ELECTROLYTIC DEPOSITION OF ZINC

Inventor: Richard B. Kessler, Jericho, N.Y.
Assignee: Lea-Ronal, Inc., Freeport, N.Y.
Filed: Feb. 1, 1973
Appl. No.: 328,782

U.S. Cl. 204/55 Y; 204/55 R
Int. Cl. C23b 5/10; C23b 5/46
Field of Search 204/55 R, 55 Y, 43, 44

References Cited
UNITED STATES PATENTS
733,028 7/1903 Goldberg ................. 204/55 R
2,451,426 10/1948 Bair et al. .......... 204/55 Y
3,318,787 5/1967 Rindt et al. ........ 204/55 Y
3,620,938 11/1971 Von Pless et al. .... 204/55 Y

FOREIGN PATENTS OR APPLICATIONS
2,086,320 12/1971 France .............. 204/55 R
1,109,479 6/1961 Germany .............. 204/55 R
1,123,172 2/1962 Germany .............. 204/55 R

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Pennie & Edmonds

ABSTRACT

An aqueous alkaline zinc bath for electroplating bright metallic zinc deposits on metal substrates is disclosed which comprises an aqueous alkaline substantially cyanide-free solution having dissolved therein at least one soluble zinc compound capable of being plated by electrolytic depositions and an effective amount of at least one substituted pyridine or quinoline compound possessing at least one amine containing substituent.

6 Claims, No Drawings
ELECTROLYTIC DEPOSITION OF ZINC

BACKGROUND OF THE INVENTION

I. Field of the Invention
This invention relates to the electrodeposition of zinc metal on metal substrates and in particular, to the electroplating baths useful therefor.

II. Description of the Prior Art
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 an 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 glycrolates 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, alkanolamines either alone or in conjunction with aldehydes to brighten the deposits as in U.S. Pat. No. 3,317,412. 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 as in German Patent No. 1,253,003. The latter baths although producing bright deposits and being comparatively more stable than previous baths, nevertheless have the serious shortcoming 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-ammine reaction products have previously been disclosed as being useful in aqueous zinc cyanide electroplating 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 these epichlorohydrinammine reaction products have been used in zinc cyanide baths, they are not good enough to meet today's standards with respect to throwing power, current density and brightness in cyanide free or substantially cyanide free baths.

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, large amounts of secondary brighteners are used in low cyanide baths to obtain an acceptable brightness.

In the United States patent application by Nobel et al. Ser. No. 268,920 filed July 3, 1972, now abandoned, and assigned to the same assignee as the present application, there is disclosed and claimed an aqueous alkaline zinc bath substantially free of cyanide 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 epichlorohydrin which water soluble reaction product contains recurring tertiary and advantageously recurring quaternary amine groups and having a molecular weight above about 250. The epichlorohydrin reaction products disclosed in the Winters' patent containing no tertiary or quaternary amine groups do not produce any advantageous results in the baths of Ser. No. 268,920 when substituted for the epichlorohydrin amine reaction products containing recurring tertiary and/or quaternary amine groups.

These zinc baths disclosed in the above-entitled application do plate bright zinc very well but in a somewhat limited current density range. A broader range of current density for producing bright zinc platings is of course highly desirable particularly in rack plating operations where high current densities are encountered. Bright deposits cannot be obtained using the baths disclosed in the above-entitled application over a range of current density from 0 to 100 asf. The deposits from these baths, for example, produce a matte or dull gray finish in the higher current density range. By use of the baths of this invention bright deposits can be obtained over a current density range from 0 to about 250 asf.

SUMMARY OF THE INVENTION
The present invention provides a cyanide free or substantially cyanide free zinc plating bath which is capable of being used in the electrolytic deposition of zinc having a brightness and throwing power equivalent or better than that which can be obtained from commercial cyanide zinc plating baths. Broadly stated, the plating baths and process of this invention involve the addition of at least one soluble zinc compound capable of being plated by electroplating deposition and an effective amount of at least one substituted pyridine or quinoline compound possessing at least one amine containing substituent.

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 one to four 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 zinicates.

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 or 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 substituted pyridine and quinoline compounds which are useful herein must possess at least one amine containing substituent.

Some examples of pyridine compounds which can be advantageously employed in the electroplating baths of this invention include pyridine compounds of the general formula

\[
\text{(I)}
\]

wherein \( R_1, R_2, R_3, R_4 \text{ and } R_5 \) each is a hydrogen atom or a halogen atom or a lower alkyl, lower alkenyl, hydroxyl, carboxylic, amino, lower alkylenc, lower alkenylcarboxylic, lower alkyleneamine group or a group resulting from the reaction of the hydroxyl, carboxylic, amino, lower alkylenc, lower alkenylcarboxylic or lower alkyleneamine group with alkyl sulfoate, alkyl lactone or epoxide and \( Z \) is nothing, \( 0^-\) or a group resulting from the reaction of (I) with a quaternizing agent, provided, that at least one of the aforesaid groups \( R_1, R_2, R_3, R_4 \text{ and } R_5 \) contains an amine nitrogen atom.

Some examples of quinoline compounds which can be advantageously employed in the electroplating baths of this invention include quinoline compounds of the general formula

\[
\text{(II)}
\]

wherein \( R_1, R_2, R_3 \text{ and } R_4 \) each is a hydrogen atom or a halogen atom or a lower alkyl, lower alkenyl, hydroxyl, carboxylic, amino, lower alkylenc, lower alkenylcarboxylic, lower alkyleneamine group or a group resulting from the reaction of the hydroxyl, carboxylic, amino, lower alkylenc, lower alkenylcarboxylic or lower alkyleneamine group with alkyl sulfoate, alkyl lactone or epoxide and \( Z \) is nothing, \( 0^-\) or a group resulting from the reaction of (II) with a quaternizing agent, provided, that at least one of the aforesaid groups \( R_1, R_2, R_3, R_4 \text{ and } R_5 \) contains an amine nitrogen atom.

An alkyl sulfoate which has been found to provide good results when reacted with the pyridines and quinolines of this invention is propane sulfoate. Other alkyl sulfoates can be advantageously employed as will be readily appreciated by one skilled in the art.

Examples of some epoxides that can be reacted with pyridines (I) and quinolines (II) include ethylene oxide, propylene oxide, epichlorohydrin, allyl glycidyl ether, 2,3-epoxybutane, 1,2-dimethyl-1,2-epoxypropyl) ether and \( \alpha,\beta\)-epoxypropionic acid.

The pyridines (I) and quinolines (II) can be quaternized with numerous known and conventional quaternizing agents such as benzyl chloride, methyl chloride, dimethylsulfate and allyl chloride.

Particularly good results have been obtained with the use of the aminopyridine of formula (I) above, such as the 2- and 3-aminopyridine; and the best results obtained to date have resulted from the use of the reaction product of the aminopyridine of formula (I), particularly the 2- and 3-aminopyridines, with epichlorohydrin. The most advantageous results are obtained by utilizing the pyridines and quinolines of formulas (I) and (II) respectively and their epichlorohydrin reaction products in conjunction with the ammonia or amino-epihaloxydrin reaction products having a molecular weight above about 250 as described in the Winters' U.S. Pat. No. 2,791,534 and as described in the above-entitled application of Nobel et al. Ser. No. 268,920, filed July 3, 1972. By use of this particular combination very bright zinc deposits can be obtained over the entire current density range of 0 to 250 a/s. The use of the pyridines and their epichlorohydrin reaction products alone extend the current density range from which bright zinc deposits can be obtained over the range obtainable in accordance with the baths described in the above-entitled application but not quite to the current density range as with the combination of these pyri-
dines and reaction products with the amine epichlorohydrin reaction products, alkylene amines or alkanolamines.

The amount of pyridine and quinoline compounds of this invention or their epichlorohydrin reaction products can be varied quite widely as will be apparent to those skilled in the art. Generally, the effect of increasing the current density range while maintaining brightness of the zinc deposits can be noticed with as little as 0.01 grams per liter of the pyridine compounds and their reaction products. In most cases it is advantageous to use about 0.1 to 1 grams per liter although much higher concentrations can be employed up to 10 grams per liter or even higher. Generally, a bright zinc coating is obtained over the full current density range before the concentration reaches 1 gram per liter, and the addition of higher amounts of the pyridine compounds does not result in any more or significant improvements. The amount of the pyridine or quinoline compounds used will not only depend upon the particular pyridine or quinoline compound employed, but the current density range desired for plating bright zinc will be apparent to those skilled in the art. If one does not desire to plate at very high current densities then lesser amounts of the pyridine can be used.

The aminopyridine-epihalohydrin reaction products can be obtained by merely heating the aminopyridine with epichlorohydrin. The particular 2-aminopyridine (formula I) used in the Examples set forth below was prepared by mixing 28 moles of 2-aminopyridine in five gallons of water and slowly adding 49.1 moles of epichlorohydrin to prevent the temperature from rising too rapidly or too high. It is preferred to keep the temperature during this phase of the reaction from rising above 90°C. The reaction mixture is then maintained at between about 75°C to 80°C for about 45 minutes and cooled. The finished product has a volume of approximately seven gallons. It is this diluted product containing approximately 27% solids that is used in the examples below and the amounts recited in the Examples are of a 27% solution.

Other epoxides, alkyl sulfones and their various homologs, isomers, saturated or unsaturated, besides the epichlorohydrin used above can be used to react with the pyridine and quinoline compounds to produce similar results so long as the reaction product remains soluble in the bath media as will be appreciated by those skilled in the art. Different proportions can also be employed. The exact formula of the reaction product is not known.

The polyelectrones or amine-epihalohydrin reaction products 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 ammonia or an alkylene amine, and an epihalohydrin. The polycondensates are in the form of a polymer containing repeating amine groups and have a molecular weight above about 250. The water soluble epihalohydrin-alkylene amine polycondensates can be prepared by direct reaction of an epihalohydrin with straight or branched chain alkyl amines or ammonia.

The term "amine" or "alkyl amine" includes ammonia as used herein with respect to the description of the alkylene amine polycondensates.
but various homologs, isomers, saturated or unsaturated so long as they are capable of reaction with an alkyl amine to produce a water soluble product containing recurring amine groups.

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

**PROCEDURE I**

102 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**

452 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 methylichloride under a pressure in the range of 2.8 to 3.5 kg/cm² 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 polyelectrolyte 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 epichlorohydrin dimethylaminopropylamine 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 one gram per liter with the specific polyelectrolyte noted above.

Additional brightness can be obtained by adding conventional brighteners such as the aldehyde brighteners including vanillin, hydroxybenzaldehyde, anisic aldehyde, bisulfite compounds of aldehydes, and so forth. The secondary brighteners mentioned above are 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. A small amount of cyanide, such as sodium cyanide, can be used in the plating solutions of this invention if 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 according to this invention can be operated at conventional amperages for zinc plating baths. For example, anywhere from about 0 to 250 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 generally 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 on steel articles inserted into the baths as cathodes.

**EXAMPLE I**

A zinc electroplating solution was prepared having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc metal</td>
<td>1.6 oz/gallon</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>16 oz/gallon</td>
</tr>
<tr>
<td>Condensation reaction product</td>
<td></td>
</tr>
<tr>
<td>of epichlorohydrin and dimethylaminopropyl amine produced by Procedure II having a molecular weight of 4000</td>
<td>6 cc/gallon</td>
</tr>
<tr>
<td>5000</td>
<td>0.04 g/gallon</td>
</tr>
<tr>
<td>Anisic aldehyde bisulfite</td>
<td></td>
</tr>
</tbody>
</table>

After electrolyzing the solution for a short period, a plating test was run in a Hull cell. A steel panel was plated at 5 amperes for 2 minutes at room temperature with no agitation. The deposit was fairly bright from 1 asf to about 90 asf. Above this current density, however, the deposit was grey, matte and non-adherent. In addition, the panel lacked sufficient brightness in the 70-90 asf range.

**EXAMPLE II**

To the bath as described in Example I was added 0.4 g/l of 3-aminopyridine. A steel panel was again plated in a Hull cell at 5 amperes for 2 minutes. The deposit was bright and uniform over the entire surface of the panel with no evidence of burning or a non-adherent deposit. The material increases the plating range by eliminating the burn and is also an excellent high current density brightener.

**EXAMPLE III**

1.5 g/l of 3-picolyamine was added to the bath described in Example I. The burned or the grey, matte and non-adherent zinc coating was eliminated over the
entire surface of the panel plated but the overall brightness of the panel over the entire current density range was not as good as when 2-aminopyridine was used.

EXAMPLE IV
0.8 g/l of 2-aminopyridine was added to the bath described in Example I and plated as described therein. This panel had similar advantageous results to the zinc plated panel described in Example II.

EXAMPLE V
0.50 ccs/l (approximately a 27% solution) of the reaction product of 2-aminopyridine and epichlorohydrin was added to the bath described in Example I and a test panel plated as described therein. The zinc deposit was uniform over the entire surface of the panel with no evidence of burning or a non-adhering deposit and the deposit was more brilliant than the deposit obtained in Example II.

EXAMPLE VI
An 80 gallon electroplating bath was prepared having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>2.4 oz/gallon</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>24 oz/gallon</td>
</tr>
<tr>
<td>Condensation reaction product of epichlorohydrin and dimethylaminopropyl amine produced by Procedure II having a molecular weight of 4000 to 5000</td>
<td>12 cc/gallon</td>
</tr>
<tr>
<td>Vanillin</td>
<td>0.1 g/gallon</td>
</tr>
</tbody>
</table>

Electrical boxes having deep recesses and sharp edges were plated in the above bath at an average current density of 60 asf. After plating, the parts showed severe burning on the outer edges.

EXAMPLE VII
To the bath in Example VI was added 0.60 g/l (27% solution) of the reaction product of 2-aminopyridine and epichlorohydrin as described above. The same parts referred to in Example VI were replated at 60 asf and showed no sign of burning.

EXAMPLE VIII
To a bath as prepared in Example I was added 0.5 g/l (27% solution) of the reaction product of 1 mole of 2-aminopyridine and 1.3 moles of ethylene oxide prepared by the above described procedure. A steel panel plated in a Hull cell at 5 amps for 2 minutes was bright from 0 to greater than 250 asf.

EXAMPLE IX
A zinc electroplating solution was prepared having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc metal</td>
<td>1.4 oz/gallon</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>20 oz/gallon</td>
</tr>
<tr>
<td>Epichlorohydrin/amine</td>
<td>12 cc/gallon</td>
</tr>
<tr>
<td>Nobel et al. S.N. 268,920</td>
<td>0.6 gm/gallon</td>
</tr>
<tr>
<td>Amine aldehyde bisulfite</td>
<td>0.3 gm/liter</td>
</tr>
</tbody>
</table>

To the above solution was added 0.60 ml/liter of a 27% solution of the reaction product of 2-aminopyridine and epichlorohydrin as described above. The resulting deposit was bright from 0-100 asf.

EXAMPLE X
A plating solution containing zinc metal at a level of 1.6 oz/gal, of sodium hydroxide at a level of 16 oz/gal with 20 cc/liter tetraethylenetetramine pentamethylamine resulted in a spongy matte deposit.

Addition to this plating solution of 1.2 cc/liter of a 27% solution of the reaction product of 2-aminopyridine and epichlorohydrin gave a semi-bright deposit at a current density range of from 0-50 asf.

EXAMPLE XI
A plating solution was prepared with the following formulation:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc metal</td>
<td>1.4 oz/gallon</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>20 oz/gallon</td>
</tr>
<tr>
<td>Epichlorohydrin/amine</td>
<td>12 cc/gallon</td>
</tr>
<tr>
<td>Nobel et al. S.N. 268,920</td>
<td>0.6 gm/gallon</td>
</tr>
<tr>
<td>Amine aldehyde bisulfite</td>
<td>0.3 gm/liter</td>
</tr>
</tbody>
</table>

A Hull Cell panel plated in the above solution at 0-250 asf possessed lustrous deposits.

1. An aqueous zincate bath having a pH of about 12 and above for electroplating bright metallic zinc deposits on substrates over a wide current density range which comprises

1. an aqueous alkaline solution containing less than about 2 oz./gal. of cyanide;
2. a soluble zinc compound dissolved therein and capable of plating zinc metal by electrolytic deposition;
3. a substituted pyridine or quinoline compound possessing at least one amino substituent in an amount sufficient to increase the brightness of the zinc deposit electrolytically deposited therefrom over an increased current density range; and
4. an amine brightening agent other than the amino substituted pyridine or quinoline compound in sufficient amount to increase the brightness of the entire deposit.

2. The bath of claim 1 wherein the substituted pyridine compound is the reaction product of an epoxide and a substituted pyridine, said reaction product being produced by reacting the epoxide and a substituted pyridine for a sufficient length of time and in a molar ratio sufficient to form the reaction product which is soluble in the aqueous zincate bath.

3. The bath of claim 2 wherein the substituted pyridine reacted is 2-aminopyridine or 3-aminopyridine and the epoxide is epichlorohydrin.

4. The bath of claim 1 wherein the amino-pyridine is 2-aminopyridine or 3-aminopyridine.

5. An aqueous zincate bath according to claim 1 in which the amine brightening agent is a water soluble reaction product of an amine and an ephalolohydrin or an amine and a polyephalohydrin containing repeating amino groups and having a molecular weight above about 250, said reaction between the amine and the ephalolohydrin and the amine and the polyephalohydrin.
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 amino groups and having a molecular weight above about 250, but below that which would render the polymer insoluble in the alkylene zincate bath.

6. The method of electrodepositing, bright metallic zinc which comprises electrodepositing zinc on a substrate over a wide current density range from an aqueous zincate bath having a pH of about 12 and above containing

1. an aqueous alkaline solution containing less than about 2 oz./gal. of cyanide;

2. a soluble zinc compound dissolved therein and capable of plating zinc metal by electrolytic deposition;

3. a substituted pyridine or quinoline compound possessing at least one amino substituent in an amount sufficient to increase the brightness of the zinc deposit electrolytically deposited therefrom over an increased current density range; and

4. an amine brightening agent other than the amino substituted pyridine or quinoline compound in sufficient amount to increase the brightness of the entire deposit.

* * * * *