

United States Patent

Kampe

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[54] **ALKALINE BRIGHT ZINC
ELECTROPLATING**

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

[51] Int. Cl. **C23b 5/12, C23b 5/46**

[58] Field of Search **204/55 R, 55 Y, 43, 44, 114; 106/1; 117/130 E**

[56] **References Cited**

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[57] **ABSTRACT**

Bright zinc is electrodeposited from alkaline zinc electrodepositing baths comprising an alkaline solution containing a source of zinc ions and an effective amount, as a brightening agent, of a bath-soluble reaction product obtained by the reaction of a nitrogen-containing heterocyclic compound with an acyclic amine having at least two functional groups separated by at least one different group, formaldehyde, and an epihalohydrin or a glycerol chlorohydrin.

26 Claims, No Drawings

ALKALINE BRIGHT ZINC ELECTROPLATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to alkaline zinc electrodepositing and more particular to new alkaline bright zinc electrodepositing baths and to the electrodeposition of bright zinc therefrom. Additionally this invention is directed to novel compositions and particularly compositions especially well suited as brightener additives for alkaline zinc electrodepositing baths.

2. Description of the Prior Art

Electrodeposition of zinc from alkaline cyanide zinc electroplating baths containing as a brightener additive a reaction product of hexamethylenetetramine with epichlorohydrin or alpha-chloroglycerol is disclosed in the prior art. Bright zinc has also been disclosed in the prior art as electrodeposited from cyanide zinc electroplating baths containing as brightener additive polyvinyl alcohol and a soluble reaction product of epichlorohydrin with ammonia or a primary amine.

The electrodeposition of bright zinc from a cyanide-free alkaline bath containing an alkanolamine, hexamethylenetetramine, or a mixture thereof is also known to the prior art.

SUMMARY OF THE INVENTION

In accordance with the present invention, I have found that bright zinc can be electrodeposited from alkaline non-cyanide and cyanide zinc electrodepositing baths comprising an alkaline solution containing a source of zinc ions and an effective amount, as a brightening agent, of a bath-soluble reaction product obtained by the reaction of a nitrogen-containing heterocyclic compound with an acyclic aliphatic primary amine containing two or more functional groups separated by one or more different groups or atoms, formaldehyde, and an epihalohydrin wherein the halogen atom is chloro or bromo or a glycerol chlorohydrin. The cyanide zinc electrodepositing bath can be a low cyanide content or a full or high cyanide content bath. The reaction product brighteners of this invention attained in the zinc electrodeposits a considerably enhanced brightening effect, range of brightness, or both, over the use of other reaction products as additives to the zinc electrodepositing baths as is shown by test data herein after set forth.

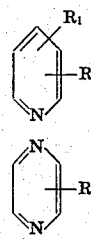
The compositions of this invention especially well suited as a brightener additive for the alkaline zinc electrodepositing baths comprise a mixture of the reaction product of the nitrogen-containing heterocyclic compound with the primary amine having two or more functional groups, formaldehyde, and the epihalohydrin or glycerol chlorohydrin, and a liquid diluent therefor. Usually the brightener additive of this invention comprises a solution of such reaction product in a liquid aqueous solvent.

It is unnecessary to recover the reaction product of this invention from the aqueous reaction product mixture, and the reaction product of this invention is utilizable as or in the brightener additive composition of this invention when in solution in the liquid diluent or solvent of the reaction mixture or mass. Other constituents can be added to the brightener additive composition, if desired, such as the brighteners and other additives of the prior art hereinafter disclosed.

The reaction product brightener herein is added to the alkaline cyanide or non-cyanide zinc electrodepositing baths herein in a minor amount, sufficient to impart brightness to the electrodeposited zinc. The reaction product brightener is usually added to the alkaline zinc electrodepositing baths herein in amount within the range of 0.1 - 10 g/l.

The nitrogen-containing heterocyclic compound reactant for forming the soluble reaction product brightener is a monocyclic or bicyclic heterocyclic compound and is usually of the formulae

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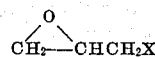


or a quinoline, wherein R is hydrogen, methyl, chloro, bromo, amino, cyano, vinyl, propanol or —COOM wherein M is hydrogen or a hydrophilic cation, for example an alkali metal, e.g. Na⁺ or K⁺, cation, R₁ is hydrogen or amino with the proviso that when R₁ is amino R is methyl, and R₂ is hydrogen, methyl or —COOM wherein M is hydrogen or a hydrophilic cation, for example an alkali metal, e.g. Na⁺ or K⁺, cation.

The acyclic amine reactant for forming the soluble reaction product brightener can be any acyclic aliphatic amine having two or more functional groups. Thus primary, secondary and tertiary amines are utilizable as the amine reactant so long as the amine has two or more functional groups. The two or more functional groups, for example —OH and —NH₂ groups, are separated by one or more different groups or atoms in the amine molecule. Exemplary of the amine reactant are monoethanolamine, diethanolamine, triethylenetriamine, tetraethylenepentamine, triethanolamine, ethylenediamine and diethylenetriamine. The functional groups in the amines enumerated immediately supra include the —NH₂, —OH, and —NH groups. By "functional group" as used herein in referring to the amine reactant having at least two functional groups is meant a group or radical capable of reacting with another reactant, group or radical in the reaction mixture, such as by an addition reaction or a condensation reaction, under the reaction conditions of the invention. It is essential that the acyclic amine reactant herein have two or more functional groups so as to be capable of forming the relatively large molecules or polymers which constitute the reaction product brightener herein.

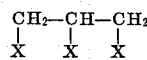
The formaldehyde reactant is conveniently utilized herein in aqueous solution, for instance as an aqueous formaldehyde solution of 37 percent formaldehyde concentration and obtainable in commerce as formalin.

The epihalohydrin reactant for forming the soluble reaction product brightener herein will usually be of the formula



wherein X is chloro or bromo. Such compounds include epichlorohydrin and epibromohydrin.

The glycerol chlorohydrin reactant will usually be of the formula:



wherein at least one but not more than two X's are hydroxy and the remaining non-hydroxy X's are chloro. Such reactant includes glycerol- α -chlorohydrin, i.e. 3-chloro-1, 2-propanediol; asym-glycerol dichlorohydrin, i.e. 2, 3-dichloro-1-propanol; and sym-glycerol dichlorohydrin, i.e. 1, 3-dichloro-2-propanol.

In the compositions of this invention which are well suited for use as brightener additives for alkaline zinc electrodepositing baths, the amount of reaction product brightener in the aqueous diluent is not especially critical and can be varied over wide limits. With lesser concentrations of the reaction product in the solutions, more of the solution can be added to the zinc electrodepositing bath if required than when greater concentrations of the reaction product. As previously disclosed herein, such brightener additive composition is ordinarily the reaction product mixture or mass taken as such from the reactor, and without recovery of the reaction product from the mixture.

Brighteners and other additive agents well known in the

prior art for cyanide zinc electroplating baths are utilizable in the non-cyanide and cyanide alkaline zinc electrodepositing baths herein together with the reaction product brightener of this invention. These prior art brighteners and addition agents including agents for inhibiting void formation and surface active agents can be added separately to the zinc electrodepositing bath or may be added as a constituent of the compositions of the present invention. When present in such additive compositions of this invention, the prior art brightener or additive can be present therein in any suitable amount. Such prior art brighteners and addition agents include, for example, aromatic aldehydes, e.g. piperonal, anisic aldehyde, vanillin, salicylaldehyde, polyvinyl alcohol, modified polyvinyl alcohol, e.g. oxidized polyvinyl alcohol, gelatin, polyether alcohols, polyesters, glue and peptone.

The reaction temperature for forming the soluble reaction product brightener herein can be room temperature. Broadly the reaction temperature can be from room temperature to reflux temperature of the reaction mixture inclusive. Higher temperature up to and including reflux temperature speed up the reaction whereas lower temperatures and room temperature require longer reaction times for formation of the reaction product.

The proportions of the reactants are not especially critical and can be varied over broad ranges.

The reaction time to yield the soluble reaction product brightener is, as is hereinbefore disclosed, dependent on the particular reaction temperature employed with room temperature reacting requiring considerably longer times, as long as 12 hours, then elevated temperatures of 60° C. and up to reflux temperature which require typically about 1-2 hours to yield the reaction product brightener.

The reaction product brightener herein is light brown to dark brown in color, and soluble in water and in the alkaline zinc electroplating baths herein. Under certain conditions, the reaction product herein may have a reddish coloration or tint in its brown color. When the reaction product is concentrated by expelling the water from the reaction product mass or mixture, the reaction product herein is a viscous semi-solid or solid.

That the reactants have reacted to form the reaction product brightener of this invention is evidenced by the evolution of heat by the exothermic reactions, a color change in the reaction mixture with the color thereof changing from a water white to a light brown to dark brown color, and the fact the the epichlorohydrin, which is initially insoluble in and suspended in the aqueous diluent, passes into solution in the aqueous diluent after reacting.

The reactants can all be mixed together and reacted together in the mixture, or they can be reacted together following a preferred sequence of adding reactants to the reactor as is hereinafter disclosed.

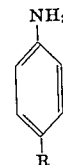
The reactants herein are reacted together to form the reaction product brightener in the presence of an aqueous liquid diluent, for example water, an aqueous solution of a 1-3 C alkanol, e.g. methanol, ethanol or propanol. When water is the diluent, which is usually the case, the water includes that contributed by the formalin as well as that contributed by any aqueous solution of another reactant or reactants, for instance an aqueous solution of the primary amine, and also the water formed by condensation reactions occurring. The amount of aqueous diluent can be varied over a wide range and the amount of water in or as the diluent is not especially critical except that when epichlorohydrin and monoethanolamine are reactants, an amount of water is utilized which is sufficient to prevent the explosive reaction of the epichlorohydrin in the presence of the monoethanolamine. The water does not appear to be an inert diluent when an epihalohydrin, for instance epichlorohydrin is a reactant, inasmuch as it is believed that the water reacts with the epichlorohydrin to open up the epoxy ring to result in two hydroxyl groups in addition to the chlorine atom.

The source of zinc ions in the aqueous alkaline electrodepositing baths herein can be zinc cyanide, $Zn(CN)_2$,

and/or an alkali metal zincate such as sodium zincate, Na_2ZnO_2 , or potassium zincate, K_2ZnO_2 , in the cyanide baths, and an alkali metal zincate such as sodium zincate or potassium zincate in the non-cyanide baths herein. The cyanide and non-cyanide alkaline baths also contain an alkaline material, usually an alkali metal hydroxide, e.g. sodium or potassium hydroxide, with the zinc-containing compound dissolved in the aqueous alkaline solution. An alkali metal carbonate, e.g. sodium or potassium carbonate may also be a constituent of the cyanide and non-cyanide alkaline baths herein.

The electrodepositing of the bright or semi-bright zinc in accordance with the invention is carried out by passing a DC electrical current, from an anode or anodes through the alkaline non-cyanide or cyanide zinc electroplating bath solution containing the reaction product brightener of this invention to a cathode or cathodes which is the article or articles or objects on which the zinc is to be electrodeposited. The electrodepositing can be carried out at room temperature and at temperatures above room temperature up to about 50° C. Current densities of 1-200 amps/sq. ft. are typically utilized. The anode or anodes may be conventional anodes well known in the art.

An aromatic amine of the formula



wherein R is -H, -NH₂ or -OH can also be a reactant herein for forming the reaction product brightener when added together with gamma picoline as the nitrogen-containing heterocyclic compound reactant. Such aromatic amine of the formula immediately supra includes aniline and p-phenylenediamine. The other reactants, viz. the acyclic amine having at least two functional groups, formaldehyde, and the epihalohydrin or glycerol halohydrin, are also reactants when such aromatic amine is utilized as a reactant together with the gamma picoline as reactant. The ratio of the aromatic amine of the formula supra to the gamma picoline as reactants is not especially critical and can be varied over a broad range.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred amine having two or more functional groups as reactant herein is monoethanolamine.

When an epihalohydrin, for instance epichlorohydrin is a reactant, the amount of water utilized in or as the aqueous diluent is preferably at least equimolar with the epichlorohydrin, more preferably a moderate or large excess of water over such equimolar amount, for instance about 600 percent excess of water over such equimolar amount.

Preferably the bath-soluble reaction product brightener herein is obtained or prepared by slowly adding an aqueous formaldehyde solution of 37 percent formaldehyde concentration known as formalin to a mixture of the amine having two or more functional groups, preferably monoethanolamine, the nitrogen-containing heterocyclic compound, and the aqueous diluent while agitating the liquid mixture. Such slow or gradual addition of the aqueous formaldehyde solution is usually over a period of about 15 to about 30 minutes. Exothermic heat is liberated during the formaldehyde addition and it may or may not be necessary to cool the reaction mixture to about room temperature or slightly above room temperature prior to the addition of the epihalohydrin. If cooling is required prior to the epihalohydrin addition, the cooling may be effected by indirect heat exchange of the reaction mixture with a fluid coolant, for instance by cooling water circulating through the jacket of a jacketed reactor, or, if desired, the cooling can be effected by simply allowing the reaction mixture to cool to about room temperature or slightly thereabove. The epihalohydrin, preferably epichlorohydrin is slowly added to the resulting liquid mixture, usually over a

period of about 20 to about 60 minutes, while agitating the mixture. Exothermic heat is liberated during the epihalohydrin addition with an attendant rise in temperature of the reaction mixture to about reflux temperature. Then refluxing of the thus-obtained reaction mixture is started and maintained or simply maintained if already started by application of heat from an outside or external heat source. Refluxing of the thus-obtained reaction mixture is carried out for a period of at least about 20 minutes, usually in the range of about 20 to about 45 minutes.

The reactants are preferably reacted to form the reaction product brightener in proportions within the molar ranges of about 0.5 - 1.5 mole of the amine having two of more functional groups, about 0.1 - 0.3 mole nitrogen-containing heterocyclic compound, about 1.0 - 3.0 moles formaldehyde, and about 0.5 - 1.5 mole epihalohydrin or glycerol chlorohydrin.

The reaction product brightener of this invention is preferably added to the alkaline cyanide or non-cyanide zinc electrodepositing baths herein in amount within the range of 0.1 - 5 g/l.

Zinc plating tests were separately carried out in alkaline non-cyanide, low cyanide and full or high cyanide content zinc electroplating baths to zinc plate Hull test panels. The plating was carried out in the Hull cell with the Hull cell panel in each test run connected as cathode in the bath. The operating conditions for the Hull cell were an operating current of 1-5 amps, usually 2 amps, room temperature of the bath, and a plating time of 5 minutes. A reaction product brightener of this invention prepared as hereafter disclosed and utilizing as the nitrogen-containing heterocyclic compound reactant for each test run that nitrogen-containing heterocyclic compound specified in the Table I hereinafter set forth was added in amount of about 1 c.c. to an alkaline zinc electroplating bath of one of the following compositions:

Zinc(oz./gal.)	Non-Cyanide Bath	Low Cyanide Bath	High Cyanide Bath
	1.0	0.98	4.7

Sodium hydroxide (oz./gal.)	10.1	10.0	11.6
Water	267 ml.	267 ml.	267 ml.

As indicated, certain of the baths were non-cyanide, i.e. were free of cyanide; certain of the baths were low cyanide baths containing 1 oz/gal. of sodium cyanide; and certain of the baths were full cyanide baths, i.e. high cyanide content baths, containing 12.7 oz/gal. of sodium cyanide.

The reaction product brightener was prepared by the following procedure:

Fifty (50) ml. water was added to a reaction vessel equipped with a reflux condenser. 31.5 g. (approximately 0.5 mole) monoethanolamine, and 6.0 g. (0.1 mole) isopropanol were added to the water in the reaction vessel. The mixture was stirred and the particular nitrogen-containing heterocyclic compound in the amount specified in Table I hereinafter was added thereto. Sixty (60.0) g. (approximately 0.75 mole) aqueous 37 percent formaldehyde was then added to the mixture in the reaction vessel while stirring the mixture, and the reaction mixture cooled to near room temperature. Forty-six (46.0) g. (0.5 mole) epichlorohydrin was then slowly added to the mixture in the reaction vessel with stirring of the mixture during such addition. The epichlorohydrin was added to the mixture over an approximately 60 minute period. The resulting reaction mixture was then refluxed for ½ hour, cooled and stored in a container.

In the Table I of test results which follows, "H cd" means a high current density of 40-100 amp/ft²; "M cd" means a middle current density of 20 amp/ft² up to 40 amp/ft²; and "L cd" means a low current density of slightly above 0 and up to 20 amp/ft². Also in the following Table I, "L-H cd" means in the low, middle and high current density ranges as set forth immediately above, "H-M cd" means in the high and middle current density ranges set forth immediately above; "M-L cd" means in the middle and low current density ranges set forth immediately above. In the Table I which follows, "Br" means a bright zinc electrodeposit, "F Br" means a fairly bright zinc electrodeposit but not as bright as "Br," "V Br" means a very bright zinc electrodeposit of a higher degree of brightness than "Br," and "Dul" as the word implies means a zinc electrodeposit substantially entirely lacking in brightness.

TABLE I

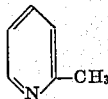
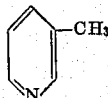

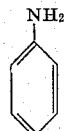
Test Run Number	Particular nitrogen containing heterocyclic compound reactant	Amount of nitrogen containing heterocyclic compound reactant utilized, mole/0.5 ml. of epichlorohydrin	Non-cyanide zinc plating bath	Low-cyanide zinc plating bath	High cyanide zinc plating bath
1	Alpha-picoline 	0.1 mole	Br, H cd	F, Br, L-H cd	F, Br, L-H cd.
2	Same as above	0.05 mole	F, Br, H-M cd	F, Br, L-H cd	F, Br, L-H cd.
3	do	0.21 mole	Br, H-M cd	Br, M cd	F, Br, M-L cd.
4	do	0.05 mole	Br, H-M cd	F, Br, L-H cd	F, Br, L and H cd.
5	Beta-picoline 	0.1 mole	F, Br, L cd	F, Br, H-L cd	F, Br, M-L cd
6	Gamma-picoline 	0.1 mole	V, Br, H-M cd	Br, H-M cd	Br, M cd
7	Gamma-picoline and aniline 	0.1 mole and 0.1 mole	F, Br, M-L cd	F, Br, L-H cd	F, Br, M cd.

Table I—Continued

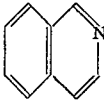
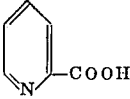
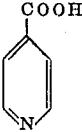
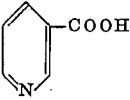

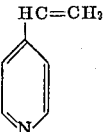


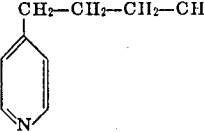
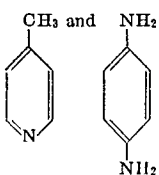
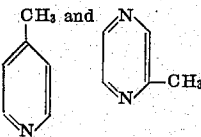
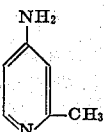
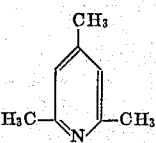
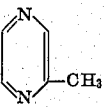
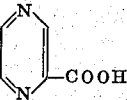
Test Run Number	Particular nitrogen containing heterocyclic compound reactant	Amount of nitrogen containing heterocyclic compound reactant utilized, mole/0.5 ml. of epichlorohydrin	Non-cyanide zinc plating bath	Low-cyanide zinc plating bath	High cyanide zinc plating bath
8.....	Isoquinoline..... 	0.05 mole.....	V, Br, M cd	Br, H-L cd	Br, H-L cd.
9.....	Same as above.....	0.05 mole.....	Br, H-L cd	Br, H-L cd	F, Br, M-L cd.
10.....	Picolinic acid..... 	0.1 mole.....	Dull, H-L cd	F, Br, H-L cd	F, Br, M-L cd.
11.....	Isonicotinic acid..... 	0.1 mole.....	Dull, H-L cd	F, Br, H-L cd	F, Br, H-L cd
12.....	Nicotinic acid..... 	0.1 mole.....	Br, H-L cd	Br, H-L cd	V, Br, H-L cd
13.....	Condensation reaction product of monoethanolamine, formaldehyde and epichlorohydrin.	Does not apply.....	F, Br, L cd	Dull, H-L cd	Dull, H-L cd
14.....	Pyridine 	0.1 mole.....	Dull, H-L cd	F, Br, H-L cd	F, Br, H-L cd
15.....	4-vinylpyridine 	0.1 mole.....	V, Br, H-M cd	Br, M-L cd	Br, M-L cd
16.....	4-cyanopyridine 	0.1 mole.....	Dull, H-L cd	F, Br, H-L cd	F, Br, H-L cd
17.....	2-chloropyridine 	0.1 mole.....	F, Br, M-L cd	F, Br, H-L cd	F, Br, M-L cd
18.....	4-propanolpyridine 	0.1 mole.....	Br, H-L cd	Br, H-L cd	Br, H-L cd
19.....	Gamma-picoline and para-phenylenediamine 	0.1 mole and 0.05 mole.....	V, Br, M cd	V, Br, H-M cd	Br, M cd

Table I—Continued

Test Run Number	Particular nitrogen containing heterocyclic compound reactant	Amount of nitrogen containing heterocyclic compound reactant utilized, mole/0.5 ml. of epichlorohydrin	Non-cyanide zinc plating bath	Low-cyanide zinc plating bath	High cyanide zinc plating bath
20.....	Same as above.....	0.08 mole and 0.025 mole.....	V, Br, M cd	Br, H-L cd	Br, M-L cd
21.....	Gamma-picoline and 2-methylpyrazine 	0.08 mole and 0.07 mole.....	V, Br, M cd	F, Br, H cd	Br, H-M cd
22.....	4-picolyamine 	0.1 mole.....	Br, M cd	Br, M-L cd	Br, H-M cd
23.....	2,4,6-collidine 	0.1 mole.....	Dull, H-L cd	Dull, H-L cd	Dull, H-L cd
24.....	2-methylpyrazine 	0.1 mole.....	Br, H-L cd	Br, H-L cd	F, Br, H-L cd
25.....	2-pyrazinecarboxylic acid 	0.1 mole.....	Dull, H-L cd	F, Br, H-L cd	F, Br, H-L cd

The good results in brightness of the electrodeposited zinc obtained utilizing the reaction product brighteners of this invention in the zinc electrodepositing baths is shown by the test results of Table I.

Additional zinc plating tests were carried out to evaluate various reaction products as brightener additives to non-cyanide, low cyanide, and full or high cyanide zinc electroplating baths. Test Runs No.'s 26-38 which follow are concerned with electroplating of zinc from non-cyanide, i.e. cyanide-free, alkaline zinc electrodepositing baths, Test Runs No.'s 39-55 which follow relate to electroplating of zinc from low cyanide content alkaline zinc electrodepositing baths, and Test Runs No.'s 56-67 also which follow are concerned with electroplating of zinc from full cyanide, i.e. high cyanide content, alkaline zinc electrodepositing baths.

The reaction product brightener for the zinc electrodepositing baths of Test Runs No.'s 26-67 hereafter set forth was prepared by combining with water 0.5 mole of the particular amine having two or more functional groups and 0.1 mole isopropanol. When a nitrogen-containing heterocyclic compound was a reactant, 0.1 mole of nicotinic acid or 0.1 mole of gamma picoline was mixed together with the aqueous mixture of the amine and isopropanol. 0.75 mole formaldehyde in aqueous solution of 37 percent formaldehyde concentration was then stirred into the thus-obtained mixture, and the resulting mixture allowed to cool to room temperature. Epichlorohydrin in the amount of 0.5 mole, or 0.5 mole of glycerol dichlorohydrin or monochlorohydrin when such reactant was used was then added slowly to mixture while stirring the mixture vigorously at room temperature for 30 minutes. The thus obtained mixture was refluxed for 30 minutes and then permitted to cool.

TEST RUN NO. 26

45 Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of 1 1/2 ml., ml. was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

50 The zinc electrodeposit on the Hull test panel was semibright in the range of about 8-15 amps/ft², and bright in the range of slightly above 0 to about 8 amps/ft².

TEST RUN NO. 27

55 Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of 1 1/2 ml., was added to an alkaline non-cyanide zinc electroplating bath of the same composition as in Test Run No. 26 in a 267 ml. Hull test cell.

60 The zinc electrodeposit on the Hull test panel was semibright in the range of about 4-37 amps/ft² and bright in the range of slightly above 0 up to about 4 amps/ft².

TEST RUN NO. 28

65 Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and gamma-picoline, in amount of 1 ml., was added to an alkaline non-cyanide zinc electroplating bath of the same composition as in Test Run No. 26 in a 267 ml. Hull test cell.

75 The zinc electrodeposit on the Hull test panel was semibright in the range of about 55-85 amps/ft².

11

TEST RUN NO. 29

Reaction product of triethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of 1 ½ ml., was added to an alkaline non-cyanide zinc electroplating bath of the same composition as in Test Run No. 26 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was semibright in the range of slightly above 0 up to about 4 amps/ft².

TEST RUN NO. 30

Reaction product of triethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of 1 ½ ml., was added to an alkaline non-cyanide zinc electroplating bath of the same composition as in Test Run No. 26 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 14–100 amps/ft².

TEST RUN NO. 31

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 32

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of slightly above 0 to 98 amps/ft².

TEST RUN NO. 33

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ¼ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was semibright in the range of slightly above 0 to about 62 amps/ft².

TEST RUN NO. 34

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of ¼ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of slightly above 0 to about 60 amps/ft².

TEST RUN NO. 35

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, and glycerol dichlorohydrin, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was dull in the range of from 0 to about 20 amps/ft², and was a burnt, dark deposit in the range of about 20 to 100 amps/ft².

12

TEST RUN NO. 36

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol dichlorohydrin and γ -picoline, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was semibright in the range of about 12 to about 40 amps/ft².

TEST RUN NO. 37

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, and glycerol monochlorohydrin, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was dull in the range of 0 to about 35 amps/ft², and a burnt, dark deposit in the range of about 35 to 100 amps/ft².

TEST RUN NO. 38

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol monochlorohydrin, and nicotinic acid in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath containing 0.99 oz./gal. Zn and 9.4 oz./gal. NaOH in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 10 to about 48 amps/ft².

That the reaction product brightener of the present invention considerably enhanced the brightening effect, the range of brightness, or both of the zinc electrodeposited from the cyanide-free zinc plating bath is shown by Test Runs No. 27, 28, 30–34, 36 and 38 wherein the plating baths contained the reaction product brightener of the invention as compared with Test Runs 26, 29, 35 and 37 wherein the baths contained as additive a reaction product not of the present invention.

TEST RUN NO. 39

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of 1 ml., was added to an alkaline, aqueous low cyanide zinc electroplating bath containing 1.09 oz./gal. Zn, 9.8 oz./gal. NaOH and 1.08 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was semibright and had an unsatisfactory cloudy appearance over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 40

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of 1 ½ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 41

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of ¼ ml., was added to an alkaline, low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 42

Reaction product of triethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of 1 ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test Cell.

The zinc electrodeposit on the Hull test panel was semi-bright over the range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 43

Reaction product of triethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of 1 ½ ml., was added to an alkaline, aqueous non-cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 10-90 amps/ft².

TEST RUN NO. 44

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright over the range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 45

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 46

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was semi-bright over the range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 47

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 20-100 amps/ft².

TEST RUN NO. 48

Reaction product of triallylamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was cloudy over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 49

Reaction product of triallylamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and

γ -picoline, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 2-40 amps/ft².

TEST RUN NO. 50

Reaction product of diethylenetriamine, aqueous formaldehyde of 37 percent formaldehyde concentration and epichlorohydrin, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was dull in the range of about 5-94 amps/ft², and semi-bright in the range of about 94-100 amps/ft².

TEST RUN NO. 51

Reaction product of diethylenetriamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ¼ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was semi-bright in the range of about 36-87 amps/ft², and bright in the range of about 87-100 amps/ft².

TEST RUN NO. 52

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol dichlorohydrin and nicotinic acid, in amount of 1 ½ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 53

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol dichlorohydrin and γ -picoline, in amount of 1 ½ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull Test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 54

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol monochlorohydrin, and γ -picoline, in amount of 1 ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 8 to 100 amps/ft².

TEST RUN NO. 55

Reaction product of ethylene diamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol monochlorohydrin, and nicotinic acid, in amount of 1 ½ ml., was added to the alkaline low cyanide zinc electroplating bath of the same composition as in Test Run No. 39 in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 6 to about 93 amps/ft².

A comparison of the zinc deposits from the low cyanide plating baths of Test Run No.'s 40, 41, 43-45, 47, 49 and 51-55 containing a reaction product brightener of the invention with the zinc deposits from the low cyanide baths of Test Run No.'s 39, 42, 46, 48 and 50 containing as additive a reac-

tion product not of the present invention, evidences the considerable increase in brightening effect, range of brightness, or both provided by the reaction product brighteners of the present invention.

TEST RUN NO. 56

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 57

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin, and γ -picoline, in amount of ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright in the range of about 2–100 amps/ft². It did not plate in the range of slightly above 0 to 2 amps/ft².

TEST RUN NO. 58

Reaction product of triethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, and epichlorohydrin, in amount of 1 ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was cloudy in the range of slightly above 0 to about 7 amps/ft² and bright in the range of about 7–100 amps/ft².

TEST RUN NO. 59

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 60

Reaction product of hexamethylenetetramine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of ¼ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps. ft² although a cloud was present in the deposit.

TEST RUN NO. 61

Reaction product of ethylene diamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and nicotinic acid, in amount of ¼ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range from slightly above 0 to 100 amps/ft².

TEST RUN NO. 62

Reaction product of ethylenediamine, aqueous formaldehyde of 37 percent formaldehyde concentration, epichlorohydrin and γ -picoline, in amount of ¼ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 63

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol dichlorohydrin and nicotinic acid, in amount of 1 ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 64

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol dichlorohydrin and γ -picoline, in amount of 1 ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 65

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol monochlorohydrin, and nicotinic acid, in amount of ¼ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 66

Reaction product of monoethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, glycerol monochlorohydrin, and γ -picoline, in amount of ¼ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was bright over the entire range of slightly above 0 to 100 amps/ft².

TEST RUN NO. 67

Reaction product of diethanolamine, aqueous formaldehyde of 37 percent formaldehyde concentration, and epichlorohydrin, in amount of ½ ml., was added to an alkaline aqueous full or high cyanide zinc electroplating bath containing 4.5 oz./gal. Zn, 10.3 oz./gal. NaOH and 13.4 oz./gal. NaCN in a 267 ml. Hull test cell.

The zinc electrodeposit on the Hull test panel was cloudy in the range of from slightly above 0 to about 4 amps/ft² and bright in the range of about 4 to 100 amps/ft².

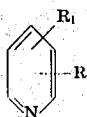
The Test Runs No. 's 56, 57, 59–66 show the good brightness and wide range of brightness provided by full cyanide, i.e. high cyanide content, alkaline zinc electrodepositing baths containing reaction product brighteners of the invention. The zinc deposits provided by the full cyanide zinc electrodepositing baths of Test Runs No. 58 and 67 containing as additive a reaction product not of this invention were bright over a narrower range than were zinc deposits from full cyanide electrodepositing baths containing reaction product brighteners of the present invention.

The term "low cyanide" content used herein with reference to the alkaline zinc cyanide electrodepositing bath means such a bath with a total cyanide content of up to 2.0 oz./gal. The terms "full cyanide" content or "high cyanide" content used herein in referring to the alkaline zinc electrodepositing bath means such a bath with a total cyanide content of 10.0 oz./gal. or higher.

What is claimed is:

1. An aqueous alkaline zinc electrodepositing bath comprising an aqueous alkaline solution containing a source of zinc ions and an effective amount, sufficient to yield a bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of a nitrogen heterocyclic compound with an acyclic amine having at least two functional groups, formaldehyde, and an epihalohydrin wherein the halogen is chloro or bromo or a glycerol chlorohydrin at a reaction temperature of from room temperature to reflux temperature inclusive.

2. The bath of claim 1 wherein the bath is a low cyanide content bath having a total cyanide content of up to 2.0 oz./gal. and wherein the nitrogen heterocyclic compound is of the formula

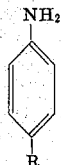


wherein R is hydrogen, methyl, chloro, bromo, amino, cyano, vinyl, hydroxypropyl or $-\text{COOM}$ wherein M is hydrogen or a hydrophilic cation and R_1 is hydrogen or amino with the proviso that when R_1 is amino R is methyl.

3. The bath of claim 2 wherein the nitrogen heterocyclic compound is a picoline.

4. The bath of claim 3 wherein the picoline is γ -picoline.

5. The bath of claim 4 wherein an additional reactant is reacted with the other reactants to form the bath-soluble reaction product, said additional reactant being an aromatic amine of the formula



wherein R is $-\text{H}$, $-\text{NH}_2$ or $-\text{OH}$.

6. The bath of claim 5 wherein the R is $-\text{NH}_2$.

7. The bath of claim 2 wherein the nitrogen heterocyclic compound is a pyridine monocarboxylic acid.

8. The bath of claim 7 wherein the pyridine carboxylic acid is nicotinic acid.

9. The bath of claim 2 wherein the nitrogen heterocyclic compound is 4-picolyamine.

10. The bath of claim 2 wherein the nitrogen heterocyclic compound is 2-chloropyridine.

11. The bath of claim 2 wherein the nitrogen heterocyclic compound is 4-vinylpyridine.

12. The bath of claim 1 wherein the bath-soluble reaction product is obtained by the reaction of the nitrogen heterocyclic compound with the amine having at least two functional groups, formaldehyde, and the epihalohydrin.

13. The bath of claim 12 wherein the epihalohydrin is epichlorohydrin and the bath-soluble reaction product is obtained by slowly adding an aqueous formaldehyde solution to a mixture of the amine having at least two functional groups, the nitrogen heterocyclic compound and an aqueous diluent while agitating the mixture, slowly adding the epichlorohydrin to the thus-obtained mixture while agitating the mixture whereby exothermic heat is liberated during the epichlorohydrin addition with an attendant rise in temperature of the mixture to about its reflux temperature, and reflux-

ing the resulting mixture for a period of at least about 20 minutes.

14. The bath of claim 1 wherein the nitrogen heterocyclic compound is a quinoline.

15. The bath of claim 14 wherein the quinoline is isoquinoline.

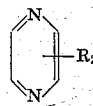
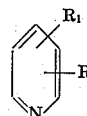
16. The bath of claim 1 wherein the bath is free of cyanide, the nitrogen heterocyclic compound reactant is selected from the groups consisting of α -, β - and γ -picolines, nicotinic acid, vinylpyridines, halopyridines wherein the halogen is chloro or bromo, picolyamines, methylpyrazines and quinolines; and the amine reactant having at least two functional groups is selected from the groups consisting of mono-, di- and triethanolamine, hexamethylenediamine, hexamethylenetetramine, ethylenediamine, diethylenetriamine and tetraethylenepentamine.

17. The non-cyanide bath of claim 16 wherein the nitrogen heterocyclic compound is selected from the group consisting of γ -picoline, nicotinic acid, 4-vinylpyridine, 2-chloropyridine, 4-picolyamine, 2-methylpyrazine and isoquinoline.

18. The bath of claim 1 wherein the nitrogen heterocyclic compound is 2-methyl pyrazine.

19. The bath of claim 1 wherein the nitrogen heterocyclic compound is γ -picoline and 2-methylpyrazine.

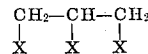
20. An aqueous alkaline zinc electrodepositing bath comprising an aqueous alkaline solution containing a source of zinc ions and an effective amount, sufficient to yield a bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of a nitrogen heterocyclic compound selected from the group consisting of those of the formulae:



and a quinoline, wherein R is hydrogen, methyl, chloro, bromo, amino, cyano, vinyl, hydroxypropyl or $-\text{COOM}$ wherein M is hydrogen or a hydrophilic cation, R_1 is hydrogen or amino with the proviso that when R_1 is amino R is methyl, and R_2 is hydrogen, methyl or $-\text{COOM}$ wherein M is hydrogen or a hydrophilic cation with an acyclic amine having at least two functional groups, formaldehyde, and an epihalohydrin of the formula



wherein X is chloro or bromo or a glycerol chlorohydrin of the formula



wherein at least one but not more than two X's is hydroxy and the remaining non hydroxy X's are chloro at a reaction temperature of from room temperature to reflux temperature inclusive, the reactants being reacted in proportions within the molar ranges of about 0.1-0.3 mole of the nitrogen heterocyclic compound, about 0.5-1.5 mole of the amine having at least two functional groups, about 1.0-3.0 moles of the formaldehyde, and about 0.5-1.5 mole of the epihalohydrin or glycerol chlorohydrin.

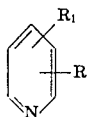
21. The bath of claim 20 wherein the amine having at least two functional groups is monoethanolamine.

22. The bath of claim 21 wherein the epihalohydrin is epichlorohydrin.

23. The bath of claim 22 wherein the bath is a low cyanide content bath having a total cyanide content of up to 2.0

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oz./gal. and the nitrogen heterocyclic compound is of the formula



wherein R is hydrogen, methyl, chloro, bromo, amino, cyano, vinyl, hydroxypropyl or —COOM wherein M is hydrogen or a hydrophilic cation and R₁ is hydrogen or amino with the proviso that when R₁ is amino R is methyl.

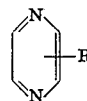
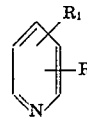
24. A method for the electrodeposition of bright zinc which comprises electrodepositing the zinc from an aqueous alkaline zinc electrodepositing bath comprising an aqueous alkaline solution containing a source of zinc ions and an effective amount, sufficient to yield a bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of a nitrogen heterocyclic compound with an acyclic amine having at least two functional groups, formaldehyde, and an epihalohydrin wherein the halogen atom is chloro or bromo or a glycerol chlorohydrin at a reaction temperature of from room temperature to reflux temperature inclusive.

25. The method of claim 24 wherein the epihalohydrin is epichlorohydrin, and the bath-soluble reaction product is obtained by slowly adding an aqueous formaldehyde solution to a mixture of the amine having at least two functional groups, the nitrogen heterocyclic compound and an aqueous diluent while agitating the mixture, slowly adding the epichlorohydrin to the thus-obtained mixture while agitating the mixture whereby exothermic heat is liberated during the epichlorohydrin addition with an attendant rise in temperature of the mixture to about its reflux temperature, and refluxing the resulting mixture for a period of at least about 20 minutes.

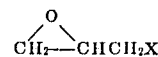
26. A method for the electrodeposition of bright zinc which comprises electrodepositing the zinc from an aqueous alkaline zinc electrodepositing bath comprising an aqueous alkaline solution containing a source of zinc ions and an effective amount, sufficient to yield a bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of a

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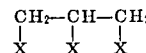
nitrogen heterocyclic compound selected from the group consisting of those of the formulae



and a quinoline wherein R is hydrogen, methyl, chloro, bromo, amino, cyano, vinyl, hydroxypropyl or —COOM wherein M is hydrogen or a hydrophilic cation, R₁ is hydrogen or amino with the proviso that when R₁ is amino R is methyl, and R₂ is hydrogen, methyl or —COOM wherein M is hydrogen or a hydrophilic cation with an acyclic amine having at least two functional groups, formaldehyde, and an epihalohydrin of the formula



wherein X is chloro or bromo or a glycerol chlorohydrin of the formula



wherein at least one but not more than two X's is hydroxy and the remaining non hydroxy X's are chloro at a reaction temperature of from room temperature to reflux temperature inclusive, the reactants being reacted in proportions within the molar ranges of about 0.1–0.3 mole of the nitrogen heterocyclic compound, about 0.5–1.5 mole of the amine having at least two functional groups, about 1.0–3.0 moles of the formaldehyde, and about 0.5–1.5 mole of the epihalohydrin or glycerol chlorohydrin.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,534 Dated April 11, 1972

Inventor(s) Marcis M. Kampe

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

Column 3, line 46, "the" (second occurrence) should read --that--. In TABLE 1, wherever recited, "F, Br" should read --F Br--; wherever recited, "V, Br" should read --V Br--; Test Run Number 18, "CH₂-CH₂-CH₂-CH" should read --CH₂-CH₂-CH₂-OH--.



Column 10, line 47, "ml." (second occurrence) should be deleted.

Signed and sealed this 28th day of November 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents