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ALKALINE BRIGHT ZINC ELECTROPLATING

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ABSTRACT OF THE DISCLOSURE

Bright zinc is electrodeposited from alkaline noncyanide or 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 melamine with formaldehyde, an acyclic amine having two or more functional groups and an epihalohydrin or a glycerol chlorohydrin. The melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product is usually utilized as brightener in the alkaline zinc baths in combination with an aromatic aldehyde as an additional brightening agent.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to alkaline zinc electrodepositing and more particularly to alkaline zinc electrodepositing baths and to a method for electrodepositing bright zinc. Additionally this invention concerns compositions especially well adapted 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 hexethylenetetramine with epichlorohydrin or alpha-chloroglycerol is disclosed in U.S. Pat. 3,227,638. Electrodeposition of bright zinc from alkaline cyanide zinc plating baths containing as brightening agent a condensation polymer of an aliphatic alkylene polyamine with furfural-sodium bisulphite and formaldehyde in the presence or absence of formaldehyde-sodium bisulphite is disclosed in U.S. Pat. 2,680,712.

The use of an aromatic aldehyde such as veratraldehyde, anisic aldehyde, piperonal, vanillin or 2,4-dichlorobenzaldehyde together with an enzyme-degraded hydrolyzed meat protein as brightener additives in acid zinc electrodepositing baths is disclosed in U.S. Pat. 3,285,840.

SUMMARY OF THE INVENTION

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 brightener additive, of the bath-soluble reaction produce obtained by the reaction of melamine with formaldehyde, an acyclic amine having two or more functional groups, and an epihalohydrin or a glycerol chlorohydrin. The melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine- glycerol chlorohydrin reaction product as sole brightener additive imparts some brightness to the electrodeposits. However such reaction product is usually used in the electrodepositing baths in combination with another brightener additive, viz, an aromatic aldehyde, e.g. piperonal, anisic aldehyde, veratraldehyde, vanillin, hydroxybenzaldehyde and 2,4-dichlorobenzaldehyde, for the reason the combination of the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-

acylic amine-glycerol chlorohydrin reaction product and the aromatic aldehyde achieves a pronounced synergistic effect in yielding bright zinc electrodeposits. The alkaline zinc electrodepositing baths herein are non-cyanide baths or cyanide baths of any cyanide content including low, medium and high cyanide content baths. In the alkaline non-cyanide zinc electrodepositing baths at least, the combination of the melamine-formaldehyde-acyclic amine-eiphalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product and the aromatic aldehyde as brighteners resulted in zinc electrodeposits of a considerably enhanced or increased brightness over that obtained by addition to the bath of each such reaction product alone as brightener.

Although we do not wish to be bound by theory, the formation of the melamine-formaldehyde-acyclic amine-epihalohydrin reaction products herein appears to involve the formation of polymeric aminoalcohols. These long chain aminoalcohol units are believed cross-linked with the epihalohydrin units to form a polymer network.

The reaction temperature for forming the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product brightener or the melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product brightener is from room temperature to reflux temperature of the reaction mixture.

The reaction time is that sufficient to obtain the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product with the total reaction time usually being at least about 3–5 hours.

The amounts of melamine, formaldehyde, acyclic amine and epichalohydrin or glycerol chlorohydrin that are reacted together are not especially critical so long as the amount of melamine reacted is insufficient to result in excessive cross-linking with attendant insoluble gel formation.

The melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product is in solution in the reaction mixture and is ordinarily not separated from the mixture. An aqueous liquid, usually water, is usually added to such reaction product-containing reaction mixture, with the water being added to such reaction mixture typically in amount of about 10–90% by weight. If desired, such reaction product-containing reaction mixture per se can be utilized as the brightener additive, i.e. without the addition of aqueous liquid to such reaction product-containing reaction mixture.

The bath-soluble melamine - formaldehyde - acrylic amine-epihalohydrin or glycerol chlorohydrin reaction product herein is utilized in the alkaline zinc electrodepositing baths each in an effective or minor amount, sufficient to yield a bright zinc electrodeposit. When the aromatic aldehyde is utilized in the alkaline zinc electrodepositing baths together with the melamine-formaldehyde-acyclic amine-epihalohydrin or glycerol chlorohydrin reaction product, the aromatic aldehyde is also utilized in the bath in an effective or minor amount, sufficient to yield a bright zinc electrodeposit. The melamine-formaldehyde-acyclic amine-epihalohydrin reaction product is usually added to the alkaline non-cyanide or cyanide zinc electrodepositing baths herein in amount within the range of 0.1 to 10 g./l. inclusive, and the melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product usually in amount within the range of 0.1 to 10 g./l. inclusive (g./l. means grams per liter of the electrodepositing bath). Due to its limited solubility in water, the aromatic aldehyde is usually utilized in the electrodepositing bath as a water-soluble aromatic aldehyde bisulfite, or the aromatic aldehyde per se may be added to the electrodepositing bath as a solution of such aldehyde itself in a water-miscible, bath-compatible organic liquid solvent, such as a lower alkanol, e.g. ethanol.

The bath - soluble melamine - formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product herein is prepared by reacting the melamine, formaldehyde, acyclic amine and epihalohydrin or glycerol chlorohydrin in the presence of an aqueous diluent, usually water, at a temperature from room temperature to reflux temperature of the reaction mixture. The formaldehyde, melamine, acyclic amine, and epihalohydrin or glycerol chlorohydrin are introduced into the reactor and reacted together in any sequence or simultaneously in the case of any two or all of these reactants. The reacting is carried out for a time sufficient to obtain the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product, which is a dark brown, viscous liquid in the case of the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product.

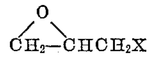
The aqueous diluent such as water utilized in the preparation of the reaction product of melamine, formaldehyde, the acyclic amine having two or more functional groups and the epihalohydrin or glycerol chlorohydrin includes the water contributed by the formalin as well as that contributed by any aqueous solution of another reactant or reactants, for instance an aqueous solution of the acyclic amine, and also the water formed by condensation reactions during formation of the reaction product or polymer. The amount of water utilized can be varied over a wide range and is not especially critical except that when the epihalohydrin is a reactant, the amount of water should be at least equimolar with respect to the epihalohydrin. The water is not believed to be an inert diluent with respect the epihalohydrin inasmuch as it appears the water reacts with the epihalohydrin, for instance epichlorohydrin, to open up the epoxy ring to result in two hydroxyl groups in addition to the chlorine.

The aromatic aldehyde bisulfite is prepared by reacting the aromatic aldehyde with an alkali metal bisulfite such as sodium bisulfite. The aromatic aldehyde, e.g. anisaldehyde, and the sodium bisulfite are supplied to a suitable separate reactor or container together with a suitable quantity of water, for instance 30 gallons of water, and the aldehyde and sodium bisulfite mixed together therein for a sufficient time, typically 30 minutes, to form the aromatic aldehyde bisulfite adduct. The sodium bisulfite is preferably used in an amount which is equimolar with respect the amount of aromatic aldehyde utilized.

The brightener additive compositions of this invention comprise a mixture of the water-soluble melamine-formaldehydehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product, and a liquid diluent or carrier, usually an aqueous liquid diluent or solvent, such as water. However any liquid diluent that is compatible with such reaction product and the alkaline zinc electrodepositing bath is utilizable. The additive compositions may also contain, if desired, other constituents such as, for example, surfactants and levelling agents, etc. The aromatic aldehyde can also be a constituent of the brightener additive composition, if desired. The amount of the soluble reaction product utilized in the brightener additive compositions herein is not especially critical and can be varied over a broad range, usually in the range of about 1%–50% by weight of the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product based on total composition). When the aromatic aldehyde is a constituent, the brightener may contain, for instance, 1%–50% of the melamine-formaldehyde-acyclic amine-epihalohydrin or glycerol chlorohydrin reaction product, 1%–15% of the aromatic aldehyde as the aromatic aldehyde bisulfite, balance water. Alternatively a water-miscible organic solvent, e.g. a lower alkanol, for example ethanol, can be used instead of the water.

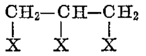
The formaldehyde reactant is conveniently utilized herein in aqueous solution, usually as an aqueous solution of 37% formaldehyde concentration and obtainable in commerce as formalin.

The epihalohydrin reactant for forming the soluble melamine-formaldehyde-acyclic amine-epihalohydrin or glycerol chlorohydrin reaction product herein will usually be of the formula:



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

If glycerol chlorohydrin is utilized as reactant in place of the epihalohydrin the glycerol chlorohydrin will usually be of the formula:



$$\underset{X}{CH_2}-\underset{X}{CH}-\underset{X}{CH_2}$$

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.

The acyclic amine reactant 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 —NH_2 groups are separated by one or more different groups or atoms in the amine molecule. Examplary of the amine reactant are monoethanolamine, diethanolamine, triethylenetriamine, tetraethylenepentamine, tetraethylenepentamine, triethanolamine, ethylenediamine and diethylenetriamine. The functional groups in the amines enumerated immediately supra include the —NH_2, —OH, and —NH groups. By "functional group" as used herein in referring to the amine reactant having at lease 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 prevailing reaction conditions. It is essential that the acyclic amine reactant have two or more functional groups so as to be capable of reacting to form the relatively large molecules of the reaction products herein.

The source of zinc ions in the aqueous alkaline electrodepositing baths herein can be zinc cyanide, $Zn(CH)_2$, and/or an alkali metal zincate such as, for example, sodium zincate, Na_2ZnO_2, or potassium zincate, K_2ZnO_2, in the cyanide baths, and an alkali metal zincate such as, for example, 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 the anode, i.e. one or more anodes, through the alkaline non-cyanide or cyanide zinc electroplating bath solution containing the reaction product brightener of this invention to the cathode, i.e. one or more cathodes, which is the object 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. Any suitable current density can be utilized for the electrodepositing and may be low, medium or high current density, for instance in the range of 1–200 amps/square foot. The anode or anodes may be conventional anodes well known in the art.

The term "low cyanide" 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" 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.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehyde-acyclic amine-glycerol chlorohydrin reaction product herein is preferably prepared by reacting an aqueous solution of formaldehyde, usually as formalin, with melamine, and the epihalohydrin. The reactants are ordinarily at room temperature at the outset of the reaction and the heat of the exothermic reaction results in the temperature of the reaction mixture rising to a temperature in the range of about 95° C. to about 100° C. The reaction mixture is preferably agitated during the reaction and the mixture may be heated by application of external heat. The reacting is carried out for a time of at least 30 minutes. That the reactants have all reacted and the addition of the epihalohydrin or glycerol chlorohydrin to the thus-formed reaction product is in order is evidenced by the disappearance of the characteristic odor of formaldehyde from the reactor and its immediate vicinity. Preferably the epihalohydrin or glycerol chlorohydrin is then reacted with the thus-formed reaction product with agitation of the reaction mixture at a temperature in the range of about 90° C. to about 100° C. and for a time sufficient to obtain a dark brown, viscous liquid reaction product.

More preferably, the melamine-formaldehyde-acyclic amine-epihalohydrin reaction product or melamine-formaldehydeacyclic amine-glycerol chlorohydrin reaction product herein is prepared by first adding the formaldehyde in aqueous solution, usually as formalin, to the melamine at a slow rate of addition which is sufficient to render the reaction between the formaldehyde and melamine self sustaining. The rate of addition of the formaldehyde to the melamine is preferably about 1–3 pounds of the formaldehyde aqueous solution, usually formalin, per minute. The reactants are ordinarily at room temperature at the outset of the reaction and the heat of the exothermic reaction results in the temperature of the reaction mixture rising to a temperature in the range of about 95° C. to about 100° C. The reaction mixture or mass is preferably not cooled while the reaction is occurring inasmuch as cessation of the reaction between the melamine and the formaldehyde tends to occur if the reaction mixture is cooled. The reaction mixture is milky or opaque in appearance at the outset of the reaction and subsequently becomes clear or substantially transparent which is indicative that the melamine has reacted with the formaldehyde. The reaction is carried out in the presence of an aqueous liquid diluent, such as water.

In this more preferred embodiment, the acyclic amine having two or more functional groups, e.g. monoethanolamine, may be present in the reactor mixed together with the melamine at the time of the addition of the formaldehyde aqueous solution. Alternatively, in this more preferred embodiment, the acyclic amine, e.g. ethanolamine, is added to the reactor after the addition of the formaldehyde aqueous solution and after the formation of the melamine-formaldehyde reaction product preferably at a slow or gradual rate which is sufficient to maintain the temperature of the reaction mixture in the range of about 95° C. to about 100° C. The rate of addition of the acyclic amine to the thus-formed reaction product is preferably about 3–8 pounds of the acyclic amine such as ethanolamine per minute. The reaction mixture is preferably stirred or mixed during the addition of the acyclic amine. After addition of the acyclic amine is completed, the reaction product is preferably mixed or stirred for an additional 30–60 minutes.

The epihalohydrin, e.g. epichlorohydrin, or glycerol chlorohydrin is then added to the thus-obtained reaction mixture in the preferred embodiment at a slow or gradual addition rate, which is sufficient to render the reaction self-sustaining and maintain the temperature of the reaction mixture in the range of about 90° C. to about 100° C. The rate of addition of the epihalohydrin or glycerol chlorohydrin to the reaction mixture is preferably about 2–5 pounds of such material per minute. The reaction mixture is preferably mixed or stirred during the addition of the epihalohydrin or glycerol chlorohydrin. After addition of the epihalohydrin or glycerol chlorohydrin is completed, the reaction product is preferably mixed or stirred for an additional 30–60 minutes. The reaction product of the melamine with the formaldehyde, ethanolamine and epichlorohydrin is dark brown in color and the reaction product is a viscous liquid.

The melamine and formaldehyde are preferably reacted together in a mole ratio in the molar range of about 1.5–4:1; the acyclic amine is preferably reacted in the mole ratio in the molar ratio range of about 0.05–0.5:2.8 of acyclic amine (calculated as ethanolamine) to melamine respectively; and the epihalohydrin is preferably reacted in a mole ratio in the molar ratio range of about 2.5–3.5:0.1 of epihalohydrin (calculated as epichlorohydrin) to melamine respectively. The glycerol chlorohydrin is preferably reacted in a mole ratio in the molar ratio range of about 2.5–3.5:0.1 of the glycerol chlorohydrin (calculated as glycerol α-chlorohydrin) to melamine respectively.

The following examples further illustrate the invention:

Example 1

One-hundred and ninety (190) lbs. of monoethanolamine was added to a jacketed stainless steel reactor equipped with a jacket for heating or cooling of the reaction mixture. 60 lbs. of melamine was also added to the reactor through its porthole. 315 lbs. of aqueous formaldehyde solution (37% formaldehyde concentration) was added to the reactor slowly, while stirring the solution. The rate of addition of the formaldehyde was about 3 pounds of the formaldehyde aqueous solution per minute. With continued stirring of the solution the solution was heated to about 96° C. to 99° C. 260 lbs. of epichlorohydrin was then added to the reactor at the rate of one pound per minute for the first one-third of the addition and at the rate of 2 pounds per minute thereafter. The reaction mixture refluxed during the addition of the epichlorohydrin and the temperature was maintained at about 93° C. without external heating. After the addition of the epichlorohydrin was completed, the reaction mixture was stirred for an additional 45 minutes, water in amount of about 25 gallons was added to the thus-obtained melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product-containing mixture, and the resulting solution cooled to about 38° C. before dumping into storage drums. The product solution, i.e. the solution obtained after the addition of the water to the reaction product-containing mixture, possessed a specific gravity of 1.84 and pH of 1.72–1.80.

Example 2

The procedure set forth in Example 1 was repeated utilizing the same reactants as in Example 1 except that glycerol chlorohydrin was utilized in this Example 2 instead of epichlorohydrin. The final product was a solution of a melamine-formaldehyde-ethanolamine-glycerol chlorohydrin reaction product.

Example 3

An alkaline non-cyanide zinc electroplating bath was prepared of the following composition and a melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing aqueous solution added thereto in the amount set forth:

Zinc metal (added as sodium zincate)	g./l.	7
NaOH	g./l.	75
Product solution containing the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product of Example 1	ml./l.	1
Anisaldehyde in solution in ethanol (10% anisaldehyde concentration)	ml./l.	1

In plating tests utilizing this aqueous bath and carried out in a Hull cell employing an operating current of 2 amps, room temperature of the bath and a plating time of 5 minutes, a bright zinc electrodeposit was plated on the test panels at from 5 to 80 a.s.f., i.e. amperes per square foot.

Example 4

An alkaline non-cyanide zinc electroplating bath was prepared of the following composition and a melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing aqueous solution added thereto in the amount indicated:

Zinc metal (added as sodium zincate)	g./l.	15
NaOH	g./l.	150
Product solution containing the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product of Example 1	ml./l.	2
Anisaldehyde bisulfite	g./l.	0.1

Plating tests were carried out utilizing this aqueous bath in a Hull cell, employing an operating current of 2 amps, room temperature of the bath, and a plating time of 5 minutes. A bright or brilliant zinc electrodeposit was plated on the test panels at from 5 to 70 a.s.f.

Example 5

An alkaline low-cyanide zinc electroplating bath was prepared of the following composition and a melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing aqueous solution added thereto in the amount indicated:

Zinc metal (added as zinc cyanide)	g./l.	10
NaCN	g./l.	10
NaOH	g./l.	90
Product solution containing the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product of Example 1	ml./l.	1
Anisaldehyde bisulfite	g./l.	0.1

In plating tests utilizing this aqueous low-CN bath and carried out in a Hull cell employing an operating current of 3 amps, room temperature of the bath, and a plating time of 5 minutes a bright zinc electrodeposit was plated on the test panels at from 2 to 80 a.s.f.

Example 6

An alkaline full cyanide zinc electroplating bath was prepared of the following composition and a melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing aqueous solution added thereto in the amount indicated:

Zinc metal (added as zinc cyanide)	g./l.	35
NaCN	g./l.	90
NaOH	g./l.	75
Product solution containing the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product of Example 1	ml./l.	1
Anisaldehyde bisulfite	g./l.	0.1

In plating tests carried out utilizing this aqueous bath in a Hull cell employing an operating current of 3 amps, room temperature of the bath, and a plating time of 5 minutes, the zinc electrodeposit on the test panels was bright or brillant at from 2 to 100 a.s.f.

Tests were carried out in a Hull cell to compare the melamine-formaldehyde-acyclic amine-epihalohydrin reaction products of this invention with a formaldehyde-ethanolamine - epichlorohydrin reaction product, as brightener additive for alkaline non-cyanide zinc plating baths. The non-cyanide zinc plating baths were aqueous solutions containing sodium zincate and sodium hydroxide and, except for the brightener additive, were of substantially identical composition for each test. The electrodeposits obtained on the Hull test panels from the bath containing the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product were bright zinc deposits. However the zinc electrodeposits obtained on the Hull test panels from the bath containing the formaldehyde-ethanol-amine-epichlorohydrin reaction product were dull to semi-bright deposits.

Example 7

A melamine-formaldehyde-ethanolamine-epibromohydrin reaction product-containing solution is prepared by the same procedure as is set forth in Example 1 and utilizing the same reactants except that epibromohydrin is utilized as a reactant in this Example 7 instead of epichlorohydrin.

Example 8

A melamine-formaldehyde-ethylenediamine-epichlorohydrin reaction product-containing solution is prepared by the same procedure as is set forth in Example 1 and utilizing the same reactants except that ethylenediamine is utilized as a reactant in this Example 8 instead of ethanolamine.

Example 9

A melamine - formaldehyde - ethanolamine - epifluorohydrin reaction product-containing solution is prepared by the same procedure as is set forth in Example 1 and utilizing the same reactants except that epifluorohydrin is utilized as a reactant in this Example 9 instead of epichlorohydrin.

Example 10

A melamine-formaldehyde-diethanolamine-epichlorohydrin reaction product-containing solution is prepared by the same procedure as is set forth in Example 1 and utilizing the same reactants except that diethanolamine is utilized as a reactant in this Example 10 instead of ethanolamine.

Example 11

A melamine-formaldehyde-triethylenetriamine-epichlorohydrin reaction product-containing solution is prepared by the same procedure as is set forth in Example 1 and utilizing the same reactants except that triethylenetriamine is utilized as a reactant in this Example 11 instead of ethanolamine.

Example 12

An alkaline non-CN zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 3 herein, except that a melamine - formaldehyde - ethanolamine-epibromohydrin reaction product-containing aqueous solution prepared in accordance with Example 7 herein is utilized as a brightener in this Example 12 instead of the melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 2 as in Example 3 and a bright zinc electrodeposit is obtained.

Example 13

An alkaline non-CN zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 3 herein, except that a melamine - formaldehyde - ethylenediamine - epichclorohydrin reaction product-containing aqueous solution prepared in accordance with Example 8 herein is utilized as a brightener in this Example 13 instead of the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 13 as in Example 3 and a bright zinc electrodeposit is obtained.

Example 14

An alkaline non-CN zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 3 herein, except that a melamine-formaldehyde-ethanolamine-epifluorohydrin reaction product-containing solution prepared in accordance with Example 9 herein is utilized as a brightener in this Example 14 instead of the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 14 as in Example 3. A bright zinc electrodeposit is obtained.

Example 15

An alkaline non-CN zinc electroplating bath is prepared of the same composition as that of the electroplating bath of Example 3 herein, except that a melamine-formaldehyde-diethanolamine - epichlorohydrin reaction product-containing solution prepared in accordance with Example 10 herein is utilized as a brightener in this Example 15 instead of the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 15 as in Example 3. A bright zinc electrodeposit is obtained.

Example 16

An alkaline non-CN zinc electroplating bath is prepared of the same composition as that of the electroplating bath of Example 3 herein, except that a melamine-formaldehyde-triethylenetriamine-epichlorohydrin reaction product-containing solution prepared in accordance with Example 11 herein is utilized as a brightener in this Example 16 instead of the melamine-formaldehyde-ethanolamine-epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 16 as in Example 3, and a bright zinc electrodeposit is obtained.

Example 17

An alkaline low-cyanide zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 5 wherein, except that a melamine-formaldehyde-ethanolamine-epibromohydrin reaction product-containing aqueous solution prepared in accordance with Example 7 herein is utilized as a brightener in this Example 17 instead of the melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 17 as in Example 5 and a bright zinc electrodeposit is obtained.

Example 18

An alkaline low-cyanide zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 5 herein, except that a melamine - formaldehyde -ethylenediamine-epichlorohydrin reaction product-containing aqueous solution prepared in accordance with Example 8 herein is utilized as a brightener in this Example 18 instead of the melamine-formaldehyde-ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 18 as in Example 5 and a bright zinc electrodeposit is obtained.

Example 19

An alkaline low-cyanide zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 5 herein, except that a melamine-formaldehyde - ethanolamine - epifluorohydrin reaction product-containing aqueous solution prepared in accordance with Example 9 herein is utilized as a brightener in this Example 19 instead of the melamine-formaldehyde-ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 19 as in Example 5 and a bright zinc electrodeposit is obtained.

Example 20

An alkaline low-cyanide zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 5 herein, except that a melamine-formaldehyde - diethanolamine - epichlorohydrin reaction product-containing aqueous solution prepared in accordance with Example 10 herein is utilized as a brightener in this Example 20 instead of the melamine-formaldehyde - ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 20 as in Example 5 and a bright zinc electrodeposit is obtained.

Example 21

An alkaline low-cyanide zinc electroplating bath is prepared of the same composition as that of the electroplating bath set forth in Example 5 herein, except that a melamine-formaldehyde - triethylenetriamine - epichlorohydrin reaction product-containing aqueous solution prepared in accordance with Example 11 herein is utilized as a brightener in this Example 21 instead of the melamine-formaldehyde-ethanolamine - epichlorohydrin reaction product-containing solution. The same plating test conditions are utilized in this Example 21 as in Example 5 and a bright zinc electrodeposit is obtained.

Although the above specific examples are given purely for purposes of illustration, it will be understood that such procedures may be altered or varied and modified without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. An alkaline zinc electrodepositing bath 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 melamine with formaldehyde, an acyclic aliphatic amine having at least two functional groups, and an epihalohydrin wherein the halogen is chloro, bromo or fluoro or a glycerol chlorohydrin, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

2. The bath of claim 1 also containing an aromatic aldehyde as an additional brightening agent.

3. The bath of claim 2 wherein the bath-soluble reaction product is obtained by reacting the melamine together with an aqueous solution of the formaldehyde, the acyclic amine, and the epihalohydrin or glycerol chlorohydrin in the presence of an aqueous diluent at a temperature in the range of from room temperature to reflux temperature of the reaction mixture.

4. The bath of claim 2 wherein the bath-soluble reaction product is obtained by reacting the melamine together with an aqueous solution of the formaldehyde and the acyclic amine in the presence of an aqueous diluent at a temperature of from room temperature to about 100° C., and then reacting the epihalohydrin or glycerol chlorohydrin with the thus-formed reaction product with agitation of the reaction mixture at a temperature in the range of about 90° C. to about 100° C.

5. The bath of claim 4 wherein the melamine, aqueous formaldehyde solution and acyclic amine are reacted together at a temperature in the range of about 95° C.

to about 100° C., and the epihalohydrin or glycerol chlorohydrin is reacted with the thus-formed reaction product at a temperature in the range of about 90° C. to about 100° C.

6. The bath of claim **4** wherein the acyclic amine is an ethanolamine.

7. The bath of claim **6** wherein the ethanolamine is monoethanolamine.

8. The bath of claim **4** wherein the epihalohydrin or glycerol chlorohydrin reactant is the epihalohydrin.

9. The bath of claim **8** wherein the epihalohydrin is epichlorohydrin.

10. The bath of claim **2** wherein the aromatic aldehyde is added to the bath as an aromatic aldehyde bisulfite.

11. The bath of claim **4** wherein the aromatic aldehyde is added to the bath as an aromatic aldehyde bisulfite.

12. The bath of claim **4** characterized by being a noncyanide alkaline zinc electrodepositing bath.

13. The bath of claim **4** characterized by being a cyanide alkaline zinc electrodepositing bath.

14. The bath of claim **13** characterized by being a low cyanide alkaline zinc electrodepositing bath.

15. The bath of claim **1** wherein the bath-soluble reaction product is present in amount of 0.1 to 10 g./l. inclusive.

16. The bath of claim **4** wherein the bath-soluble reaction product is present in amount of 0.1 to 10 g./l. inclusive.

17. A method for the electrodeposition of bright zinc which comprises passing a direct electrical current from an anode through an alkaline zinc electrodepositing bath to a cathode on which the zinc is to be electrodeposited, the electrodepositing bath comprising an 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 melamine with formaldehyde, an acyclic aliphatic amine having at least two functional groups, and an epihalohydrin wherein the halogen is chloro, bromo or fluoro or a glycerol chlorohydrin, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

18. The method of claim **17** wherein the bath also contains an aromatic aldehyde as an additional brightening agent.

19. The method of claim **18** wherein the bath-soluble reaction product is obtained by reacting the melamine together with an aqueous solution of the formaldehyde, the acyclic amine, and the epihalohydrin or glycerol chlorohydrin in the presence of an aqueous diluent at a temperature in the range of from room temperature to reflux temperature of the reaction mixture.

20. The method of claim **18** wherein the bath-soluble reaction product is obtained by reacting the melamine together with an aqueous solution of the formaldehyde and the acyclic amine in the presence of an aqueous diluent at a temperature of from room temperature to about 100° C., and then reacting the epihalohydrin or glycerol chlorohydrin with the thus-formed reaction product with agitation of the reaction mixture at a temperature in the range of about 90° C. to about 100° C.

21. The method of claim **20** wherein the melamine, aqueous formaldehyde solution and acyclic amine are reacted together at a temperature in the range of about 95° C. to about 100° C., and the epihalohydrin or glycerol chlorohydrin is reacted with the thus-formed reaction product at a temperature in the range of about 90° C. to about 100° C.

22. The method of claim **20** wherein the acyclic amine is an ethanolamine.

23. The method of claim **22** wherein the ethanolamine is monoethanolamine.

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