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3,393,135

BRIGHT ZINC ELECTRO-PLATING

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7 Claims. (Cl. 204—55)

ABSTRACT OF THE DISCLOSURE

This invention concerns alkaline zinc cyanide electroplating enabling bright, lustrous zinc deposits without the necessity of a subsequent bright dipping, and involving the use as an addition agent in the electroplating bath of a bath-soluble polyethylenimine, preferably a soluble lower alkyl-substituted polyethylenimine wherein one or more of the hydrogen atoms is susbtituted by a 1–3C alkyl radical or a substitution derivative of such alkyl-substituted polyethylenimine wherein one or more of the alkyl hydrogens is substituted by a bath-compatible organic radical, for example the carboxyl, esterified carbonyl, aldehyde, acetyl, ether, carboxyl, or cyano radical, or the hydroxy or amino radical or group.

This invention relates to the art of electroplating zinc. It is particularly concerned with new zinc cyanide plating bath compositions, for plating metallic substrata or articles, for instance, those of steel or copper, and new addition agent compositions enabling the bath compositions to produce bright, lustrous zinc deposits without the necessity of subsequent bright dipping operations. This invention is also concerned with a new method for plating bright, lustrous zinc deposits.

Prior art commercial bright zinc cyanide plating baths are characterized by a distinct tendency to produce bright but yellowish, off-white deposits having an objectionable colored surface film. This defect can partially be offset by the use of multiple addition agents, which has numerous disadvantages, so it is general practice to remove this objectionable colored surface film with a bright dip. Such bright dips remove some zinc as well as the surface film and therefore are objectionable on this score as well as on the basis of their cost and the cost of an added operation and rinse in the finishing process.

Another fault inherent in zinc cyanide plating bath addition agents now in commercial use is bath instability which require frequent removal of such agents to maintain optimum operating plating bath composition. In addition, most of these agents produce objectionable bath contaminants as products of their oxidation, hydrolysis, polymerization or decomposition—thus requiring frequent bath purification to remove such contaminants.

One object of this invention is to provide new and improved alkaline zinc cyanide plating bath compositions which produce on metallic substrates or articles bright, lustrous, while, unstained and uncolored zinc deposits, without the requirements of a subsequent bright dipping treatment.

Another object of this invention is to provide new addition agent compositions for alkaline zinc cyanide plating baths and which enable the production of the bright, lustrous, white, unstained and uncolored zinc deposits without subsequent bright dipping operations.

A further object is to provide a new and improved method for electroplating bright, lustrous zinc on metallic substrates or articles.

Additional objects and advantages will be readily apparent as the invention is hereinafter described in detail.

The addition agents of my invention produce white, bright, unstained zinc deposits directly from the zinc

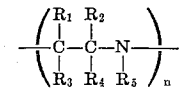
cyanide plating bath, thus eliminating the need for using a subsequent bright dip, thereby preserving all the zinc deposited on the base metal surface as a protection against corrosion.

The new and improved alkaline zinc cyanide plating bath of this invention is provided by adding to the prior alkaline zinc cyanide plating baths a minor amount of a bath-soluble, unsubstituted or lower alkyl-substituted polyethylenimine or a derivative of the last-mentioned lower alkyl-substituted polyethylenimine wherein one or more alkyl hydrogens is substituted by a bath-compatible organic radical as hereinafter disclosed, either in solid form or as a solution in a bath-compatible inert liquid solvent. These bath-soluble, unsubstituted or lower alkyl-substituted polyethylenimines and derivatives thereof are designated and referred to herein by the generic term "a bath-soluble polyethylenimine" or "polyethylenimine."

The polyethylenimine of the addition agent composition of the present invention is soluble and stable in alkaline zinc cyanide plating baths, thus contributing greatly to both stability and economy of operation; and such addition agent compositions greatly improve the overall throwing power of the plating bath as well as the covering power in low current density areas, thus providing superior corrosion protection for such areas as well as greater uniformity of deposit thickness on all areas being plated.

The polyethylenimine which I prefer to use is a lower alkyl-substituted polyethylenimine, that is, a polyethylenimine in which one or more of the hydrogens is substituted by a lower alkyl, i.e., a 1-3C alkyl, radical such as methyl, ethyl, n-propyl or isopropyl, and including their substitution derivatives in which one or more alkyl hydrogens is substituted by a bath-compatible organic radical such as, for example, carboxyl, esterified carboxyl, aldehyde, acetyl, ether, carbonyl, and other bath-compatible organic radicals, the hydroxy or amino radicals, either singly or in combination, the important consideration being that the polyalkylethylenimine is sufficiently soluble in the plating bath to be effective as an addition agent.

The polyethylenimine additive herein is characterized by a molecular structure made up of a plurality of repeating units of the formula:



in which R_1, R_2, R_3, R_4, and R_5 are from the group of hydrogen, lower alkyl radicals, i.e., methyl, ethyl, n-propyl or isopropyl and their substitution derivatives wherein one or more alkyl hydrogen is substituted by the bath-compatible organic radical as previously disclosed herein, and n is an integer of within the range generally about 5–300, preferably about 5–265. The value of n can be varied to control the molecular weight of the polymer so as to provide within the range aforesaid maximum effective addition agent action at various current densities as desired, as well as the bath solubility of the compound. The actual value of n in any instance will also depend on the nature of the substituent R groups, some of which contribute to the solubility of the polymer, while others detract therefrom. The actual composition of any specific addition agent will therefore be determined by the R groups, and the value of n, so balanced as to secure the addition agent effect desired and required bath solubility. The polyethylenimine additive herein has a molecular weight of preferably 1,000–50,000.

The polyethylenimine used is a minor amount, sufficient to impart brightness to the electrodeposited zinc and to improve throwing power of the bath as well as covering

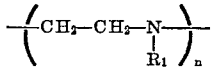
power in low current density areas. Such amount will vary depending on the structure of the polyethylenimine, its solubility, the bath composition and results desired, but will generally be small in amounts ranging from about 0.004 to about 0.1 oz./gallon of bath for optimum results. In general, the actual amount used is not critical since bath solubility is usually the limiting factor.

The unsubstituted polyethylenimine herein is obtainable in commerce. The substituted polyethylenimines herein are obtained by contacting the monomer in aqueous solution at normal temperature with either HCl, H_2SO_4, $AlCl_3$, H_3PO_4 or CO_2 as catalyst, whereby polymerization is effected to obtain the polyethylenimine. The substituted ethylenimine monomers for preparation of the substituted polyethylenimines are prepared in accordance with the preparation procedure set forth, in the following publications.

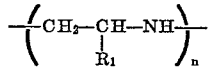
(1) H. Ulrich & W. Harz (to I. G. Farben Industrie), U.S. Pat. 2,182,306 (1939)
(2) G. D. Jones et al., J. Org. Chem., 9, 125–147 (1944)
(3) Funke & Benoit, Bull. Soc. Chem. Fr. 5, 20, 1021–3 (1953)
(4) Dornow & Schacht, Ber. 82, 464 (1949)
(5) Bestian, Ann. 566, 210–244 (1950)
(6) Chance et al., Text, Res. J., 30, 305–311 (1960)
(7) Houben-Weyl (Engen Miller, Ed.) "Methoden der Organischen Chemie," 4th Ed., vol. 11/2, pp. 227–265, G. Thieme, Stuttgart (1958)
(8) Le Breque, "Studies With Three Alkylating Agents as Housefly Sterilants," paper presented before Entomological Soc. of Amer. November 1960; see also Chem. Wk. p. 95, Mar. 18, 1961.

The following specific types of polyloweralkylethylenimines are cited as examples of my new and novel addition agents for zinc cyanide electroplating baths. R_1, R_2, R_3, R_4, and R_5 in such compounds and n have the meaning previously disclosed herein.

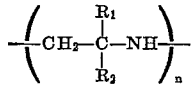
(1) Poly-N-loweralkylethylenimines



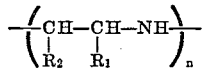
(2) Poly-2-loweralkylethylenimines



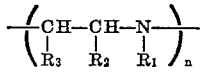
(3) Poly-2,2-di-loweralkylethylenimines



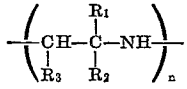
(4) Poly-2,3-di-loweralkylethylenimines



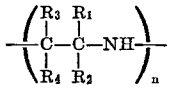
(5) Poly-1,2,3-tri-loweralkylethylenimines



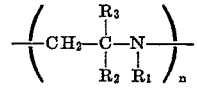
(6) Poly-2,2,3-tri-loweralkylethylenimines



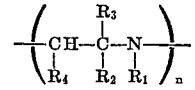
(7) Poly-2,2,3,3-tetraloweralkylethylenimines



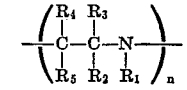
(8) Poly-1,2,2-tri-loweralkylethylenimines



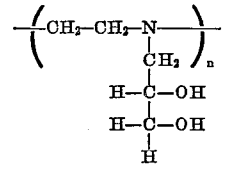
(9) Poly-1,2,2,3-tetra-loweralkylethylenimines



(10) Poly-1,2,2,3,3-penta-loweralkylethylenimines

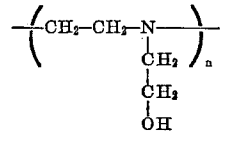


(11) Poly-N (polyhydroxy-loweralkyl) ethylenimines

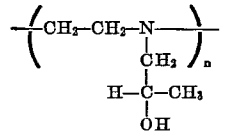


(12) Poly-N-hydroxy-loweralkylethylenimines

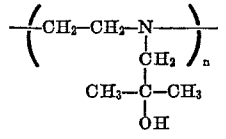
(a)



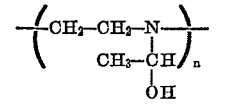
(b)



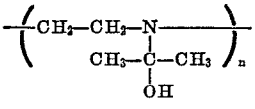
(c)



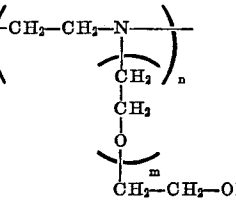
(d)



(e)

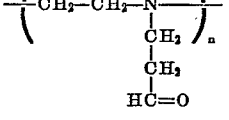


(13) Poly-N-(polyethylene ether) ethylenimines



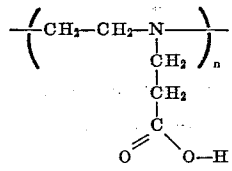
Ethylene oxide derivatives of (1) above wherein m is 1–5.

(14) Poly-N-loweralkylaldehydeethylenimines

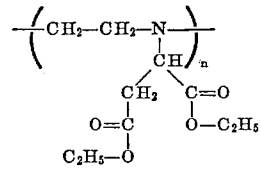


(15) Poly-N-(propionic acid) ethylenimines

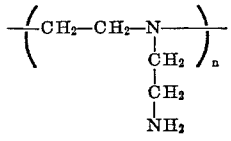
(a)



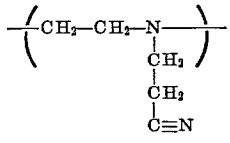
(b)



(16) Poly-N-(loweralkylamino) ethylenimines



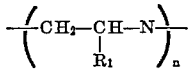
(17) Poly-N-loweralkylcyanoethylenimines



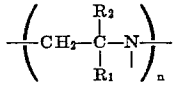
(18) Substitution derivatives of the polyethylenimine compounds in Examples 11 to 17 inclusive wherein one or more of the hydrogens of the ethylenimine unit portion of the molecule is substituted by a 1-3C alkyl.

The ethylene portion of the repeating units can have any of the following structures:

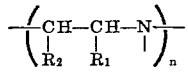
(a) Poly-2-loweralkyl



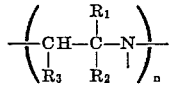
(b) Poly-2,2-di-loweralkyl



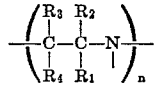
(c) Poly-2,3-di-loweralkyl



(d) Poly-2,2,3-tri-loweralkyl



(e) Poly-2,2,3,3-tetra-loweralkyl



While my new polyalkylethylenimine addition agents are effective in any operable commercial aqueous zinc cyanide plating bath formulation, I may cite the following specific example as one preferred embodiment of my invention.

Bath composition

Zinc cyanide—$Zn(CN)_2$—67.5 grams/l.=9 oz./gal.
Sodium cyanide—NaCN—45.0 grams/l.=6 oz./gal.

Sodium hydroxide—NaOH—82.5 grams/l.=11 oz./gal.
Poly-N-hydroxyethylethylenimine—0.075–0.3 grams/l.= .01–.04 oz./gal.

Operating conditions for plating with the bath

Temperature ° F	80
Cathode current density amps./sq. ft	5–30

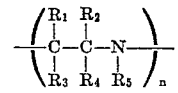
The poly-N-hydroxyethylethylenimine addition agent of the bath composition set forth immediately supra has a molecular weight of about 30,000.

The addition agent composition of this invention is preferably added to the zinc plating bath as an aqueous solution. The concentration of the solution may vary throughout substantially the solubility range of the polyethylenimine with typical concentration of the polyethylenimine in water being 1–50 weight percent of the polyethylenimine.

What is claimed is:

1. In an aqueous alkaline zinc cyanide electroplating bath the improvement which comprises having present in the bath a minor amount, sufficient to impart brightness to electrodeposited zinc, of a bath-soluble polyethylenimine.

2. The plating bath of claim 1 wherein the polyethylenimine is a lower alkyl-substituted polyethylenimine selected from the group consisting of those having a molecular structure made up of a plurality of repeating units of the formula:



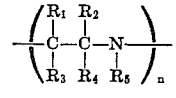
wherein at least one of R_1, R_2, R_3, R_4 and R_5 is a 1-3C alkyl radical and any remaining non-alkyl R is hydrogen, and substitution derivatives thereof wherein one or more alkyl hydrogens is substituted by a radical selected from the group consisting of a bath-compatible organic radical, hydroxy and amino radicals, and *n* is an integer of about 5–265.

3. The alkaline zinc cyanide plating bath composition of claim 2 containing from about 0.004 to about 0.1 oz./gallon of the polyethylenimine.

4. The plating bath of claim 2 wherein the bath-compatible organic radical of the substitution derivative is selected from the group consisting of carboxyl, esterified carboxyl, aldehyde, acetyl, ether, carbonyl and cyano radicals.

5. In a method for the electroplating of zinc, the improvement whereby a bright, lustrous, unstained zinc electrodeposit free of an objectionable colored surface film is obtained without the requirement of a subsequent bright dipping operation which comprises effecting the electroplating of the zinc from an aqueous alkaline zinc cyanide electroplating bath composition containing a minor amount, sufficient to impart brightness to electrodeposited zinc, of a bath-soluble polyethylenimine.

6. The method of claim 5 wherein the polyethylenimine is a lower alkyl-substituted polyethylenimine selected from the group consisting of those having a molecular structure made up of a plurality of repeating units of the formula:



wherein at least one of R_1, R_2, R_3, R_4 and R_5 is a 1-3C alkyl radical and any remaining non-alkyl R is hydrogen, and substitution derivatives thereof wherein one or more alkyl hydrogens is substituted by a radical selected from the group consisting of a bath-compatible organic radical, hydroxy and amino radicals, and *n* is an integer of about 5–265.

7. The method of claim 6 wherein the bath-compatible organic radical of the substitution derivative is selected from the group consisting of carboxyl, esterified

carboxyl, aldehyde, acetyl, ether, carbonyl and cyano radicals.

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2,853,444	9/1958	Pye et al.	204—55 XR

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HOWARD S. WILLIAMS, *Examiner.*

G. KAPLAN, *Assistant Examiner.*

Disclaimer

3,393,135.—*William E. Rosenberg*, Parma, Ohio. BRIGHT ZINC ELECTROPLATING. Patent dated July 16, 1968. Disclaimer filed Dec. 16, 1968, by the assignee, *Enthone, Incorporated.*

Hereby enters this disclaimer to claims 1 and 5 of said patent.

[*Official Gazette April 29, 1969.*]