omitted. This treatment was followed by a dip in a solution of one volume of concentrated nitric acid and one volume of

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water for about 5 seconds. The articles were then immersed in a bath having the following composition.

	Optimum Concentration (Ounces per Gallon)	Preferred Range (Ounces per Gallon)
Zinc Cyanide.....	10	1 to 30
Sodium Cyanide.....	8.5	4 to 54
Sodium Hydroxide.....	10	5 to 20
Sodium Carbonate.....	6	0.1 to 12
Sodium Sulfide.....	0.05	0.01 to 0.07
Temperature.....	75° F.	50 to 120° F.

The time of treatment and current densities in this example were the same as Example 1, and the silver plate was plated thereon in a similar manner.

Example 3

Aluminum articles of E.C. aluminum and alloy 6101, 6063, 7075, 3003, 2024, 2014, 355, 356 and 380 were processed similarly as in Example 1 except that again the Rochelle salts were eliminated in the preliminary cleaning or etching solution, and this was followed by a dip in one volume of 48% hydrofluoric acid, four volumes of concentrated nitric acid and five volumes of water. The articles were then rinsed and immersed in a bath having the following composition.

	Optimum Concentration (Ounces per Gallon)	Preferred Range (Ounces per Gallon)
Zinc Cyanide.....	10	1 to 30
Sodium Cyanide.....	8.5	4 to 54
Sodium Hydroxide.....	10	5 to 20
Sodium Carbonate.....	6	0.1 to 12
Sodium Potassium Tartrate.....	8	4 to 12
Silver Cyanide.....	0.03	0.001 to 0.1
Sodium Sulfide.....	0.05	0.01 to 0.07
Polyvinyl Alcohol.....	0.15	0.01 to 0.4
Temperature.....	75° F.	50 to 120° F.

Again, the times of treatment and current densities were the same as those in Example 1 above.

The sodium cyanide and sodium hydroxide in the bath or water solution serve as solvents for the zinc cyanide which the latter in turn serves to provide the zinc ion which is deposited as zinc metal. The sodium cyanide and sodium hydroxide also serve to control the degree of ionization of zinc. Sodium hydroxide, and, to some extent, sodium cyanide provide proper pH conditions of the cathode film on the aluminum during the zinc displacement step and during electrodeposition of the zinc. For any particular concentration of zinc cyanide, there should preferably be a suitable corresponding amount of sodium cyanide and sodium hydroxide. The ratio of zinc cyanide to sodium cyanide may vary with the concentration. For example, with concentrations of zinc around 1 ounce per gallon, the ratio of zinc cyanide to sodium cyanide should be of the order of 1 to 3.8, lower concentrations requiring higher ratios. At 0.5 and 0.25 ounce of zinc cyanide per gallon, the required ratios of zinc cyanide to sodium cyanide for best results are of the order of 1 to 4 and 1 to 5, respectively. At high concentrations, the ratio may range from 1 to 0, and as high as 1 to 3.1. If, in the bath, the concentration of sodium cyanide is less than the stoichiometric amount required to dissolve the zinc cyanide, sufficient sodium hydroxide is necessary to complete the solution. Generally speaking, below about 4 ounces of zinc cyanide per gallon chemical creates control problems and operating sensitivity increases inversely proportional to the concentration. Above 5 ounces per gallon of zinc cyanide, the choice of bath concentration largely becomes a matter of economics, though, of course, such higher concentrations can be used. Some sodium hydroxide is required in the bath. When the proper zinc cyanide-sodium cyanide ratio is used, the amount of sodium hydroxide

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can vary over wide limits. For example, with the zinc cyanide concentration as low as 0.25 ounce per gallon, the sodium hydroxide may be as low as 2 ounces per gallon. Higher concentrations of sodium hydroxide are preferable for higher zinc cyanide concentrations and the desired range lies between 4 and 10 ounces per gallon. Higher concentrations than 10 ounces per gallon, of course, may be used although no significant advantages appear to be obtained. It will be realized that other alkali metals may be used in lieu of sodium in the bath compounds.

The Rochelle salt, in general, where used, serves to aid, as pointed out above, in the removal of insoluble compounds like magnesium and manganese hydroxide. Under many conditions, the zinc electrolyte will function satisfactorily without it, but it is useful again, as pointed out above, for alloys having a rather large concentration of elements which are insoluble in sodium hydroxide. The sodium carbonate in the bath helps to stabilize the pH of the bath and aids in producing uniformly bright deposits of good texture. Under many conditions, this salt is not essential but to some degree it does improve the quality of the electrodeposited zinc coating. In many cases, sodium carbonate is produced in the bath by reaction with carbon dioxide in the air. The sodium sulfide serves in the role of a bath purifier precipitating lead, cadmium and other sulfides which are insoluble in cyanide solutions. Such metals in sufficient quantity would reduce the brightness of the zinc coating. However, if the chemicals originally used in the bath are of suitable purity, the sodium sulfide may be omitted. The brightener or polyvinyl alcohol used generally improves the brightness, density and tensile strength of the zinc coating and provides for better over-all bonding.

By this invention, there are provided improved processes for electroplating aluminum and alloys thereof. Using such processes, wide ranges of aluminum alloys can be treated under relatively flexible conditions such as time, current density, temperature and solution composition.

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

1. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide and alkali potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution of zinc cyanide, alkali cyanide, alkali hydroxide and alkali sulfide until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath with the article as the cathode at current densities up to the order of 1500 amperes per square foot at temperatures ranging from about 50° F. to 120° F. until a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc coated article.

2. The method of claim 1 in which the electrolyte bath contains about from 1 to 30 ounces zinc cyanide, 4 to 54 ounces alkali cyanide, 5 to 20 ounces alkali hydroxide and 0.01 to 0.07 ounce alkali sulfide per gallon of electrolyte.

3. The method of claim 2 wherein the electrolyte also contains from 0.1 to 12 ounces of alkali carbonate per gallon of electrolyte.

4. The method of claim 2 wherein the electrolyte also contains from 0.1 to 12 ounces alkali carbonate, from 4 to 12 ounces sodium potassium tartrate, from 0.001 to 0.1 ounce silver cyanide and 0.01 to 0.4 ounce polyvinyl alcohol per gallon of electrolyte.

5. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide

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and alkali potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution of zinc cyanide, alkali cyanide, alkali hydroxide and alkali sulfide until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature of from about 50° F. to about 120° F. with the article as the cathode in the amount of from about 10 to 15,000 ampere-seconds per square foot whereby a thin electrodeposit of zinc is applied thereon, and (5) electrodepositing a metal coating on said zinc coated article.

6. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide and sodium potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution of zinc cyanide, alkali cyanide, and alkali hydroxide until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at 50° F. to 120° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot whereby a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc coated article.

7. The method of claim 1 wherein said article after step 1 is treated in an acid bath.

8. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide and sodium potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution containing by weight per gallon of solution about 10 ounces zinc cyanide, 8.5 ounces alkali cyanide, 10 ounces alkali hydroxide, 6 ounces alkali carbonate and 0.05 ounce alkali sulfide until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature of from about 70° F. to 90° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot until a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc coated article.

9. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide and alkali potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution containing by weight per gallon of solution about 10 ounces zinc cyanide, 8.5 ounces alkali cyanide, 10 ounces alkali hydroxide, 6 ounces alkali carbonate, 8 ounces Rochelle salt, 0.03 ounce silver cyanide, 0.05 ounce alkali sulfide and 0.15 ounce polyvinyl alcohol until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature of from about 70° F. to 90° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot whereby a thin electrodeposit of zinc is applied thereto and (5) electrodepositing a metal coating on said zinc coated article.

10. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide and alkali potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution containing by weight per gallon of solution about

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10 ounces zinc cyanide, 8.5 ounces alkali cyanide, 10 ounces alkali hydroxide and 0.05 ounce alkali sulfide until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature of about 70° F. to about 90° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot until a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc coated article.

11. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum article in a hot bath containing alkali hydroxide and sodium potassium tartrate, (2) removing said article from said bath and rinsing said article, (3) immersing said article in a bath comprising an aqueous solution containing by weight per gallon of solution from about 0.25 to 40 ounces of zinc cyanide, from 1.3 ounce up to the saturation amount of alkali cyanide, and from 2.5 ounces to the saturation amount of alkali hydroxide, until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature from about 50° F. to 120° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot until a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc-coated article.

12. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide, (2) treating said article with an acid dip, (3) rinsing said article, (4) immersing said article in a bath comprising an aqueous solution of zinc cyanide, alkali cyanide, alkali hydroxide, and alkali sulfide, until a thin displacement coating of zinc is deposited thereon, (5) passing a direct electric current through said bath at a temperature of from about 50° F. to 120° F. with the

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article as the cathode at current densities up to the order of 1500 amperes per square foot until a thin electrodeposit of zinc is applied thereto, and (6) electrodepositing a metal coating on said zinc-coated article.

13. The method of claim 12 in which the electrolyte bath contains from about 1 to 30 ounces of zinc cyanide, 4 to 54 ounces alkali cyanide, 5 to 20 ounces alkali hydroxide, and 0.01 to 0.07 ounce alkali sulfide per gallon of electrolyte.

14. The method of preparing an aluminum containing article for the application thereon of an electroplated metal coating which comprises (1) immersing said aluminum base article in a hot bath containing alkali hydroxide, (2) treating said article with an acid dip, (3) immersing said article in a bath comprising an aqueous solution of zinc cyanide, alkali cyanide, alkali hydroxide, and alkali sulfide, until a thin displacement coating of zinc is deposited thereon, (4) passing a direct electric current through said bath at a temperature of 50° F. to 120° F. with the article as the cathode at current densities up to the order of 1500 amperes per square foot until a thin electrodeposit of zinc is applied thereto, and (5) electrodepositing a metal coating on said zinc-coated article.

15. The method of claim 14 in which the electrolyte bath contains from about 1 to 30 ounces of zinc cyanide, 4 to 54 ounces alkali cyanide, 5 to 20 ounces alkali hydroxide, and 0.01 to 0.07 ounce alkali sulfide per gallon of electrolyte.

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