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(54) Zinc plating baths and additives therefor.

(57) An alkaline, cyanide-free zinc plating bath contains a betaine such as N-benzyl pyridinium betaine and a reaction product of an epihalohydrin and a heterocyclic nitrogen compound such as imidazole.

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1.

This invention relates to zinc plating baths and additives therefor and in particular alkaline aqueous plating baths for the electrodeposition of zinc.

Alkaline zinc plating baths used to contain cyanide and gave bright zinc deposits, but because of toxicity problems present day baths tend to be cyanide free, and these give less satisfactory deposits. Many additives have been proposed to improve the deposits from cyanide free alkaline zinc plating baths. Among these additives are aromatic aldehydes and ketones, polyalkylene glycols, polyamines, sulphones and sulphonates, polyphosphates, silicates, Group VI and Group VII metals and reaction products of a compound comprising a heterocyclic ring with at least 2 ring nitrogen atoms, and an epihalogenohydrin (see BP 1553265).

We have found that adding to an alkaline, preferably cyanide-free, zinc plating bath (a) a betaine containing a quaternary nitrogen atom and a carboxylic or sulphonic acid group and (b) a reaction product of an epihalohydrin with a heterocyclic compound containing a nitrogen ring atom can give a bath which may produce bright, ductile zinc deposits over a wide range of current densities.

Additives (a) and (b) appear to work together in a synergistic fashion since neither additive alone, when added to an alkaline cyanide free zinc plating bath, produces bright zinc deposits over a wide range of current densities.

Our invention therefore provides according to a first aspect a brightening composition for a zinc plating bath comprising (a) a betaine containing a quaternary nitrogen atom and a carboxylic or sulphonic acid group and (b) a reaction product of an epihalohydrin and a heterocyclic compound containing a nitrogen ring atom.

The betaine is an organic compound which is an internal salt having a zwitterionic, polar character so that it has a cationic

group and an anionic group within its molecule. The cationic group is a quaternary nitrogen atom. The anionic group is a carboxylic or sulphonic acid group which is joined to the quaternary nitrogen atom via at least one carbon atom and usually via a chain of up to six carbon atoms.

The quaternary nitrogen atom typically forms part of a five-membered or preferably six-membered heterocyclic ring which is usually unsaturated, preferably aromatic and may have two nitrogen ring atoms as in imidazolinium and pyrazinium compounds or preferably one nitrogen ring atom as in pyrrolium and pyridinium compounds, all other atoms in the heterocyclic ring being preferably carbon atoms. The betaine may contain attached to the heterocyclic ring, especially in a fused relationship thereto, a carbocyclic ring, preferably six-membered, especially unsaturated, e.g. an aromatic ring as in a betaine derived from benzimidazole or quinoxaline or more preferably from indole, quinoline or isoquinoline. It is preferred, however, that the betaine contain no ring other than the said heterocyclic ring. One or more carbon ring atoms in the betaine may each be substituted by a group such as: hydroxide; cyanide; amino or amido, optionally substituted by an alkyl group having from one to four carbon atoms; hydrazino or hydrazido; halide, e.g. bromide or chloride; alkyl, alkenyl or alkynyl, each preferably of 1-6 carbon atoms, e.g. methyl, ethyl, propyl, vinyl, or allyl; carboxylic acid; carboxylic ester of an alkyl group having from one to four carbon atoms. Preferred betaines are quaternary derivatives of pyridine compounds such as, for example, pyridine, 4-cyanopyridine, picolinic acid, 2-picoline, nicotinamide and butyl nicotinate.

The carboxylic or sulphonic acid group may be joined directly to a carbon ring atom either in the said heterocyclic ring or, less preferably, in any carbocyclic ring which may be attached thereto. Alternatively, the acid group may be a substituent in an alkyl group

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which is joined directly to the quaternary nitrogen atom. Examples of betaines which have the acid group joined to the heterocyclic ring at the quaternary nitrogen atom are isoquinoline N-betaine and indole N-propyl sulphobetaine. Preferred pyridinium betaines include propyl nicotinate N-betaine and 4-picoline N-butyl sulphobetaine. Instead of or in addition to the acid group there may be joined to the quaternary nitrogen atom a hydrocarbon group, generally a monovalent group such as an alkyl, alkenyl or alkynyl group usually having from one to four carbon atoms, e.g. methyl or allyl, an aralkyl group e.g. of 7 to 19 carbon atoms such as benzyl, or less preferably an aryl group e.g. an aromatic hydrocarbyl group of 6 to 18 carbon atoms such as phenyl. The hydrocarbon group may be a divalent group such as an alkylene or aralkylene group e.g. methylene or xylylene which joins two heterocyclic rings in a bis quaternary such as para-xylylene bis (pyridine 3-carboxylate). The hydrocarbon group may be unsubstituted or may be substituted by one or more groups such as alkyl or alkoxy having from one to four carbon atoms, phenyl, halogen, hydroxy and cyanide. Examples of monovalent optionally substituted hydrocarbon groups are 4-methyl benzyl, 4-chloro benzyl, allyl and propargyl. The acid group is generally joined to a carbon ring atom and is preferably joined at the 3- or 4- position, more preferably at the 3- position especially where the acid group is the only substituent on any carbon ring atom, particularly in a pyridinium betaine.

Pyridinium 4-sulphonates, pyridinium 4-carboxylates, especially pyridinium 3- sulphonates and more especially pyridinium 3- carboxylates are preferred, e.g. N-allyl pyridinium 3- carboxylate, N-ethyl pyridinium 3- carboxylate and N-(4-chloro benzyl) pyridinium 3-carboxylate. The most preferred compounds are N-methyl pyridinium 3-carboxylate and especially N-benzyl pyridinium 3-carboxylate.

The epihalohydrin may be epibromhydrin or preferably epichlorhydrin. The heterocyclic compound contains at least one nitrogen ring atom usually in a six-membered or preferably five-membered heterocyclic ring. The ring preferably contains at least two nitrogen ring atoms, usually two or three, especially two. The nitrogen ring atoms may be secondary or tertiary nitrogen atoms but preferably the ring contains at least one secondary nitrogen ring atom. More preferably it also contains at least one tertiary nitrogen ring atom. Aromatic heterocyclic compounds are preferred, which the nitrogen atom or atoms form part of the aromatic ring. The heterocyclic compound preferably consists of one six-membered or especially five-membered ring, optionally substituted by at least one group such as: hydroxide; halide, e.g. chloride; amino; alkoxy, alkanoyl or hydrocarbon such as alkyl, alkenyl or alkynyl usually having from one to four carbon atoms, e.g. ethoxy, acetyl, butyl, allyl. Examples of these substituted heterocyclic compounds are: 1,4-diethyl piperazine; 2,5-dimethyl piperazine; 1-acetyl pyrrole; 4-hydroxy, 2-amino imidazole. Less preferably the heterocyclic compound comprises in addition to one heterocyclic ring, also in a fused or unfused relationship thereto a carbocyclic ring or a second heterocyclic ring, preferably six-membered especially unsaturated, e.g. an aromatic ring containing up to two nitrogen heteroatoms, as in for example, purine, pteridine, benzimidazole and their derivatives.

The first or only heterocyclic ring preferably contains only carbon and nitrogen ring atoms but may also contain other ring atoms such as sulphur or oxygen, as in, for example 1,2,3 oxadiazole and benzothiadiazine. Examples of suitable heterocyclic compounds are triazines, triazoles, preferably diazines and more preferably diazoles such as imidazole and substituted imidazoles, such as: 1-methyl imidazole; 1-ethyl imidazole; 2-methyl imidazole; 1,4-dimethyl imidazole; 1-ethyl, 2-methyl imidazole; 1-oxymethyl imidazole (hydroxymethyl imidazole); 5-ethyl, 4-hydroxy imidazole;

1-vinyl imidazole. Other useful compounds are piperazine and substituted piperazines, e.g. piperazines with at least one hydrocarbon substituent such as 1,4-dimethyl piperazine.

The reaction product may be prepared, for example, by dissolving the heterocyclic compound in a solvent such as water, adding the epihalohydrin in a molar ratio of from 1:0.5 to 1:8, e.g. from 1:1 to 1:4 and allowing them to react at a temperature of from 40°C to the boiling point, e.g. from 50°C to 90°C, such as 70-85°C, for e.g. from 1 to 10 hours until reaction is complete. The resulting solution of reaction product may be used as such in compositions of our invention. There is no need to isolate the reaction product (b) from solution before adding the betaine (a) to it.

Compositions comprising mixtures of (a) and (b) in which the molar ratio of the betaine (a) to the heterocyclic compound used in preparing (b) is from 1:1 to 1:30, preferably from 1:4 to 1:25, such as from 1:6 to 1:20, e.g. from 1:7 to 1:14, are particularly effective as brightening agents for aqueous alkaline zinc plating baths. It is convenient to prepare such compositions as aqueous solutions by mixing an aqueous solution of (a) with an aqueous solution of (b) prepared by the method suggested above. The resulting aqueous composition preferably contains from 0.01 to 1 moles more preferably from 0.02 to 0.5 moles, especially from 0.04 to 0.2 moles of betaine (a) per litre of solution. It generally contains a quantity of reaction product (b) prepared from 0.01 to 10 moles, usually from 0.1 to 4 moles especially from 0.4 to 2 moles of heterocyclic compound per litre of solution.

According to a second aspect our invention provides an aqueous solution comprising from 0.01 to 1 mole per litre of solution of a betaine containing a quaternary nitrogen atom and a carboxylic or sulphonic acid group and a reaction product of an epihalohydrin with

a heterocyclic compound containing a nitrogen ring atom, the quantity of reaction product per litre of solution being derived from 0.01 to 10 moles heterocyclic compound in a ratio of from 1 to 30 moles of heterocyclic compound per mole of betaine.

The aqueous solution comprising betaine and reaction product may be used as a brightening agent for an aqueous alkaline zinc plating bath and will generally be added thereto in proportions of from 1 to 100 ml, e.g. from 2 to 25 ml of aqueous solution per litre of zinc plating bath. The aqueous solution preferably contains in addition polyvinyl alcohol in the proportions of from 1 to 100g per litre of aqueous solution.

According to a third aspect our invention provides an alkaline aqueous, preferably cyanide-free, zinc plating bath comprising (a) a betaine containing a quaternary nitrogen atom and a carboxylic or sulphonie acid group and (b) a reaction product of an epihalohydrin with a heterocyclic compound containing a nitrogen ring.

There is also provided in our invention a method of forming a zinc deposit on an article by electrodeposition thereupon from said alkaline aqueous zinc plating bath. Furthermore, there is provided by our invention an article comprising a zinc deposit produced by said method.

A bath of our invention will generally be operated under strongly alkaline conditions e.g. at a pH above 12 and preferably above 13. This pH is usually obtained by adding to water an alkali metal hydroxide such as potassium hydroxide or preferably sodium hydroxide in amounts such as to form aqueous solutions containing from 30 to 180g preferably from 60 to 130g of sodium hydroxide per litre of solution. A barrel plating bath usually contains slightly more sodium hydroxide per litre of solution than a rack plating bath. A barrel plating bath may, for example, contain from

90 to 130g e.g. 110g of sodium hydroxide per litre of solution and a rack plating bath may contain from 60 to 100g e.g. 80g of sodium hydroxide per litre of solution.

Zinc may be added to the bath in the form of a bath-soluble zinc compound such as zinc oxide or zinc hydroxide or, less preferably, a zinc salt such as zinc sulphate, or zinc metal. The bath will generally contain from 4 to 15g preferably from 6 to 13g of zinc per litre of solution. A barrel plating bath usually contains slightly more zinc per litre of solution than a rack plating bath. A barrel plating bath may, for example, contain from 9 to 13g e.g. 11g of zinc per litre of solution and a rack plating bath may contain from 6 to 10g e.g. 8g of zinc per litre of solution. The weight ratio of sodium hydroxide to zinc is usually from about 8:1 to about 12:1, preferably 10:1, in both barrel plating and rack plating baths.

The bath may contain from 2×10^{-5} to 10^{-2} moles preferably from 5×10^{-5} to 5×10^{-3} moles especially from 10^{-4} to 3×10^{-3} moles, e.g. from 2×10^{-4} to 10^{-3} moles of betaine (a) per litre of solution. Additive (b) may be present in concentrations per litre of solution prepared from 5×10^{-4} to 5×10^{-2} moles preferably from 8×10^{-4} to 3×10^{-2} moles especially from 10^{-3} to 2×10^{-2} moles, e.g. from 2×10^{-3} to 10^{-2} moles of heterocyclic compound. Additives (a) and (b) may be added separately, preferably in aqueous solution or mixed together especially in the form of an aqueous composition according to the second aspect of this invention.

An alkaline zinc plating bath may be produced by mixing water, zinc compound, sodium hydroxide and additives (a) and (b). A bath consisting of these components may generally be used to electrodeposit bright, ductile zinc over a wide range of current densities, up to 100 amperes per square foot (ASF) (11 A dm^{-2}), or even 150 ASF (17 A dm^{-2}). It is particularly useful over the range from 0.1 to 100 ASF (from 0.011 to 11 A dm^{-2}) and especially

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advantageous from 60 to 100 ASF (from 6.5 to 11 dm^{-2}). This extension of the bright plating range to current densities above 60 ASF (6.5A dm^{-2}) means that bright plated articles can be produced at higher average current densities and in shorter times. One advantage of this wide bright plating range is that there is usually no need to add any subsidiary brighteners, e.g. carbonyl compounds such as aromatic aldehydes with their problems of instability and breakdown products. Polyalkylene polyamines especially those of formula $\text{H}_2\text{N}-(\text{CH}_2)_n\text{NH}_x\text{H}$ where n is from 2 to 4 and x is from 8 to 150 are preferably substantially absent. The bath usually contains from 0.005 to 10 gram per litre of solution of polyvinyl alcohol to reduce the haziness of the bright zinc deposit. Complexants such as gluconate and ethylene diamine tetraacetic acid may optionally be present in concentrations of up to 1 gram of complexant per litre of solution.

A typical plating bath may be prepared by dissolving sodium hydroxide in water adding zinc oxide and diluting the solution to working concentrations with more water. Generally heavy metal contaminants will be removed from the bath before use by a conventional method e.g. by using the bath to electrodeposit at less than 10 ASF (1.1A dm^{-2}) for at least one ampere hour per litre of solution. An aqueous mixture of additives (a) and (b) in suitable proportions and generally mixed with polyvinyl alcohol may then be added and the bath may be used to electrodeposit bright, ductile zinc over a wide range of current densities.

The plating baths are used to plate articles having metal surfaces e.g. ferrous metal surfaces such as iron or steel or nonferrous metal surfaces such as zinc or brass surfaces.

The invention is illustrated by the following examples:-

Example 1

An aqueous solution of a reaction product (R) was prepared by mixing imidazole (0.18 moles) with water (70g) adding epichlorhydrin (0.33) moles and refluxing at 80°C for 4 hours.

An alkaline aqueous cyanide free zinc plating bath was prepared which had the following compositions per litre of solution:

8g	zinc added as zinc oxide;
80g	sodium hydroxide;
0.15g	N-benzyl pyridinium 3-carboxylate;
4ml	aqueous solution of reaction product (R) prepared above
0.1g	polyvinyl alcohol
	balance water

Heavy metal contaminants were removed by plating for 1 amp hour per litre. The bath was used to electrodeposit zinc on to a steel Hull cell panel at a current of 2A at 25°C for 10 minutes, and a bright ductile zinc deposit was obtained over the current density range from 0.1 to 150 ASF (from 0.011 to 17A dm⁻²).

Example 2 - Comparative example

a) A bath was prepared to the following formulation:-

8g Zinc added as zinc oxide
80g Sodium hydroxide
0.5ml N-benzyl pyridinium 3 carboxylic acid (30%
solution)
0.1g Polyvinyl Alcohol
1g Sodium gluconate
to 1 litre water.

The bath was prepared by dissolving the sodium hydroxide in 35% of the added water to give a hot concentrated solution. Zinc oxide was then added slowly with stirring and was readily soluble. The bath was cooled to 20°C, and the gluconate dissolved.

Heavy metal contaminants were removed by treatment at 20°C with 1 gpl zinc dust for 10 mins. followed by filtration. The polyvinyl alcohol was then added as a 10% solution in water, followed by the N-benzyl pyridinium 3 carboxylic acid. The bath was then made up to 1 litre with the remainder of the added water.

The bath was used to electrodeposit zinc on to a steel Hull Cell panel at a current of 3 amperes for 10 minutes, using a zinc anode.

The deposit was dark and burnt looking, and had no promise as a commercial bright zinc.

Increasing the amount to 2 ml of 30% solution had no improving effect.

- b) A similar bath was made up and purified in the same way, but the N-benzyl pyridinium 3 carboxylic acid was replaced by various amounts of the reaction product prepared in Example 1.

Results were as follows:-

2 ml/1 R bright deposit 2 - 20 ASF dull
below 2 ASF burn above 20 ASF.

3 ml/1 R bright deposit 2 - 30 ASF.

4 ml/1 R bright deposit 2 - 50 ASF.

This shows that neither constituent alone is capable of producing a bright deposit over an extended current density range (cf. Example 1).

Example 3

A steel component was thoroughly cleaned in an alkaline soap cleaner, rinsed, and etched in 50% v/v hydrochloric acid, rinsed and immersed in a zinc plating bath made up as in Example 1 for twenty minutes at an average current density of 20 ASF at 20°C to give deposit of approximately 8 microns. The deposit, after rinsing, was immersed in a proprietary blue passivation composition for 15 seconds to give a pleasing blue tint to the electrodeposited zinc.

After air-drying for twenty-four hours the component was heated in an oven at 150°C for ten minutes to test adhesion - no blistering was experienced.

CLAIMS

1. A brightening composition for a zinc plating bath comprising (a) a betaine containing a quaternary nitrogen atom and a carboxylic or sulphonic acid group and (b) a reaction product of an epihalohydrin with a heterocyclic compound containing a nitrogen ring atom.
2. A composition according to claim 1, wherein the molar proportion of (a) to said heterocyclic compound used to prepare (b) is from 1:1 to 1:30.
3. A composition according to either of claims 1 and 2 comprising an aqueous solution containing from 0.01 to 1 moles of (a) per litre and from 0.01 to 10 moles of (b) per litre.
4. A composition according to any foregoing claim wherein (a) comprises a five membered or six membered aromatic heterocyclic ring, wherein said quaternary nitrogen atom forms part of said ring and said carboxylic or sulphonic acid group is attached either to said ring or to an alkyl substituent joined directly to said quaternary nitrogen atom.
5. A composition according to any foregoing claim wherein (a) is a pyridinium carboxylate or pyridinium sulphonate.
6. A composition according to claim 5, wherein (a) is N-methyl pyridinium 3 carboxylate or N-benzyl pyridinium 3 carboxylate.
7. A composition according to any foregoing claim, wherein (b) is a reaction product of epichlorhydrin or epibromhydrin with a heterocyclic compound comprising at least one, five or six-membered aromatic heterocyclic ring and containing a total of two or three nitrogen atoms in said at least one ring.

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8. A composition according to claim 7, wherein (b) is a reaction product of epichlorhydrin with imidazole or a substituted imidazole.
9. An alkaline, aqueous, zinc plating bath comprising, as a brightener therefore, a composition according to any foregoing claim.
10. A bath according to claim 9 substantially free from cyanide.
11. A bath according to either of claims 9 and 10, comprising from 30 to 180 gms per litre sodium hydroxide, from 4 to 15 gm per litre dissolved zinc, from 2×10^{-5} to 10^{-2} moles of (a) and from 5×10^{-4} to 5×10^{-2} moles per litre of (b).
12. A method of electrodepositing zinc from a plating bath according to any of claims 9 to 11.
13. Plated articles having thereon a layer of zinc deposited by the method of claim 12.
14. A method for the preparation of compositions according to any one of claims 1 to 8, wherein said epichlorhydrin is added to an aqueous solution of said heterocyclic compound in a mole ratio of from 1:0.5 to 1:8, the solution is maintained at a temperature between 40°C and boiling point until reaction is substantially completed to form a solution of (b) and an aqueous solution of (a) is added to said solution of (b).
15. A method for the preparation of an electroplating bath according to any of claims 9 to 11, wherein zinc or an alkali solution zinc compound is mixed with water and sodium hydroxide, together with (a) and (b) either together or separately.



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>GB - A - 2 009 790</u> (M & T CHEMICALS INC.) + Claims + --	1,4-6, 9,10	C 25 D 3/22
	<u>GB - A - 1 394 637</u> (M & T CHEMICALS INC.) + Claims + --	1,4-6, 9,10	
	<u>GB - A - 1 381 939</u> (E.I. DU PONT DE NEMOURS AND COMPANY) + Claims + --	1,4-6, 9,10	TECHNICAL FIELDS SEARCHED (Int. Cl.)
	<u>US - A - 4 169 772</u> (R.K. LOWERY et al.) + Claims + --	1,7-10	C 25 D
	<u>US - A - 4 166 778</u> (S. ACIMOVIC et al.) + Claims + --	1,3-10	
	<u>US - A - 4 093 523</u> (J.A. HENRICKS et al.) + Claims + --	1,4-6, 9,10	CATEGORY OF CITED DOCUMENTS
	<u>US - A - 4 045 306</u> (G. SENGE et al.) + Claims + ----	1,7-10	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search		Date of completion of the search	Examiner
VIENNA		13-04-1981	SLAMA