United States Patent [19]

Nobel et al.

[11] 3,869,358

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[54] **ELECTROLYTES FOR THE ELECTROLYTIC DEPOSITION OF ZINC**

[75] Inventors: **Fred I. Nobel; Barnet D. Ostrow,** both of Roslyn, N.Y.

[73] Assignee: **Lea-Ronal, Inc.,** Freeport, N.Y.

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[21] Appl. No.: **412,817**

Related U.S. Application Data

[63] Continuation of Ser. No. 268,920, July 3, 1972, abandoned, which is a continuation-in-part of Ser. No. 17,302, March 6, 1970, abandoned, which is a continuation-in-part of Ser. No. 640,339, May 22, 1967, abandoned.

[52] **U.S. Cl.** ..... **204/55 Y,** 204/DIG. 2, 204/55 R

[51] **Int. Cl.** **C23b/5/10,** C23b 5/46

[58] **Field of Search** ..... 204/55 R, 55 Y, 43 Z, 44, 204/114; 106/1

[56] **References Cited**

UNITED STATES PATENTS

2,451,426	10/1948	Bair et al.	204/55 Y
2,791,554	5/1957	Winters	204/55 Y
3,227,638	1/1966	Burnson	204/55 Y
3,317,412	5/1967	Dahlmann	204/55 R

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Pennie & Edmonds

[57] **ABSTRACT**

An aqueous alkaline zinc bath is used for electroplating bright metallic zinc deposits on metal substrates said plating bath containing less than about 2 oz./gal. of cyanide therein, and comprising an aqueous alkaline solution having dissolved therein a soluble zinc compound capable of being plated by electrolytic deposition and a water soluble reaction product of an amine and an epihalohydrin containing recurring tertiary and/or quaternary amine groups and having a molecular weight above about 250 in an amount from at least about 0.1 gm./liter.

10 Claims, No Drawings

ELECTROLYTES FOR THE ELECTROLYTIC DEPOSITION OF ZINC

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of Ser. No. 268,920, filed July 3, 1972 which in turn was a continuation-in-part of Ser. No. 17,302, filed Mar. 6, 1970 which was a continuation-in-part of Ser. No. 640,339, filed May 22, 1967, all now abandoned.

BACKGROUND OF THE INVENTION

The field of this invention relates to electrolyte solutions or baths useful for the electrolytic deposition of metallic zinc on various substrates well known in the art of the electrolytic deposition of zinc.

The major portion of zinc plating is done today from alkaline solutions containing a soluble zinc compound and substantial quantities of sodium cyanide. This sodium cyanide solution plates zinc that is semi-bright, and in order to obtain bright zinc deposits, a large variety of brighteners are added to the plating solutions. These brighteners are well known in the art and include a wide variety of compounds, such as aldehydes, ketones, thiourea, organic acid salts, and so forth.

These cyanide-containing baths are obviously objectionable due to the poisonous nature of the cyanides and present serious problems of disposal, particularly since waste disposal has become and important national problem in this country and elsewhere.

As a result of the waste disposal problem with the cyanide baths, much effort has been put into development of cyanide-free electrolytes which will eliminate this serious waste disposal problem.

Some cyanide-free or substantially cyanide-free zinc plating baths are in existence today, and most of these baths appear to be based on a solution of sodium zincate with excess sodium hydroxide. High pH alkali zincate baths when used without brightening or addition agents yield deposits that are dull, spongy and of poor appearance. It has been proposed to overcome these deficiencies by adding glycolates to increase smoothness of deposits but commercially acceptable bright plates were not obtainable. It has also been proposed to add, to the high pH zincate baths, alkanol amines either alone or in conjunction with aldehydes to brighten the deposit. Baths of the latter type were not sufficiently stable, did not produce commercially acceptable bright deposits, and the plating range over which these fairly bright deposits were obtained was not commercially competitive with presently developed bright cyanide baths. It has further been proposed to incorporate in the high pH zincate baths alkylene amines such as ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine, either alone or in conjunction with an aldehyde compound. The latter baths although producing bright deposits and being comparatively more stable than previous baths, nevertheless has the serious short-coming of a very narrow bright plating range as well as poor throwing power. These factors made such baths commercially unacceptable according to today's requirements.

In most cases, production experience has indicated that even these so-called cyanide-free solutions or baths require small quantities of sodium cyanide to make them commercially operative, particularly with respect to bright deposits according to today's requirements.

Epichlorohydrin-amine reaction products have previously been disclosed as being useful in aqueous zinc cyanide electroplating baths, but not to applicants' knowledge in cyanide free or substantially cyanide free zinc plating baths. The Winters' U.S. Pat. No. 2,791,554, for example, discloses the use of epichlorohydrin reaction products with ammonia or primary amines in conventional zinc cyanide baths using 10 to 12 ounces/gallon of zinc cyanide. Although epichlorohydrin-primary amine reaction products, containing recurring primary amine groups, have been used in zinc cyanide baths, they are not good enough to meet today's standards for non-cyanide or low cyanide zinc baths with respect to throwing power, current density and brightness and of course cannot aid in solving the pollution problems because of the presence of the cyanide. In addition, the ethylene diamineepichlorohydrin reaction product produced according to the Example beginning at line 68, column 2 of the Winters' patent substituting ethylene diamine for the ammonia in the amount specified at lines 49–55, column 3 was prepared and analyzed for amine content according to the well-known method published in *Quantitative Organic Analysis via Functional Groups* by Dr. Sidney Siggia, J. Wiley & Sons Inc. 3rd Edition, page 450, "Determination of Amines in Mixtures: Primary, Secondary and Tertiary Amines via Schiff Base and Acetylation Approach (Siggia, Hanna, Kervenski, Anal. Chem. 22 page 1295 in 1950)". The results showed that the Winters' product contained 13.7 percent primary amine groups, 14.2 percent secondary amine groups, less than 0.5 percent tertiary amine groups, and no quaternary amine group. The figure 0.5 percent for the tertiary amine groups is within experimental error and thus the product can be said to contain no tertiary amine groups for all practical purposes and certainly the tertiary amine groups, if any, are not "recurring" as required according to this invention.

The Burnson U.S. Pat. No. 3,227,638 discloses the use of a cyclic amine, namely, hexamethylenetetramine reacted with epichlorohydrin, again in cyanide electroplating baths. The use of this reaction product in conventional zinc cyanide baths, low cyanide baths (about 2 oz./gal.) or even in cyanide-free baths results in insufficient or poor stability of the bath which is unacceptable to meet today's standards. In addition, the use of large amounts of secondary brighteners are used in low cyanide baths to obtain an acceptable brightness.

SUMMARY OF THE INVENTION

The present invention provides a zinc plating bath which can be completely devoid of cyanide and which is capable of being used in the electrolytic deposition of zinc having a brightness and throwing power close to or better than that which can be obtained from commercial cyanide zinc plating baths. Broadly stated, the plating bath of this invention contains an alkaline soluble zinc compound and a water soluble polyelectrolyte which is the reaction product of an epihalohydrin and an alkylene amine resulting in a plating bath having excellent stability over a long period of time and at the same time producing semi-bright zinc deposits over a wide current density plating range with good throwing power to meet the requirements demanded by the plating industry today.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The alkaline soluble zinc salts which can be used in the plating baths according to this invention can be of any zinc compound soluble in an alkaline medium capable of being plated by electrolytic deposition. Examples of such zinc compounds and salts are well known in the art and include, for example, zinc sulfate, zinc acetate, and zinc oxide. Other alkaline soluble zinc compounds can of course be used, as will be apparent to those skilled in the art.

The amount of zinc metal in the bath is not critical and can be varied, as known in the art, with respect to other known zinc plating baths. Preferably, however, the zinc metal content of the baths of this invention is between about 1 to 4 ounces per gallon.

The zinc metal content can be supplied to the bath by means of a conventional soluble zinc anode or by the use of an insoluble anode and by direct addition of the appropriate alkaline soluble zinc compound to the plating solution.

The alkalinity can be supplied to the aqueous baths by any alkaline material so long as it is capable of dissolving the zinc compound used in the aqueous bath to the desired extent. For example, both sodium hydroxide and potassium hydroxide can be used to supply the alkalinity. Sodium hydroxide is preferable, however, since sodium hydroxide has better solubility with respect to alkali zincates.

The amount of alkaline compound, such as sodium hydroxide, should advantageously be in excess of that required to form the sodium zincate. The amount of excess of free sodium hydroxide is not critical, so long as it is sufficient to keep all the zinc in solution and prevent any precipitation of the zinc from taking place.

The pH of the electrolyte solutions according to this invention can of course be varied to obtain optimum results as will be apparent to those skilled in the art. The pH of the electrolyte solutions of this invention are, however, advantageously maintained at 12 and above.

The polyelectrolytes useful as additives according to this invention for producing bright zinc platings from cyanide-free or substantially cyanide-free electrolytes are water-soluble polycondensates, of an alkylene amine, and an epihalohydrin. The polycondensates are in the form of a polymer containing repeating tertiary and/or quaternary amine groups and have a molecular weight above about 250 but below that which would render the polycondensates water insoluble or insoluble in the electrolyte solution. Advantageously the condensates have a molecular weight above 1000. Polyelectrolytes with molecular weight in the range between 4,000 and 5,000 are particularly advantageous.

Polymeric amines reacted with compounds having functional groups capable of reacting with the amine may also be used as additives according to this invention provided that the polymeric products contain recurring tertiary or quaternary amine units and have a molecular weight in excess of 250, preferably above 1,000.

The water soluble epihalohydrin-alkylene amine polycondensates containing recurring tertiary and/or quaternary groups can be prepared by direct reaction of an epihalohydrin with straight or branched chain alkyl amines and subsequently reacted to form the recurring tertiary and/or quaternary amine groups, such as by a conventional quaternization reaction as set forth in Procedure II below.

Polycondensates containing recurring primary and/or secondary amine groups do not produce the advantageous results of this invention when used in noncyanide or low cyanide zinc plating baths as are obtained by the use of the polycondensates containing recurring tertiary and/or quaternary amine groups and therefore do not meet the zinc plating standards of wide current density ranges, brightness, throwing power, etc. desired by the plating industry today.

The presence of some primary and/or secondary amine groups in the polycondensates used according to this invention is permissible so long as there are a sufficient number of recurring tertiary and/or quaternary amine groups present in the polycondensate to accomplish the objects of this invention. The number or amount of primary or secondary amine groups permissible in the polycondensates will depend upon the particular amine used to form the polycondensate as well as other variables and can be determined by routine experimentation by one skilled in the art. The presence of secondary amine groups are more easily tolerated in the polycondensates than primary amines.

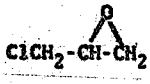
Lower alkyl amines are advantageous for reaction with the epihalohydrin and some examples of amines that can be used according to this invention include trimethyl amine, triethanolamine, dimethyl amino propylamine, diethyl amino propylamine, n-n′ dimethyl amine ethylamine, n-n′ dimethyl n′ methyl propylene diamine, and so forth. For example, the methyl, ethyl and propyl groups can be interchanged in various manners in the above mentioned amines.

Although the polycondensates containing recurring tertiary amines are quite advantageous when used in cyanide free or low cyanide zincate baths, the polycondensates containing quaternary amine groups are particularly advantageous.

The amine group can be quaternized by known processes using known quaternizing agents, such as methyl chloride, methyl sulfate, allyl chloride, benzyl chloride, butene chloride, hexyl chloride and propargyl chloride. Although it is not necessary, if the resulting polymer already contains recurring tertiary and/or quaternary amine groups, it is advantageous to quaternize the amines after reaction with the epihalohydrin by a process such as set forth in Procedure II below.

The polycondensates of this invention containing repeating tertiary or quaternary amine groups can be prepared using primary amines or mono amines in the initial reaction with an epihalohydrin and the resulting polymer further reacted to form the recurring tertiary and/or quaternary amine groups such as by subjecting the polymer to a quaternization reaction as set forth in Procedure II below. Thus the products of the Winters' patent as described above, could be converted into polymers containing recurring tertiary and/or quaternary groups by subjecting the polymers to quaternization with methyl chloride as set forth in Procedure II below, and thus be rendered useful according to this invention.

The epihalohydrins that can be used according to this invention include not only the well known



but various homologs, isomers, saturated or unsaturated so long as they are capable of reaction with an alkylamine, alkyl polyamine or polymerized amines to produce a water soluble product containing recurring tertiary and/or quaternary amine groups. Other compounds having similar reactivity with epihalohydrins, such as cloro-ethylene glycol might also be used as will be apparent to those skilled in the art.

The water soluble polymers can also be prepared by polymerizing epichlorohydrin by known manners and then reacting the polyepihalohydrin with an alkyl amine to produce a polymer having recurring tertiary and/or quaternary amine groups. Depending on the amine used, and other reaction conditions, the resulting product may have to be quaternerized, for example, by a process similar to that set forth in Procedure II below to insure the presence of recurring tertiary and/or quaternary amine groups. A polymer produced according to the procedure is set forth below in Example IV.

PROCEDURE I

One hundred and two grams of dimethylaminopropylamine are added to a three-necked round flask containing 612 grams of water. The flask is placed in a water bath and is equipped with an agitator, a thermometer and a funnel with stopcock. After the solution is cooled to and maintained at 25°C., 161 grams of epichlorohydrin are added to the aqueous solution in the flask slowly over a period of an hour. The molar ratio of the epichlorohydrin to the dimethylaminopropylamine is 1.75:1. The reaction is allowed to proceed for an additional 30 minutes after all the epichlorohydrin is added to the aqueous solution and thereafter, the reaction product is acidified to a pH of about 6 with sulfuric acid.

PROCEDURE II

Four hundred and fifty-two grams of dimethylaminopropylamine in 820 ml. of water is reacted with 368 grams of epichlorohydrin (0.9:1 molar ratio of the epichlorohydrin to the dimethylaminopropylamine) in a round flask in the same manner as described in Procedure I. After the reaction is completed, the resultant product is put in an autoclave together with 110 grams of sodium hydroxide, and is heated therein to 50°C. under agitation. 300 grams of methyl chloride under a pressure in the range of 2.8 to 3.5 kg/Cm^2 is then used to flush the autoclave and thereafter the autoclave is cooled and the contents are emptied. The resultant solution is adjusted to a solid content of 50 percent and a pH of about 6.

The amount of polyelectrolytes which can most advantageously be used according to this invention will of course vary to some extent depending upon the particular polyelectrolyte selected for use and the brightness of the zinc plating desired. When a basic solution containing sodium zincate and free sodium hydroxide is used, the deposit is a matte gray color with no luster at all. As small quantities of the polyelectrolyte are added, the deposit becomes semi-bright, and as additional polyelectrolyte is added, brighter plating will be obtained until maximum brightness is obtained. Additional amounts of the polyelectrolyte could of course be used if desired. Generally, the addition of 0.1 gram per liter of an epichlorohydrindimethylaminopropylamine condensation product in a sodium zincate bath containing free sodium hydroxide will change the zinc plating from a matte gray color with no luster at all to a semi-bright plating; and as additional amounts of this polyelectrolyte are added, brighter deposits will be obtained. Optimum results have been obtained with about 1.2 to 1.5 grams per liter with the specific polyelectrolyte noted above.

We have also discovered that brilliant deposits that are leveled can be produced with a plating bath of this invention in which there is dissolved, in addition to the polyelectrolyte, a conventional aldehyde brightening agent. The combined brightening and leveling effects by the synergistic action of the two additives is not expected because aldehyde brightening agents in zinc cyanide or other zinc baths do not exhibit leveling effects. We further noticed that the amount of aldehyde that is required to give increased brightness is less than that required in the prior zinc baths.

Suitable aldehyde brighteners include vanillin, hydroxybenzaldehyde, anisic aldehyde, bisulfite compounds of aldehydes, and so forth. The polyelectrolytes of this invention are the primary brighteners and are required in every case to give good results. The secondary brighteners mentioned above are thus optional for obtaining even brighter zinc plates if desired. The amount of such secondary brighteners, such as anisic aldehyde, can be varied quite widely, as will be apparent to those skilled in the art. For example, anisic aldehyde can be used in combination with the polyelectrolytes in an amount as low as 0.1 grams per liter and up to one gram per liter and even more. Other secondary brighteners useful in noncyanide or low cyanide zinc baths can also be used alone or preferably in combination with the secondary aldehyde brighteners.

A small amount of cyanide, such as sodium cyanide, can be used in the plating solutions of this invention is desired. However, the advantageous results of this invention are not obtained if the amount of cyanide exceeds about 2 oz./gal. The presence of cyanide is, however, not essential for the production of bright zinc plate in accordance with the present invention.

The baths can be operated at conventional amperages for zinc plating baths. For example, anywhere from 0 to 50 amps per square foot as determined by the Hull-Cell evaluation can be used. It is advantageous, however, to utilize between about 25 to 50 amps per square foot, and 25 amps per square foot is generelly recommended for production plating.

Various articles can of course be plated according to this invention, as is well known in the art. The zinc plating takes place on the cathode, and the majority of zinc plating is done in steel articles inserted into the baths as cathodes.

EXAMPLE I

Zinc metal as Zinc Sulfate	2 oz./gal.	(12g./l.)
Sodium Hydroxide	16 oz./gal.	(150g./l.)
Condensation reaction product of Epichlorohydrin and Dimethylaminopropylamine (Prepared according to Procedure 1 and having a molecular weight in the range between 4000–5000)	1.0 g./l.	
Hydroxybenzaldehyde	0.04 g./l.	

EXAMPLE II

Zinc metal as Zinc Oxide	3 oz./gal.
Sodium Hydroxide	32 oz./gal.
Quaternized condensation reaction product of Epichlorohydrin Dimethylaminopropylamine (Prepared according to Procedure II and having a molecular weight in the range between 4000–5000)	1.5 g./l.
Vanillin	0.06 g./l.

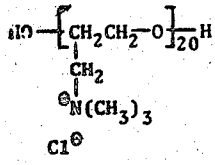
EXAMPLE III

Zinc metal as Zinc Acetate	1.5 oz./gal.
Potassium Hydroxide	25 oz./gal.
Condensation reaction product of Epichlorohydrin Dimethylaminopropylamine (Prepared according to Procedure II and having a molecular weight in the range between 4000–5000)	0.5 g./l.
Anisic Aldehyde (as the bisulfate)	0.2 g./l.

All of the above baths were operated utilizing a steel cathode at 25 amps per square foot, and bright zinc deposits were obtained in all instances.

EXAMPLE IV

Zinc metal as Zinc Sulfate	2 oz./gal.	(15 g./l.)
Sodium hydroxide	27 oz./gal.	(200 g./l.)
Methyl quaternary of Polyepichlorohydrin (having a molecular weight of approximately 2000) Represented by the following formula:	0.75 g./l.	



In the above bath operated utilizing a steel cathode at 25 amps per square foot, a plate of uniform brightness was obtained.

We claim:

1. An aqueous alkaline zincate bath suitable for depositing bright metallic zinc deposits and containing less than about 2 oz./gal. of cyanide therein, said bath comprising an aqueous alkaline solution having dissolved therein:

a. a soluble zinc compound capable of being plated by electroytic deposition; and

b. at least about 0.1 gm./l of a water soluble polymer containing repeating tertiary and/or quaternary amine groups, said polymers having been prepared by (i) polymerizing an aliphatic amine with an epihalohydrin, said polymerization being carried out for a sufficient length of time, and said reactants being present in such a molar ratio, so as to produce a polycondensate having repeating tertiary and/or quaternary amine groups ahd having a molecular weight above about 250 but below that which would render the polycondensate water insoluble or insoluble in the alkaline zincate bath.

2. The aqueous alkaline zincate bath of claim 1 wherein a secondary aldehyde brightener is dissolved therein in a sufficient amount to increase the brightness of the deposit.

3. The aqueous alkaline zinc bath of claim 1 in which the soluble polymer containing repeating tertiary amine groups is reacted with a sufficient amount of a quaternizing agent to convert amine groups to repeating quaternary amine groups.

4. An aqueous alkaline zincate bath suitable for depositing bright metallic zinc deposits and containing less than about 2 oz./gal of cyanide therein, said bath comprising an aqueous alkaline solution having dissolved therein:

a. a soluble zinc compound capable of being plated by electrolytic deposition; and

b. at least about 0.1 gm./l of a water soluble polymer containing repeating tertiary and/or quaternary amine groups, said polymers having been prepared by (i) polymerizing an aliphatic amine comtaining a primary amine group with an epihalohydrin, said polymerization being carried out for a sufficient length of time, and said reactants being present in such a molar ratio, so as to produce a polycondensate having repeating secondary amine groups and having a molecular weight above about 250 but below that which would render the polycondensate water insoluble or insoluble in the alkaline zincate bath, and (ii) reacting said polycondensate with a sufficient amount of a quaternizing agent to convert repeating secondary amine groups into repeating tertiary and/or quaternary amine groups.

5. The aqueous alkaline zincate bath of claim 4 wherein a secondary aldehyde brightener is dissolved therein in a sufficient amount to increase the brightness of the deposit.

6. An aqueous alkaline zincate bath suitable for depositing bright metallic zinc deposits and containing less than about 2 oz./gal. of cyanide therein, said bath comprising an aqueous alkaline solution having dissolved therein:

a. a soluble zinc compound capable of being plated by electrolytic deposition; and

b. at least about 0.1 gm/l of a water soluble polymer containing repeating tertiary and/or quaternary amine groups, said polymers having been prepared by (i) reacting and aliphatic amine containing a secondary or tertiary amine group with a polyepihalohydrin, said reaction being carried out for a sufficient length of time and said reactants being present in such a molar ratio, so as to produce a polycondensate having repeating tertiary and/or quaternary amine groups and having a molecular weight above about 250 but below that which would render the polycondensate water insoluble or insoluble in the alkaline zincate bath.

7. The aqueous alkaline zincate bath of claim 6 wherein a secondary aldehyde brightener is dissolved therein in a sufficient amount to increase the brightness of the deposit.

8. The aqueous alkaline zinc bath of claim 6 in which the soluble polymer containing repeating tertiary amine groups is reacted with a sufficient amount of a quaternizing agent to convert amine groups to repeating quaternary amine groups.

9. An aqueous alkaline zincte bath suitable for depositing bright metallic zinc deposits and containing less than about 2 oz./gal. of cyanide therein, said bath commprising an aqueous alkaline solution having dissolved therein:

a. a soluble zinc compound capable of being plated by electrolytic deposition; and

b. at least about 0.1 gm./l of water soluble polymer comprising repeating tertiary and/or quaternary amine groups, said polymers having been prepared by (i) reacting an aliphatic amine containing a primary amine group with a polyepihalohydrin, said reaction being carried out for a sufficient length of time and said reactants being present in such a molar ratio, so as to produce a reaction product having repeating secondary amine groups and having a molecular weight above about 250 but below that which would render the polycondensate water insoluble or insoluble in the alkaline zincate bath and (ii) reacting the reaction product of the polyepihalohydrin containing the secondary amine groups with a sufficient amount of a quaternizing agent to convert repeating secondary amine groups into repeating tertiary and/or quaternary amine groups.

10. The aqueous alkaline zincate bath of claim 9 wherein a secondary aldehyde brightener is dissolved therein in a sufficient amount to increase the brightness of the deposit.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,869,358

DATED : March 4, 1975

INVENTOR(S) : Fred I. Nobel et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 30 "become and" should read --become an--.

Column 6, line 55, "done in steel" should read --done on steel--.

Column 7, line 43 "$^{\bullet}N(CH_3)_3$" should read --$^{\oplus}N(CH_3)_3$--.

Column 7, line 66 "groups ahd" should read --groups and--.

Column 9, line 1 "zincte bath" should read --zincate bath--.

Column 9, line 4 "commprising" should read --comprising--.

Signed and Sealed this

Twenty-seventh Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks