

SPECIFICATION

Ductile bright zinc electroplating bath and process

- 5 The present invention relates to an improved solution and process for electrodepositing bright zinc coatings. 5

It is known to employ zinc electroplating solutions for purposes of depositing corrosion resistant and decorative plating deposits upon a variety of substrates as exemplified by iron and steel. In order to enhance the brightness of the plating deposit, a variety of additive agents have previously been proposed or used. Typical of such brightening and/or additive agents are those disclosed in United States Patent Nos. 3,853,718, 3,974,045 and 4,045,306. It is conventional commercial practice to employ more than one such brightening agent in a zinc plating bath in order to attain the characteristics desired of the deposit. 10

A continuing problem associated with known zinc plating baths is the inability of the baths to produce consistently fully bright zinc deposits over broad operating pH ranges and over a broad range of current densities. Additionally, the deposition of a zinc plate of high ductility is also difficult to attain. 15

The zinc plating bath and process of the present invention overcomes many of the problems and disadvantages associated with prior art solutions and techniques by providing a zinc plating bath featuring a brightening agent which enhances the flexibility and versatility of the bath producing excellent fully bright zinc deposits over broad pH and current density ranges, while at the same time producing a zinc deposit which has excellent ductility characteristics. 20

The present invention can be used for a range of baths including alkaline cyanide-free zinc, alkaline cyanide zinc, and acid zinc including the sulphate, chloride and fluoroborate types, whereby exceptionally ductile plating deposits of full brightness are attached over a broad operating pH and current density range. The brightening agent comprises an aqueous bath soluble cationic alkylated condensation polymer obtained by alkylating a condensation polymer of an epihalohydrin and a heterocyclic compound containing at least 2 nitrogen atoms with a trialkyl ammonio-halo-alkyl halide salt such as 3-halo-2-hydroxy propyl trialkyl ammonium halide and 2-halo-ethyl-trialkyl ammonium halide, of which the chlorine halide derivatives are preferred. 25

The brightening agent of the present invention is advantageously employed either alone or in combination with one or more other brightening agents such as aromatic aldehydes, pyridine quaternaries, polyvinyl alcohols, polyethers, polyglycidols, ethoxylated naphthols or aromatic carbonyl compounds. 30

The improved brightening agent of the invention comprises a bath soluble cationic alkylated condensation polymer obtained by alkylation of a polymer which is the reaction product of an epihalohydrin compound and a heterocyclic compound having a five or six membered ring containing at least two nitrogen atoms, the ratio of epihalohydrin to heterocyclic compound being in the range of 0.5 to 1 mole: 1 mole, with an alkylating agent corresponding to the formula: 35



Wherein:

- 45 R represents a $-(CH_2-CH_2)-$ or a $(CH_2-CHOH-CH_2)-$ group, 45
R' represents an alkyl group of 1 to 4 carbons, and
X represents a Cl, Br or I atom,

the ratio of alkylating agent to heterocyclic compound being in the range 0.1 to 0.5 moles: 1 mole. The heterocyclic compound may comprise a 5 or 6 membered heterocyclic compound containing at least 2 nitrogen atoms in the ring and may additionally be substituted by amino groups, alkyl groups containing from 1 to 4 carbon atoms, carboxy groups, hydroxy groups, or carbonyl groups, such as acetyl groups. The substituents could also comprise a condensed aromatic ring system as in benzotriazole. Typical of the heterocyclic compounds which may be used to produce the brightening agent are those set forth in Table 1. 50

TABLE 1

imidazole	1,2,3-triazole	
2-methylimidazole	tetrazole	
60 2,4-dimethylimidazole	1,3,5-triazine	60
4-hydroxy-2-aminoimidazole	benzotriazole	
5-ethyl-4-hydroxyimidazole	tolyltriazole	
pyrazole		

- 65 The specific heterocyclic compound or mixture of heterocyclic compounds is reacted with an 65

epihalohydrin compound or mixtures thereof in a mole ratio of from about 0.5 up to about 1 mole epihalohydrin per mole of heterocyclic compound. While epibromohydrin and epiodohydrin can be employed, epichlorohydrin at present constitutes the preferred material. In accordance with a preferred embodiment of the present invention, the heterocyclic compound is utilized in a slight molar excess, whereby the resultant polymer has terminal heterocyclic groups which facilitate the subsequent alkylation reaction. Polymers comprising about 1 mole of heterocyclic compound and about 0.9 moles epihalohydrin are particularly preferred. The polymerization reaction is carried out in an aqueous medium at elevated temperatures up to about the boiling point of the solution with temperatures of from about 40°C up to about 95°C being suitable. Polymerization reaction times of from about one hour up to about 15 hours are usually adequate to produce the desired degree of polymerization.

An alkylating agent is added in an amount of about 0.1 up to about 0.5 moles per mole of heterocyclic compound to the resultant solution containing the condensation polymer. Particularly satisfactory results are obtained when the alkylating agent is employed in amounts of about 0.2 moles to 0.3 moles per mole of heterocyclic compound. The alkylating agent or quaternizing agent comprises a trialkyl ammonio-halo-alkyl halide compound having a structural formula as follows:



Wherein:

R represents a $-(CH_2-CH_2)-$ or $-(CH_2CHOHCH_2)-$ group,

R' represents an alkyl group of 1 to 4 carbons; and

X represents a Cl, Br or I atom.

Alkylating agents in which R comprises an ethyl group can generically be described as 2-haloethyl trialkyl ammonium halide while compounds in which R is 2-hydroxy propyl can be generically defined as 3-halo-2-hydroxy-propyl-trialkyl ammonium halide. Compounds in which the halogen is chlorine are preferred. A particularly satisfactory compound is 3-chloro-2-hydroxy-propyl trimethyl ammonium chloride.

The alkylation of the condensation polymer is performed by adding the alkylating agent to the aqueous reaction solution containing the polymer and continuing heating at the prescribed temperature for an additional period of time to complete alkylation. Alkylation reaction periods of from about one half hour up to about three hours are usually satisfactory.

In accordance with a preferred embodiment of the present invention, appropriate amounts of other brightening agents for example aromatic aldehydes, pyridine quaternaries, polyvinyl alcohols, polyethers, polyglycidols, exthoxylated naphthols, and aromatic carbonyl compounds may be admixed in appropriate amounts with the alkylated polymer to provide an optimum mixture of brighteners.

In the process of the present invention, the cationic alkylated polymer is added in controlled amounts to any one of a variety of zinc plating baths, either alone or in combination with additional conventional brighteners, thereby providing improved brightening effects in alkaline cyanide-free zinc, alkaline cyanide zinc, and acid zinc electroplating baths including the sulphate, chloride or fluoroborate types. The magnitude of brightness of the zinc deposit will vary somewhat depending upon the specific type of zinc plating bath in which the additive is used. Preferably, the cationic alkylated polymer is employed in concentrations of from about 0.001 g/l up to about 25.0 g/l.

The invention may be put into practice in various ways and a number of specific examples will be given to illustrate the invention; examples 1 to 4 being examples of the method of preparation of the brightener and Examples 5 to 11 being examples of electroplating baths incorporating the brightener.

EXAMPLE 1

A cationic alkylated polymer brightening agent was prepared by forming an aqueous solution containing 0.9 moles imidazole and 0.91 moles epichlorohydrin which was heated to a temperature of about 95°C for a period of 15 hours. Thereafter, 0.45 moles of 3-chloro-2-hydroxy-propyl-trimethyl ammonium chloride were added and heating of the reaction mixture was continued for an additional period of one hour to complete the alkylation reaction. The resultant reaction medium after cooling is diluted with water to a concentration of about 385 g/l to make a stock solution prior to use.

EXAMPLE 2

A cationic alkylated polymer brightener was prepared in accordance with the conditions and sequence of steps as described in Example 1 employing the following reactants:

Reactant	Moles
Imidazole—	1.0
Epichlorohydrin—	0.9
3-chloro-2-hydroxy propyl trimethyl ammonium chloride	0.2

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EXAMPLE 3

A cationic alkylated polymer brightener was prepared in a manner similar to that described in Example 1 employing the following reactants:

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Reactant	Moles
Pyrazole—	1.0
Epichlorohydrin—	0.9
3-chloro-2-hydroxypropyl trimethyl ammonium chloride	0.2

20

EXAMPLE 4

A cationic alkylated polymer brightener was prepared in accordance with the procedure described in Example 1 employing the following reactants:

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Reactant	Moles
Triazole—	1.0
Epichlorohydrin—	0.9
3-chloro-2-hydroxypropyl trimethyl ammonium chloride	0.2

35

EXAMPLE 5

An aqueous zinc electroplating solution was prepared incorporating the ingredients at the following concentrations:

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Ingredient	Concentration
Zn	7.5 g/l
NaOH	98 g/l
Brightener (Example 1)	1 g/l

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The brightener employed corresponded to the cationic alkylated polymer prepared in accordance with Example 1. The plating bath was operated at a pH of about 14 at a temperature of about 24°C in a standard Hull cell at two amperes. The test panel was observed to have a ductile and bright zinc deposit at current densities between 10 and 80 amps per square foot (ASF), (1.1 to 8.6 amps per square decimetre (ASD)).

EXAMPLE 6

A zinc plating solution was prepared incorporating the constituents in the concentrations as set forth below:

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Ingredient	Concentration
5 Zn (from Zn SO ₄)	75 g/l
H ₃ BO ₃	22.5 g/l
Brightener (Example 1)	20 mg/l

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- 10 The solution has a pH of 4.5 and a test panel was plated at 60 ASF (6.5 ASD). The resultant panel was found to have a fully bright and ductile zinc deposit but was observed to have poor recessed coverage. The latter characteristic is typical of acid zinc sulphate solutions. 10

EXAMPLE 7

- 15 An aqueous zinc electroplating solution was prepared incorporating the ingredients in the concentrations as set forth below: 15

Ingredient	Concentration
20 Zn	18 g/l
NaOH	75 g/l
NaCN	45 g/l
Brightener (Example 1)	50 mg/l

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- 25 25

A steel test panel was plated in a Hull cell at two amperes and at a temperature of 26°C and a pH of greater than 13. The test panel was bright between 1-60 ASF (0.1 to 6.5 ASD).

- 30 **EXAMPLE 8** 30

An acid zinc chloride plating solution was prepared incorporating the ingredients in the concentrations as set forth below:

Ingredient	Concentration
35 Zn (from Zn Cl ₂)	35 g/l
Cl (from KCl or NH ₄ Cl)	165 g/l
Brightener (Example 1)	0.75 g/l

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- 40 40

A test panel was plated in the foregoing solution at a pH of 5.5 and at a current density of 40 ASF (4.3 ASD) and at a temperature of 21°C and a pH of 5.5. The test panel had a bright to semi-bright appearance.

- 45 45

EXAMPLE 9

An alkaline, cyanide-free zinc plating solution was prepared incorporating the following ingredients:

Ingredient	Concentration
50 Zn (from Zn O)	8.0 g/l
NaOH	85.0 g/l
55 Brightener (Example 4)	2.0 g/l

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- The solution was plated at a temperature of 22°C in a Hull cell at 2 amperes at a pH of greater than 13. The deposit is bright between 5-75 ASF (0.5 to 8.1 ASD) and is very ductile. 60
- To further illustrate the improved results achieved by the present invention, the following tests were conducted in pursuance of the teachings in Example 1 of U.S. Patent No. 3,954,575: 60

EXAMPLE 10

Ingredient	Concentration
5 Zn (from Zn O)	7.5 g/l
NaOH	75 g/l
Brightener (from USP 3,954,575)	1 g/l

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- 10 The plating bath is operated at a temperature of 24°C in a standard Hull cell at 2 amperes at a pH of greater than 13. The test panel was observed as having a cloudy, streaky and semi-bright appearance between 10–80 ASF (1.1 to 8.6 ASD) and dull dark appearance below 10 ASF (1.1 ASD). 10

15 EXAMPLE 11 15

Ingredient	Concentration
20 Zn (from ZnSO ₄)	75 g/l
H ₃ BO ₃	22.5 g/l
Brightener (from USP 3,954,575)	20 mg/l

20

- 25 The solution has a pH of about 4.5, and a test panel is plated in a Hull cell at 2 amperes. The panel was black and cloudy throughout its dimensions with relatively poor recess coverage below 10 ASF (1.1 ASD). The results should be compared to those of example 6 which differs only in the brightener. 25

30 CLAIMS 30

1. A brightener for aqueous zinc electroplating solutions comprising a bath soluble cationic alkylated condensation polymer obtained by alkylation of a polymer which is the reaction product of an epihalohydrin compound and a heterocyclic compound having a five or six membered ring containing at least two nitrogen atoms, the ratio of epihalohydrin to heterocyclic compound being in the range 0.5 to 1 mole: 1 mole, with an alkylating agent corresponding to the formula: 35



40 Wherein: 40

R represents a $-(CH_2-CH_2)-$ or a $-(CH_2-CHOH-CH_2)-$ group,
 R' represents an alkyl group of 1 to 4 carbons, and
 X represents a Cl, Br or I atom,

- 45 the ratio of alkylating agent to heterocyclic compound being in the range 0.1 to 0.5 moles: 1 mole. 45

2. A brightener as claimed in Claim 1 in which the heterocyclic compound is used in a molar excess relative to the epihalohydrin compound.

3. A brightener as claimed in Claim 1 or 2 in which, the said epihalohydrin is used in an amount of 0.9 moles and alkylating agent is used in an amount of 0.2 to 0.3 moles. 50

4. A brightener as claimed in Claim 1, 2 or 3 in which the epihalohydrin compound comprises epichlorohydrin.

5. A brightener as claimed in Claim 1, 2, 3 or 4 in which the alkylating agent comprises 3-chloro-2-hydroxy-propyl trimethyl ammonium chloride.

- 55 6. A brightener as claimed in any one of claims 1 to 5 as specifically described herein with reference to examples 1 to 4. 55

7. An aqueous zinc electroplating solution comprising zinc ions and an effective amount of a bath soluble cationic alkylated condensation polymer as claimed in any one of claims 1 to 6.

8. An aqueous zinc electroplating solution as claimed in Claim 7 which contains the bath soluble cationic alkylated condensation polymer in concentrations from 0.001 g/l to 25.0 g/l. 60

9. An aqueous zinc electroplating solution as claimed in Claim 7 or Claim 8 substantially as specifically described herein with reference to any one of examples 5 to 9.

10. A method of electrodepositing a bright zinc plating on a substrate which comprises electrodepositing zinc from an aqueous zinc plating solution as claimed Claim 7, 8 or 9.

- 65 11. A method of electrodepositing zinc as claimed in Claim 10 substantially as specifically 65



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- | Ingredient | Concentration |
|---------------------------------|---------------|
| 5 Zn (from Zn O) | 7.5 g/l |
| NaOH | 75 g/l |
| Brightener (from USP 3,954,575) | 1 g/l |
- 10 The plating bath is operated at a temperature of 24°C in a standard Hull cell at 2 amperes at a pH of greater than 13. The test panel was observed as having a cloudy, streaky and semi-bright appearance between 10–80 ASF (1.1 to 8.6 ASD) and dull dark appearance below 10 ASF (1.1 ASD).
- 15 **EXAMPLE 11**
- | Ingredient | Concentration |
|---------------------------------|---------------|
| 20 Zn (from ZnSO ₄) | 75 g/l |
| H ₃ BO ₃ | 22.5 g/l |
| Brightener (from USP 3,954,575) | 20 mg/l |
- 25 The solution has a pH of about 4.5, and a test panel is plated in a Hull cell at 2 amperes. The panel was black and cloudy throughout its dimensions with relatively poor recess coverage below 10 ASF (1.1 ASD). The results should be compared to those of example 6 which differs only in the brightener.
- 30 **CLAIMS**
1. A brightener for aqueous zinc electroplating solutions comprising a bath soluble cationic alkylated condensation polymer obtained by alkylation of a polymer which is the reaction product of an epihalohydrin compound and a heterocyclic compound having a five or six membered ring containing at least two nitrogen atoms, the ratio of epihalohydrin to heterocyclic compound being in the range 0.5 to 1 mole: 1 mole, with an alkylating agent corresponding to the formula:
- $$[X-R-N(R')_3]^+X^-$$
- 40 Wherein:
R represents a $-(CH_2-CH_2)-$ or a $-(CH_2-CHOH-CH_2)-$ group,
R' represents an alkyl group of 1 to 4 carbons, and
X represents a Cl, Br or I atom,
- 45 the ratio of alkylating agent to heterocyclic compound being in the range 0.1 to 0.5 moles: 1 mole.
2. A brightener as claimed in Claim 1 in which the heterocyclic compound is used in a molar excess relative to the epihalohydrin compound.
3. A brightener as claimed in Claim 1 or 2 in which, the said epihalohydrin is used in an amount of 0.9 moles and alkylating agent is used in an amount of 0.2 to 0.3 moles.
- 50 4. A brightener as claimed in Claim 1, 2 or 3 in which the epihalohydrin compound comprises epichlorohydrin.
5. A brightener as claimed in Claim 1 2, 3 or 4 in which the alkylating agent comprises 3-chloro-2-hydroxy-propyl trimethyl ammonium chloride.
- 55 6. A brightener as claimed in any one of claims 1 to 5 as specifically described herein with reference to examples 1 to 4.
7. An aqueous zinc electroplating solution comprising zinc ions and an effective amount of a bath soluble cationic alkylated condensation polymer as claimed in any one of claims 1 to 6.
8. An aqueous zinc electroplating solution as claimed in Claim 7 which contains the bath soluble cationic alkylated condensation polymer in concentrations from 0.001 g/l to 25.0 g/l.
- 60 9. An aqueous zinc electroplating solution as claimed in Claim 7 or Claim 8 substantially as specifically described herein with reference to any one of examples 5 to 9.
10. A method of electrodepositing a bright zinc plating on a substrate which comprises electrodepositing zinc from an aqueous zinc plating solution as claimed Claim 7, 8 or 9.
- 65 11. A method of electrodepositing zinc as claimed in Claim 10 substantially as specifically



described herein with reference to any one of Examples 5 to 9.

12. An article whenever provided with a zinc electrodeposit by a method as claimed in Claim 10 or Claim 11.

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