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METHOD AND COMPOSITIONS FOR ZINC COATING ALUMINUM

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17 Claims. (Cl. 117—130)

This application is a continuation-in-part of our co-pending application Serial No. 124,375 filed July 17, 1961, now abandoned.

This invention relates to metal coating and more particularly to a method for applying zinc to aluminum and its alloys as a base for subsequently electroplating metals, and compositions useful in such method. The term "aluminum" as used herein is intended to include also alloys of aluminum.

Electroplating aluminum has in the past been difficult because of the natural oxide coating which is irregular and nonconducting and the fact that aluminum has such a high electro potential that a perfectly clean aluminum surface would dissolve in the conventional copper plating solutions. Under these conditions aluminum metal dissolves at the same time that copper (or other metal) is deposited on to the aluminum surface. This results in a loose, non-adherent coating. Many efforts have been made to obviate these difficulties. One of the experimenters in this field was E. H. Hewitson whose method described in United States Patent 1,627,900 was somewhat of an improvement over prior methods but still in commercial practice produced blistering and poor adhesion of the final plating over the zinc coating. Another solution was to anodize the aluminum surface in a phosphoric acid electrolyte. The resulting coating was adherent and uniform but porous and costly. The commercial disadvantages of this process were that the anodizing step was costly; that different anodizing conditions were necessary for various aluminum alloys; that pure aluminum was difficult to plate, evidently because metallic impurities are necessary to conduct a current through the oxide layer; the anodized surface was characterized by high resistance and a resulting low current density in the cavities or in the center of large objects which in turn resulted in uneven plating thickness.

Another attempted solution to the problem was known as the Vogt process which involved heat treating, much manual labor and was not adaptable to automatic plating machines.

Aluminum electroplating is commonly carried out today by the zinc immersion process, the first step of which is the solution of the aluminum oxide layer from the aluminum according to the equation:

(1) $Al_2O_3.H_2O+2NaOH\rightarrow 2NaH_2AlO_3$ aq.

The aluminum surface is then in equilibrium with the hydrated aluminate ions according to the equation:

(2) $Al+4OH^-\rightleftarrows H_2AlO_3^-+3e^-+H_2O$

The standard oxidation potential of this equilibrium as stated by W. M. Latimer in "Oxidation Potentials," on page 264 is—E=2.35 volts. There are several factors which influence this potential. The actual half cell potential of the aluminum surface in contact with the alkaline solution is dependent upon the activity of the OH^- ion, the activity of the $H_2AlO_3^-$ ion, the concentration of the water and the composition of the surface of the aluminum alloy. Furthermore, there may be local differences in concentrations of the aluminate ion and therefore local differences in actual voltage between the zinc ions in the sodium zincate solution and the aluminum surface because of the fact that the oxide layer on aluminum and its alloys is often irregular in thickness and composition. As a result, the zinc deposit is irregular and blisters occur in the subsequently deposited metal.

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The second step in the process is the galvanic reduction of the zinc ion. The standard half cell reaction is:

(3) $Zn(OH)_4^=+2e\rightleftarrows Zn+4OH^-$
$E_o=-1.21$ volts

Of course, in combining Equation 2 and Equation 3 the completed potential would still be dependent upon the activities of the ions involved. The complete reaction may be described by equation:

(4) $2Al+3Zn(OH)_4^=\rightarrow 3Zn+2H_2AlO_3^-+4OH^-+2H_2O$

The standard potential for this reaction is 2.35 volts -1.21 volts$=1.14$ volts. In actual practice the potential difference between the aluminum and zinc must be less than the standard potential difference. It has been found that a potential difference between aluminum metal and zinc ions of .013 volt after 20 seconds immersion gave the best results in an aqueous solution of 500 g./l. NaOH and 100 g./l. ZnO.

According to the present invention the addition of small amounts of an alkali metal gluconate or heptagluconate such as sodium gluconate, or sodium heptagluconate, greatly increases the quality of the zinc coating produced by immersion and the subsequent metal coating.

Zincate baths suitable for use in this invention can have the following composition with water being used to form the bath solution:

Ingredient:	Grams per liter of bath solution
Alkali metal gluconate or heptagluconate	1 to 200
Zinc oxide	10 to 200
Alkali metal hydroxide	100 to 700

The alkali metal gluconate or heptagluconate is advisably used in the bath in the range of 5 to 25 gm./liter of aqueous bath solution with the desired operating concentration being about 10 gm./liter. All amounts of ingredients specified herein as well as in the claims unless otherwise stated are per liter of solution and not amounts added to a liter of water.

Sodium gluconate, potassium gluconate, sodium heptagluconate and potassium heptagluconate are specific materials which can be used in the baths.

Sodium hydroxide and potassium hydroxide are the alkali metal hydroxides most suitable for use in the baths.

The baths can be readily prepared by combining the ingredients in water. It is sometimes desirable to add the zinc oxide, which is insoluble in water, to an aqueous alkali metal hydroxide solution in which it is soluble. The alkali metal gluconate or alkali metal heptagluconate usually can be dissolved either before or after the other ingredients.

The zincate bath can be prepared by the plater. However, some platers would prefer to be supplied with the bath already formulated with a specified composition ready for use, or a concentrated bath which can be diluted as desired. Such liquid compositions can be readily

shipped, such as in drums, carboys, or in tank cars or trucks.

In order to facilitate some aluminum platers' operation it is considered advisable to provide various dry premix compositions for their use. One particular composition which facilitates the zinc coating operation is a dry composition comprising an admixture of an alkali metal hydroxide, zinc oxide and an alkali metal gluconate or heptagluconate. Such a composition can have the following ranges of ingredients:

DRY PARTICULATE COMPOSITION

Ingredient:	Parts by weight
Alkali metal hydroxide	100 to 700
Zinc oxide	10 to 20
Alkali metal gluconate or heptagluconate	1 to 200

Such compositions are readily prepared by thoroughly mixing together the specified materials until a uniform heterogenous particulate mixture is obtained. Such compositions are convenient for packing, shipping and use and assure proper ratios of each of the ingredients being used. Zincate baths are prepared by combining such compositions with water in the proper amount.

A specific dry particulate composition could contain a ratio of 2 parts by weight of sodium gluconate, 18 parts by weight of zinc oxide and 80 parts by weight of sodium hydroxide. From about 2 to 7 pounds of such a dry composition can be dissolved in water to make a gallon of zincate bath solution.

Commercial compositions can also be made by combining the zinc oxide and alkali metal gluconate or heptagluconate without including the alkali metal hydroxide. Such compositions are useful in adjusting the make-up of the zincate bath apart from the necessary addition of the alkali metal hydroxide and this flexibility is desired on occasion by the aluminum platers. Such dry particulate compositions can contain the following ranges of ingredients:

DRY PARTICULATE COMPOSITION

Ingredient:	Parts by weight
Zinc oxide	10 to 20
Alkali metal gluconate or heptagluconate	1 to 200

Specific compositions can contain a ratio of one part by weight of sodium gluconate or heptagluconate in intimate admixture with 10 parts by weight of zinc oxide.

The zincate baths are advisably used at a temperature of about 60 to 120° F. to effect forming the zinc coating. Immersion of the aluminum in the zincate bath for about 5 seconds or longer gives a useful application of zinc. There is usually no need for the immersion to continue longer than 5 minutes. Also, the necessary immersion time diminishes as the temperature increases. Generally, however, the immersion time is about 15 seconds to about two minutes.

It is, of course, clear that one can use gluconic acid or heptagluconic acid instead of the alkali metal salts thereof in the dry compositions disclosed above or in the preparation of the zincate baths because these acids would be converted to the salts immediately upon contact with an aqueous alkali metal hydroxide solution. These acids and their salts are considered equivalents which can be used interchangeably in this invention.

Panels of aluminum alloy were processed as follows:

Example I

(1) Cleaned in a solution containing soda ash, trisodium phosphate, caustic soda, tetrasodium pyrophosphate and a suitable wetting agent such as alkyl aryl sulfonate.

(2) Rinsed.

(3) Pickled in commercial nitric acid 50% by volume of 42° Bé. at 80° F.

(4) Rinsed.

(5) Dipped in an aqueous sodium zincate bath one minute at 75° F. The bath solution consisted of water and:

	g./l.
Sodium hydroxide	500
Zinc oxide	100
Sodium gluconate	10

(6) Rinsed.

(7) Copper plated in the following aqueous solution for a period of one minute:

Copper cyanide	oz./gal.	5.5
Rochelle salt	oz./gal.	8.0
Sodium cyanide	oz./gal.	6.8
Sodium carbonate	oz./gal.	4.0
Sodium bicarbonate	oz./gal.	0.2
pH		10.2
Temperature	°F.	128
Current density	amps./sq. ft.	22

(8) Rinsed and dried with a stream of dry air.

The aluminum alloy panels were tested for adherence and blistering by subjecting them to extreme temperature change. The panels were first heated to 500° F. in liquid polyethylene glycol for a period for two minutes and then plunged into cold water. The panels were then rinsed, dried and examined for blisters. The plating was found to be adherent and free from blisters.

The copper cyanide electroplating bath of step 7 may be followed by suitable electroplating baths for cadmium, nickel, silver, zinc, tin or iron.

Example II

The same procedure as in Example I was carried out with the exception that the sodium gluconate was omitted from the bath of step 5. The result was that numerous blisters were found in the copper plate and the panel was unsuitable for further electro-deposition.

Example III

The same procedure was carried out as in Example I except that the aqueous sodium zincate bath of step 5 consisted of:

Sodium hydroxide	g./l.	375
Zinc oxide	g./l.	70
Sodium gluconate	g./l.	10

No blisters were found after testing as set forth in Example I.

Example IV

The same procedure as in Example III was carried out with the exception that the sodium gluconate was omitted in the aqueous sodium zincate bath and the electroplated panel had blisters after the temperature change test.

Example V

The same procedure as in Example I was carried out with the exception that the following bath was used in lieu of the bath in step 5 of Example I:

Zinc oxide	g./l.	100
Sodium hydroxide	g./l.	500
Copper cyanide	g./l.	2
Sodium cyanide	g./l.	4
Sodium gluconate	g./l.	5

No blisters were found after the temperature change test.

Example VI

The same procedure was carried out as in Example V with the exception that the sodium gluconate was omitted and blisters were found on the copper plated coating after the temperature change test.

Example VII

The same procedure was carried out as in Example I with the exception that the bath in step 5 consisted of:

Zinc oxide ----------g./l..	100
Sodium hydroxide ----------g./l..	525

Blisters were found after the temperature change test.

Example VIII

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	100
Sodium hydroxide ----------g./l..	525
Potassium gluconate ----------g./l..	5

No blisters were found after the temperature change test.

Example IX

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	50
Sodium hydroxide ----------g./l..	250

Blisters were found after the temperature change test.

Example X

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	50
Potassium hydroxide ----------g./l..	300

Blisters were found after the temperature change test.

Example XI

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	50
Potassium hydroxide ----------g./l..	300
Potassium gulconate ----------g./l..	20

No blisters were found after the temperature change test.

Example XII

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	50
Sodium hydroxide ----------g./l..	300

Blisters were found after the temperature change test.

Example XIII

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	50
Sodium hydroxide ----------g./l..	300
Sodium gluconate ----------g./l..	100

No blisters were found after the temperature change test.

Example XIV

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	100
Sodium hydroxide ----------g./l..	500
Gluconic acid ----------g./l..	20

No blisters were found after the temperature change test.

Example XV

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	100
Sodium hydroxide ----------g./l..	525
Sodium gulconate ----------g./l..	2

No blisters were found after the temperature change test.

Example XVI

The same procedure was carried out as in Example I with the exception that instead of the zincate bath of step 5 the following solution was used:

Zinc oxide ----------g./l..	60
Sodium hydroxide ----------g./l..	300
Sodium gluconate ----------g./l..	10

No blisters were found after the temperature change test.

All of the zincate baths described in these examples can be prepared by adding a dry particulate mixture containing the ingredients in the same ratio as specified in the examples to water to make a solution of the stated concentration. Similarly, a premix of the zinc oxide and alkali metal gluconate or heptagluconate can be prepared having the stated amounts of each material and such a premix then added to water followed by the base, or to water already containing the alkali metal hydroxide.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

What is claimed is:

1. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 100 to 700 gm./liter of an alkali metal hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates, at 60 to 120° F. for a time of at least 5 seconds and sufficient to apply an appreciable zinc coating on the aluminum.

2. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 100 to 700 gm./liter of sodium hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of sodium gluconate, at 60 to 120° F. for a time of at least 5 seconds and sufficient to apply an appreciable zinc coating on the aluminum.

3. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 100 to 700 gm./liter of potassium hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of potassium gluconate, at 60 to 120° F. for a time of at least 5 seconds and sufficient to apply an appreciable zinc coating on the aluminum.

4. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 100 to 700 gm./liter of an alkali metal hydroxide, 10 to 200 gm./liter of zinc oxide and 5 to 25 gm./liter of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates, at 60 to 120° F. for a time of at least 5 seconds and sufficient to apply an appreciable zinc coating on the aluminum.

5. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 100 to 700 gm./liter of an alkali metal hydroxide, 10 to 200 gm./liter of zinc oxide and

1 to 200 gm./liter of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates at 60 to 120° F. for about 15 seconds to about 5 minutes.

6. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 375 gm./liter of sodium hydroxide, 100 gm./liter of zinc oxide and 10 gm./liter of sodium gluconate at 60 to 120° F. for about 15 seconds to 5 minutes.

7. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting af water, 375 gm./liter of sodium hydroxide, 70 gm./liter of zinc oxide and 10 gm./liter of sodium gluconate at 60 to 120° F. for about 15 seconds to 5 minutes.

8. A method of applying zinc to aluminum, including alloys thereof, for subsequently electroplating metals thereon which comprises immersing the aluminum in a bath consisting of water, 525 gm./liter of sodium hydroxide, 100 gm./liter of zinc oxide and 5 gm./liter potassium gluconate at 60 to 120° F. for about 15 seconds to 5 minutes.

9. A solution comprising water, 100 to 700 gm./liter of an alkali metal hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates.

10. A solution comprising water, 100 to 700 gm./liter of sodium hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of sodium gluconate.

11. A solution comprising water, 100 to 700 gm./liter of potassium hydroxide, 10 to 200 gm./liter of zinc oxide and 1 to 200 gm./liter of potassium gluconate.

12. A dry particulate composition consisting essentially of a ratio of 100 to 700 parts by weight of an alkali metal hydroxide, 10 to 20 parts by weight of zinc oxide and 1 to 200 parts by weight of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates.

13. A dry particulate composition consisting essentially of a ratio of 100 to 700 parts by weight of sodium hydroxide, 10 to 20 parts by weight of zince oxide and 1 to 200 parts by weight of sodium gluconate.

14. A dry particulate composition consisting essentially of a ratio of 10 to 20 parts by weight of zinc oxide and 1 to 200 parts by weight of a member of the group consisting of alkali metal gluconates and alkali metal heptagluconates.

15. A dry particulate composition consisting essentially of a ratio of 10 to 20 parts by weight of zinc oxide and 1 to 200 parts by weight of sodium gluconate.

16. A dry particulate composition consisting essentially of a ratio of 100 to 700 parts by weight of sodium hydroxide, 10 to 20 parts by weight of zinc oxide and 1 to 200 parts by weight of potassium gluconate.

17. A dry particulate composition consisting essentially of a ratio of 10 to 20 parts by weight of zinc oxide and 1 to 200 parts by weight of potassium heptagluconate.

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RICHARD D. NEVIUS, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,235,404 February 15, 1966

Floyd Mickelson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 44, for "gulconate" read -- gluconate --; column 7, line 8, for "375" read -- 500 --; line 15, for "af" read -- of --; column 8, line 9, for "zince" read -- zinc --.

Signed and sealed this 31st day of January 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents