United States Patent [19]

Creutz

[11] **3,853,718**

[45] **Dec. 10, 1974**

[54] **METHOD TO IMPROVE ZINC DEPOSITION EMPLOYING MULTI-NITROGEN QUATERNARIES**

[75] Inventor: **Hans-Gerhard Creutz,** Westland, Mich.

[73] Assignee: **Oxy Metal Finishing Corporation,** Warren, Mich.

[22] Filed: **Jan. 5, 1973**

[21] Appl. No.: **321,429**

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

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

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

[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 X
3,393,135	7/1968	Rosenberg	204/55 Y
3,642,589	2/1972	Nobel et al.	204/44
3,655,534	4/1972	Kampe	204/55 R

FOREIGN PATENTS OR APPLICATIONS

1,910,466	9/1970	Germany	204/55 R
1,915,653	10/1970	Germany	204/55 R
1,480,997	4/1967	France	204/55 R

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—B. F. Claeboe

[57] **ABSTRACT**

An alkaline electroplating bath comprising alkali metal zincate, and an effective zinc brightening amount of a bath soluble multiple quaternary compound which is the reaction product of a polyalkylene imine and an organic ammonium halide which contains a halogen which will quaternarize a nitrogen of the polyalkylene imine.

42 Claims, No Drawings

METHOD TO IMPROVE ZINC DEPOSITION EMPLOYING MULTI-NITROGEN QUATERNARIES

BACKGROUND TO THE INVENTION

Various plating baths have been employed for the electrodeposition of zinc. A preferred means is one that does not employ cyanide ions, due to the difficulty in disposing of cyanide ions in waste effluents. Some conventional zinc brighteners produce a bright deposit, but only over a narrow current density range. The high current density areas generally result in a spongy or burnt deposit. It has been found that bright zinc deposits that are dendrite free, are obtained when compounds containing multinitrogen quaternary sites are employed.

Some zinc brighteners have been described is U.S. Patents; 3,296,105; 3,317,412; 3,393,135; 3,472,743; 3,672,971; and German Pat. No. 1,232,800.

SUMMARY OF THE INVENTION

Described is an electroplating bath useful for the electrodeposition of zinc, comprising an alkaline electrolyte preferably containing alkali zincate and also containing a reaction product of a polyalkylene imine and an ammonium halide which has a halogen which may react with the nitrogen of the polyalkylene imine to produce a plurality of nitrogen quaternary sites.

DESCRIPTION OF PREFERRED EMBODIMENTS

A method is described for obtaining a bright zinc deposit from an alkaline bath, preferably a cyanide-free alkaline zincate bath, wherein the bath contains a brightening amount of the reaction product of a polyalkylene imine and an organic ammonium halide, which contains a halogen which may react with the nitrogen of the polyalkylene imine to produce a plurality of nitrogen quaternary sites.

Zincate plating baths are those which are generally obtained by mixing zinc oxide and caustic, such as sodium or potassium hydroxide.

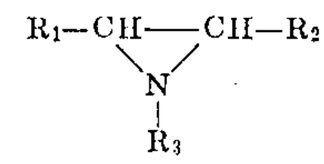
The amount of alkali metal hydroxide that may be employed ranges from about 100 to 200 grams per liter, while the amount of alkali metal zincate ranges from 10 to 150 grams per liter, preferably about 20 to 70 grams per liter.

The processing parameters are such that normally atmospheric temperature and pressure is employed, although temperatures up to 55° C. may also be employed, and even more preferably about 15° to 45° C. The cathode current density ranges from about 5 to 100 amps. per sq. ft., while the anode current density ranges from about 10 to 35 amps. per sq. ft., where the zinc deposition can occur with agitation.

The zinc brightening agent that may be employed in the present invention is one that employs as a reactant a polyalkylene imine. It is to be appreciated that the reaction product that is to be used as a zinc brightener in the present invention is one that should be soluble in the aqueous alkaline system. The polyalkylene imine that is employed is a lower alkyl substitute of polyethylene imine, that is a polyethylene imine in which one or more of the hydrogens is substituted by a lower alkyl, such as a one to three carbon alkyl radical, such as methyl, ethyl, and n-propyl or isopropyl and including the substitution derivatives in which one or more alkyl hydrogen is substituted by a bath compatible organic radical, such as for example, carboxyl, esterified carboxyl, aldehyde, acetyl, ether carbonyl, and other bath compatible radicals, such as the hydroxy or amino radicals. It is most preferred that the polyalkylene imine be unsubstituted polyethylene imine which are generally available to the public.

The polyethylene imine can be expressed as the polymerization product of the compound of Formula I;

I

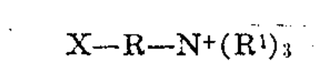


wherein R_1 and R_2 may be hydrogen, alkyl of from one to three carbon atoms and R_3 may be hydrogen, alkyl or hydroxy alkyl of from one to three carbon atoms, such as hydroxy ethyl and hydroxy propyl, cyanoethyl, cyanopropyl and benzyl.

The polyalkylene imine, preferably unsubstituted polyethylene imine, may range from 300 to 1,000,000 in molecular weight.

The zinc brightening agent that is to be employed in the present case preferably has a plurality of nitrogen quaternary ammonium sites. One of the quaternaries is in the repeating polyalkylene imine unit, while the side chain attached to the quaternary of the polyalkylene imine would be the second site for a quaternary nitrogen. The multiple nitrogen quaternary that may be employed in the present case is one that may be obtained by reacting the compound of Formula II;

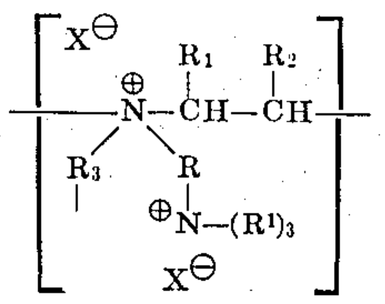
II



with the aforementioned polyalkylene imine, wherein R may be alkylene, or hydroxy substituted alkylene, wherein the number of carbon atoms is up to six carbon atoms, preferably up to four carbon atoms, and even more preferably three carbon atoms; and R^1 may have up to 10 carbon atoms per R^1 group, wherein R^1 is independently selected from the group consisting of hydrogen, alkyl, aryl, aralkyl and hydroxy or halo substituted derivatives thereof, and the like.

When one quaternizes the nitrogen of the Formula I polymerization products with the compound of Formula II, one may obtain products having some repeating units of Formula III;

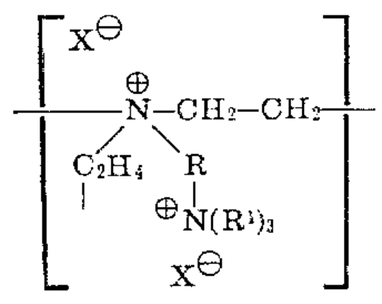
III



It is to be appreciated that when one uses a compound of formula I for polymerization, the product has a mixture of primary, secondary and tertiary amines. The polymerized product may be cross-linked. In general, the low molecular weight PEI probably have few if any cross-linkages. Therefore, as the molecular weight increases, the amount of cross-linking in the product will increase. Accordingly, when polyethylene imine (PEI) is polymerized to obtain a cross-linked product, the PEI is reacted with a compound of for-

mula II, repeating units of the product can be expressed by Formula IV;

IV



In all of the above formulas, X may be a halogen, such as chloro or bromo and the like.

The compound of formula II, may be prepared by reacting a tertiary amine with a suitable reactant which will form the quaternary amine and also have a halogen available which can in turn quaternarize at least one of the nitrogens of the polyalkylene imine.

A suitable reactant for the reaction with a tertiary amine to produce the compounds of formula II would be epichlorohydrin; preferably this reaction is performed in the presence of hypochlorous acid.

A suitable tertiary amine may be trimethyl amine, triethyl amine, tributyl amine, tridecyl amine, tribenzyl amine, triphenyl amine, and the like.

The most preferred reactant with polyethylene imine is the product resulting from reacting epichlorohydrin with trimethyl amine.

As can be appreciated, other agents may be present in the bath in order to impart other desirable characteristics such as improving the throwing power of the bath to low current density areas, and improving the bath solubility of the components. Suitable agents are anisaldehyde, glue, polyvinyl alcohol, the glycerol esters of polyvinyl alcohols, having a molecular weight of 5,000 to 20,000. Other polymers that may be employed are gelatin, peptone, and the like. In addition, chelating agents, or agents that can form a complex with the zinc in the bath may also be employed, such as nitrilo triacetic acid and the various alkali metal salts, such as the sodium salt, ethylene diamine tetra acetic acid, and its water soluble salts, such as sodium and the like.

A preferred polyethylene imine that may be used as a reactant with a compound of formula II, is one having a molecular weight ranging from 250 to 400,000, preferably 600 to 60,000, wherein the percentage of primary, secondary, and tertiary nitrogens is about 25 to 50 to 25.

A zincate bath that may be employed in the present invention is as follows:

MATERIALS	RANGE GRAMS PER LITER	PREFERRED GRAMS PER LITER
Zinc Oxide	5 – 50	8 – 30
Sodium Hydroxide	50 – 250	100 – 200
Multiple quaternary brightening agent	0.5 – 50	2 – 15

The bath pH normally is alkaline, having a range of about 10 to 14. The bath pH may be adjusted by the addition of sodium hydroxide.

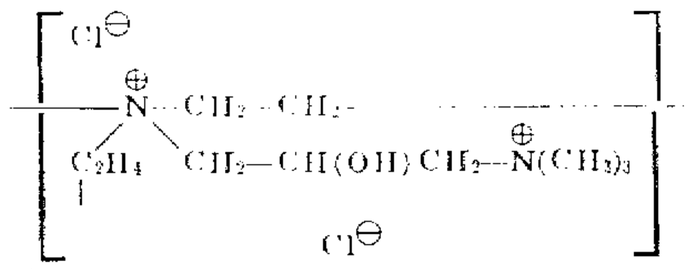
EXAMPLE I

1.5 percent zinc oxide was mixed with 15 percent of dry caustic soda. 500 cc.'s of water were then added and the slurry mixed until all the solids were dissolved. The solution was cooled and diluted to one gallon. Steel test panels were plated in a Hull cell at 1 amp. for ten minutes. The deposit was dark and spongy.

To the solution was added 1 percent by weight (about 10 grams per liter) of a compound obtained as follows:

To a solution of 93 grams of polyethylene imine (1,800 molecular weight with percentage of primary, secondary and tertiary amine being, 25, 50 and 25 percent) in 326 grams of water there was added 398 grams of (3-chloro-2 hydroxypropyl) trimethyl ammonium chloride (chloride concentration was 140.5 g/l; 49.5 grams chloride) followed by addition of 43 grams of 50 percent sodium hydroxide solution. The mixture was heated to reflux (103°C) and refluxed for 30 minutes. After cooling, the solution (750 ml, 821 grams) was analyzed for chloride content. The chloride concentration was 112.9 g/l corresponding to 84.5 grams of chloride. Total chloride formed in the reaction was 35.0 grams (theoretical 37.7 grams). The resulting product contains as a portion of its polymeric structure the multiple quaternary nitrogen having repeating units as in formula V;

V



The plating test was repeated and the cathode this time was smooth.

EXAMPLE II

Following the procedure of Example I, the solution was further added to with the addition of 200 milligrams per liter of anisaldehyde bisulfite. The plating was repeated with the result that a bright zinc deposit was obtained.

In order to improve the efficacy of the zinc electroplating bath, various other materials may be added.

Suitable additional materials are the nitrogen quaternaries which are zinc brighteners, such as those described in U.S. Pat. No. 3,318,787 and U.S. Pat. No. 3,411,996, the subject matter of which is incorporated here by reference. The preferred organic quaternaries are those that are bath soluble and are substituted by such groups as carboxylic esters, carboxamides, substituted carboxamides, carboxy groups and nitrile. The amount of the quaternary that may be used may range from about 0.005 to about 5 grams per liter. It is to be appreciated when the quaternary is substituted by a carboxy group, that an inner salt, i.e., a betaine can be formed, such as described in U.S. Pat. No. 3,411,996.

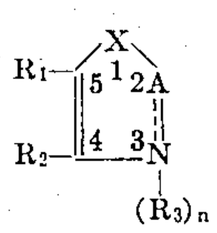
The most preferred quaternary is a pyridine compound whereby the nitrogen has been quaternized by suitable goups. Suitable quaternizing groups are benzyl chloride, allyl bromide, and the like. The most preferred quaternary is that obtained by quaternizing nicotinic acid (or 3-methyl or ethyl-nicotinate) with benzyl chloride.

It has also been found that significantly improved zinc brightening effects are obtained when other suit-

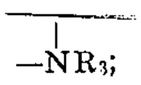
able heterocyclic compounds and the multiple quaternary of the present invention are added to the zinc bath. The use of these two compounds results in a wider current density plating range, thereby improving the brightness of zinc in the low current density area.

Suitable heterocyclic compounds are those described in Ser. No. 244,938, filed Apr. 17, 1972, now abandoned.

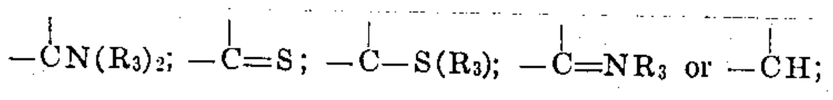
Such compounds are generally used in amounts ranging from about 0.005 to about 10 grams per liter and are generally of the structure;



wherein X is —S— or



A is

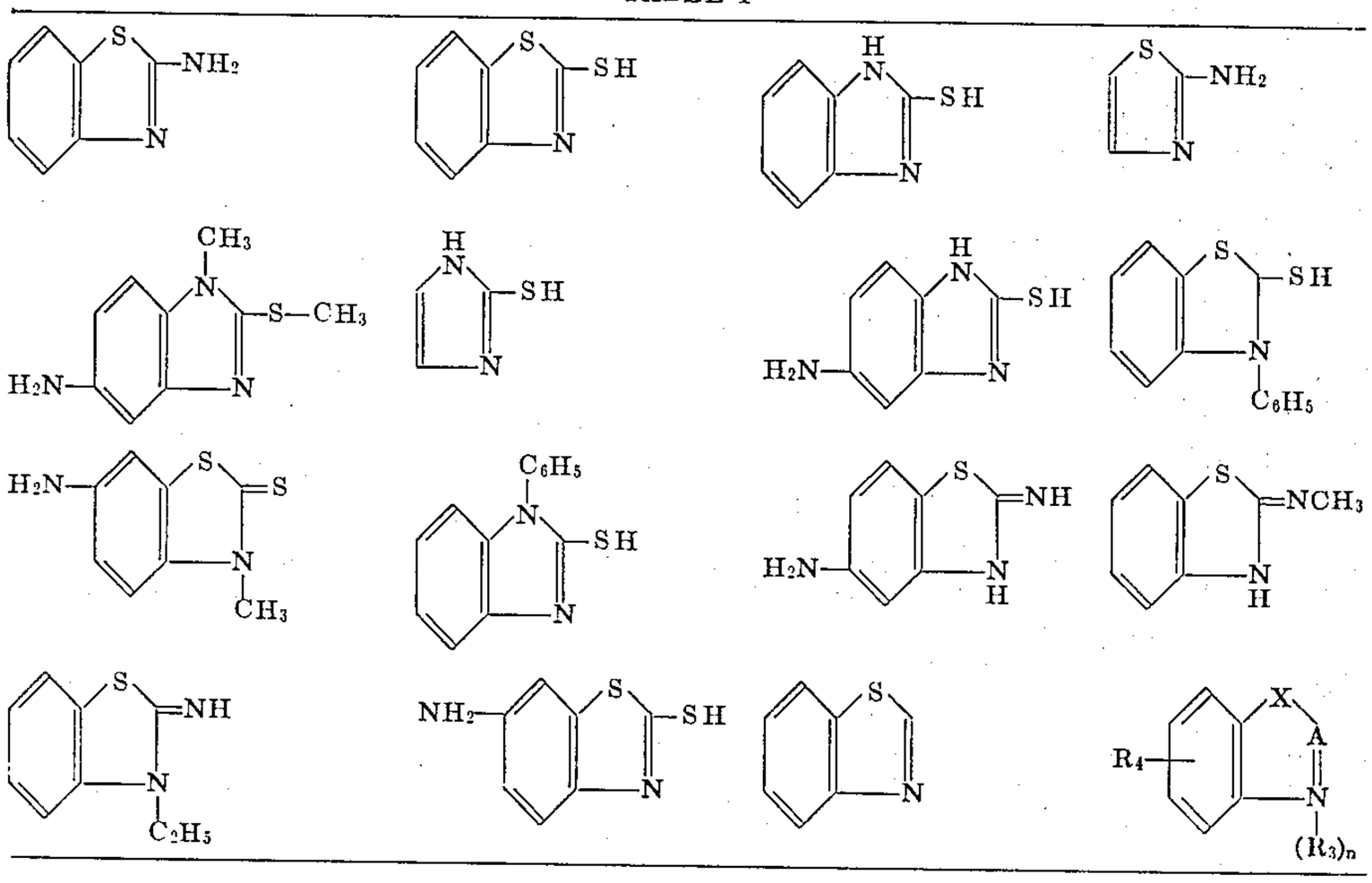


n is 0 to 1; when *n* is zero, nitrogen is doubly bonded to carbon in position 2;

R_1 and R_2 may be hydrogen, alkyl of one to four carbon atoms; phenyl; or may be joined to form a six membered aromatic carbocyclic ring; and

R_3 is hydrogen, alkyl of one to four carbon atoms or phenyl.

TABLE I



Some of the heterocyclic compounds that may be employed are as follows: (See Table No. I) wherein R_4 is a "water solubilizing group."

By "water solubilizing group" is meant any substituent on the six membered carbocyclic ring which will improve the water solubility of the compound. Such groups are hydroxy, alkoxy, such as methoxy or ethoxy and the like, carboxy, amino, and the like. In addition R_4 may be other groups which are not detrimental to the electrodeposition of zinc such as chloro, bromo, cyano (—CN), nitro and the like.

EXAMPLE III

Other examples of suitable zinc brightening baths are as follows;

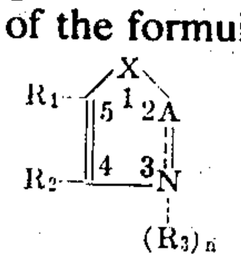
(a)	12	g/l zinc (as metal)
	120	g/l NaOH
	10	g/l multiple quaternary of example I
	50	mg/l 2 amino benzothiazole
	150	mg/l anisaldehydebisulfite
(b)	15	g/l zinc (as metal)
	150	g/l NaOH
	5	g/l multiple quaternary of example I
	10	mg/l betaine of benzylchloride-nictoinic acid
	100	mg/l 2-mercaptobenzothiazole
(c)	10	g/l zinc (as metal)
	100	g/l NaOH
	7.5	g/l multiple quaternary of example I
	50	mg/l 2-aminobenzothiazole
	20	mg/l methylnicotinate of benzylchloride quaternary
	100	mg/l anisaldehydebisulfite
(d)	16	g/l zinc (as metal)
	130	g/l NaOH
	3	g/l multiple quaternary of example I
	0.5	g/l betaine of benzylchloride-nicotinic acid

It is to be appreciated that some cyanide ions may be present in the baths of the present case. This can normally occur in a conversion of a cyanide bath to the zincate bath of the present case or may be present to improve the efficiency of the zincate bath.

What is claimed is:

1. An aqueous alkaline zinc electroplating bath comprising alkali metal zincate, and about 0.5 to about 50 grams per liter of a zinc brightening agent in the form of a bath soluble multiple quaternary compound which is the reaction product of a polyalkylene imine having a molecular weight from about 300 to 1,000,000, and an organic quaternary ammonium halide which contains a halogen which will quaternize a nitrogen of the polyalkylene imine in a ratio of one mole of organic ammonium halide to two mole-units of the polyalkylene imine.

2. The bath of claim **1**, further comprising about 0.005 g/l to about 10 g/l of a third soluble nitrogen heterocyclic compound of the formula:



wherein X is —S— or —NR_3; and

A is independently selected from the group consisting of —CN $(R_3)_2$; —C═S; ═C—R_3; —C═NR_3 and ═C—H;

n is 0 to 1; when n is 0, nitrogen is doubly bonded to carbon in A;

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl of one to four carbon atoms; phenyl; and may be joined together to form a six membered aromatic benzene ring and R_3 is hydrogen, alkyl of one to four carbon atoms or phenyl.

3. The bath of claim **2,** wherein X is —S—.

4. The bath of claim **2,** wherein X is —N—R_3.

5. The bath of claim **2,** wherein A is —C—S—(R_3).

6. The bath of claim **2,** wherein R_3 is hydrogen.

7. The bath of claim **2,** wherein the third nitrogen heterocyclic compound is amino benzothiazole.

8. The bath of claim **2,** wherein the third nitrogen heterocyclic compound is an amino-2-mercaptobenzothiazole.

9. The bath of claim **1,** wherein to produce the multiple quaternary compound, the imine is reacted with a compound of the formula;

$$X - R - N^+ (R')_3 X^-$$

wherein R is selected from the group consisting of alkylene and hydroxy substituted alkylene; R′ is independently selected from the group consisting of hydrogen, alkyl, aryl, aralkyl and the hydroxy or halo derivatives thereof; and X is halogen.

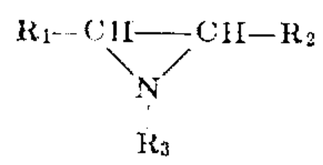
10. The bath of claim **9,** wherein R is a hydroxy substituted alkylene.

11. The bath of claim **10,** wherein R contains up to three carbon atoms.

12. The bath of claim **9,** wherein R is —CH_2—CH(OH) CH_2—.

13. The bath of claim **9,** wherein R′ is alkyl of one to four carbon atoms.

14. The bath of claim **9,** wherein the imine is the polymerization product of a compound of the formula;



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen and alkyl of from one to three carbon atoms; and R_3 is independently selected from the group consisting of hydrogen, alkyl of from one to three carbon atoms, hydroxy alkyl of from one to three carbon atoms, cyano alkyl wherein the alkyl has from one to three carbon atoms and benzyl.

15. The bath of claim **1,** further comprising a second bath soluble quaternary nitrogen compound in the amount from about 0.005 g/l to about 5.0 g/l.

16. The bath of claim **15,** wherein the second nitrogen compound is a heterocyclic compound.

17. The bath of claim **16,** wherein the second quaternary compound is a pyridine compound present in an amount ranging from about 0.005 to about 5 grams per liter.

18. The bath of claim **17,** wherein the pyridine compound is quaternized by a benzyl chloride.

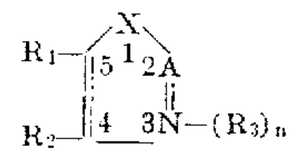
19. The bath of claim **1,** further comprising a zinc brightening agent containing an aldehyde group, said agent being present in an amount of between about 0.010 g/l to about 0.5 g/l.

20. The bath of claim **19,** wherein the aldehyde is anisaldehyde.

21. The bath of claim **1,** wherein the polyalkylene imine is polyethylene imine.

22. A method of depositing zinc from an alkaline zine electroplating bath, comprising passing an electric current from an anode through the bath of claim **1** to a cathodic workpiece for a period of time sufficient to form a zinc deposit.

23. The method of claim **22,** further comprising about 0.005 g/l to about 10 g/l of a third bath soluble nitrogen heterocyclic compound of the formula;



wherein X is —S— or NR; and

A is independently selected from the group consisting of —CN $(R_3)_2$; —C═S; ═C—R_3; —C═NR_3 and ═C—H;

n is 0 to 1; when n is 0, nitrogen is doubly bonded to carbon in A;

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl of one to four carbon atoms; phenyl; and may be jointed together to form a six membered aromatic benzene ring and R_3 is hydrogen, alkyl of one to four carbon atoms or phenyl.

24. The method of claim **23,** wherein X is —S—.

25. The method of claim **23,** wherein X is —N—R_3.

26. The method of claim **23,** wherein A is —C—S(R_3).

27. The method of claim **23,** wherein R_3 is hydrogen.

28. The method of claim **23,** wherein the nitrogen heterocyclic compound is amino benzothiazole.

29. The method of claim **23,** wherein the nitrogen heterocyclic compound is an amino-2-mercaptobenzothiazole.

30. The method of claim **22,** wherein the imine is reacted with a compound of the formula;

$$X - R - N^+ (R')_3 X^-$$

wherein R is selected from the group consisting of alkylene, and hydroxy substituted alkylene; R′ is independently selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, and the hydroxy or halo substituted derivative thereof; and wherein X is a halogen.

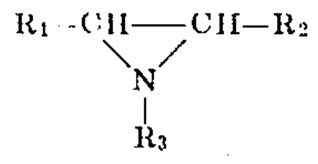
31. The method of claim **30,** wherein R is a hydroxy substituted alkylene.

32. The method of claim **30,** wherein R contains up to three carbon atoms.

33. The method of claim **30,** wherein R is —CH_2—CH(OH) CH_2—.

34. The method of claim **30,** wherein R′ is alkyl or one to four carbon atoms.

35. The method of claim **30,** wherein the imine is the polymerization product of a compound of the formula;



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen and alkyl of from one to three carbon atoms; and R_3 is independently selected from the group consisting of hydrogen, alkyl of from one to three carbon atoms, hydroxy alkyl of from one to three carbon atoms, cyanoalkyl wherein the alkyl has from one to three carbon atoms and benzyl.

36. The method of claim **22,** further comprising a second bath soluble quarternary nitrogen compound in the amount from about 0.005 g/l to about 5.0 g/l.

37. The method of claim **36,** wherein the quaternary compound is a pyridine compound present in an amount ranging from about 0.005 to about 5 grams per liter.

38. The method of claim **37,** wherein the pyridine compound is quaternized by a benzyl chloride.

39. The method of claim **36,** wherein the second nitrogen compound is a heterocyclic compound.

40. The method of claim **22,** further comprising a zinc brightening agent containing an aldehyde group, said agent being present in an amount of between about 0.010 g/l to about 0.5 g/l.

41. The method of claim **40,** wherein the aldehyde is anisaldehyde.

42. The method of claim **22,** wherein the polyalkylene imine is polyethylene imine.

* * * * *