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3,745,099

ALKALINE BRIGHT ZINC ELECTROPLATING

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Int. Cl. C23b 5/10
U.S. Cl. 204—55 R 17 Claims

ABSTRACT OF THE DISCLOSURE

Semi-bright zinc is electrodeposited from alkaline zinc electrodepositing baths comprising an alkaline solution containing a source of zinc ions and an effective amount, as a brightening agent, of a bath-soluble reaction product obtained by the reaction of melamine with formaldehyde. In another embodiment the brightening agent is the bath-soluble reaction product of melamine with formaldehyde and an epihalohydrin or a glycerol chlorohydrin. The melamine-formaldehyde reaction product and melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction product are usually each utilized as brightener in the alkaline zinc baths in combination with a formaldehyde-acyclic amine-epihalohydrin reaction product wherein the acyclic amine has two or more functional groups.

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 semi-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 hexamethylenetetramine with epichlorohydrin or alpha-chloroglycerol is disclosed in the prior art. The electrodeposition of bright zinc from alkaline cyanide zinc plating baths containing as brightening agent a condensation polymer of an aliphatic alkylenepolyamine 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 electrodeposition of bright zinc from cyanide-free zinc baths containing an alkanolamine, hexamethylenetetramine, or a mixture thereof is disclosed in U.S. Pat. 3,317,412.

SUMMARY OF THE INVENTION

Semi-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 product obtained by the reaction of melamine with formaldehyde. Although the melamine-formaldehyde reaction product as sole brightener additive imparts some semi-brightness to the zinc electrodeposits, the melamine-formaldehyde reaction product is usually used in the electrodepositing baths in combination with another brightener additive, viz a formaldehyde-acyclic amine-epihalohydrin reaction product wherein the acyclic amine has at least two functional groups for the reason the combination of the melamine-formaldehyde reaction product and the formaldehyde-acyclic amine-epihalohydrin reaction product exhibits a pronounced synergism in imparting brightness to the 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 malamine-formaldehyde reaction product and the formaldehyde-acyclic amine-epihalohydrin reaction product as brighteners resulted in zinc electrodeposits of a considerably enhanced or increased brightness over that obtained with addition to the bath of each such reaction product alone as brightener.

In another embodiment of the invention, the brightening agent in the alkaline zinc electrodepositing baths herein is a bath-soluble melamine-formaldehyde-epihalohydrin reaction product. Alternatively, glycerol chlorohydrin is the reactant in the formation of the reaction product in place of the epihalohydrin. The soluble melamine-formaldehyde-epihalohydrin reaction product or melamine-formaldehyde-glycerol chlorohydrin reaction product as sole brightener in the baths results in some semi-brightness being imparted to the zinc electrodeposits. However the melamine-formaldehyde-epihalohydrin or -glycerol chlorohydrin reaction product is usually used in the electrodepositing baths in combination with another brightener additive, which is a formaldehyde-acyclic amine-epihalohydrin reaction product wherein the acyclic amine has at least two functional groups, inasmuch as the combination of the melamine-formaldehyde-epihalohydrin or -glycerol chlorohydrin reaction product and the formaldehyde-acyclic amine-epihalohydrin reaction product is a synergistic combination from the standpoint of imparting brightness to the zinc electrodeposits. Further, the combination of the melamine-formaldesyde-epihalohydrin reaction product and the formaldehyde-acyclic amine-epihalohydrin reaction product as brightener was found to considerably extend the current density range in the high current density region over which the semi-bright zinc was deposited. This extension of the current density range was in the range of a 50 to 150 amps per square foot extension.

Although we do not wish to be bound by theory, the formation of the melamine-formaldehyde reaction products herein appears to involve the condensation reaction of melamine and formaldehyde with the subsequent formation of melamine-methylol compounds. The polymerization of the melamine-methylol compounds then occurs. The formation of the melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction products herein appears to involve the formation of cross-linked polymeric networks.

The reaction temperature for forming the melamine-formaldehyde reaction product brightener is from room temperature to reflux temperature of the reaction mixture. The reactants are usually at room temperature when brought together, and the heat of the exothermic reaction between the melamine and formaldehyde results in the temperature of the reaction mixture rising to the reflux temperature of the reaction mixture.

The reaction time is that sufficient to obtain the melamine-formaldehyde reaction product and is usually at least about 1 hour and typically about 2–3 hours. The formation of the melamine-formaldehyde reaction product is indicated by the reaction mixture changing to a clear, substantially transparent or water-white state from a milky or opaque white color.

The amounts of melamine and formaldehyde 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 of the reaction product.

The melamine-formaldehyde reaction product herein is of a clear, non-milky color and is soluble in water. The

reaction product is in solution in the reaction product mixture and is ordinarily not separated from the mixture. An aqueous liquid, usually water, is usually added to the melamine-formaldehyde reaction product-containing mixture to prepare the brightener additive composition herein. The water is added to the reaction product-containing mixture typically in a weight ratio of about 1–4:1 of the water to the reaction product-containing mixture respectively. The melamine-formaldehyde reaction product-containing reaction mixture itself can, if desired, be utilized as the brightener additive, i.e. without the addition of aqueous liquid to such reaction product-containing reaction mixture.

The reaction temperature for forming the melamine-formaldehyde-epihalohydrin reaction product brightener or the melamine-formaldehyde-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-epihalohydrin reaction product or melamine-formaldehyde-glycerol chlorohydrin reaction product with the total reaction time usually being at least about 2½–3 hours.

The amounts of melamine, formaldehyde and epihalohydrin 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 insoluble gel formation.

The melamine - formaldehyde - epihalohydrin reaction product or melamine-formaldehyde-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 mixture, with the water being added to such reaction mixture typically in amount of about 1–4:1 respectively. 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 reaction product or bath-soluble melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction product herein are utilized in the alkaline zinc electrodepositing baths each in an effective or minor amount, sufficient to impart semi-brightness to the zinc electrodeposit. When the bath-soluble formaldehyde-acyclic amine-epihalohydrin reaction product wherein the acyclic amine has two or more functional groups is utilized in the alkaline zinc electrodepositing baths together with the melamine-formaldehyde-epihalohydrin or -glycerol chlorohydrin reaction product, which is usually the case, the formaldehyde-acyclic amine-epihalohydrin reaction produce is also utilized in the bath in an effective or minor amount, sufficient to impart semi-brightness to the zinc electrodeposit. The melamine-formaldehyde reaction product is usually added to the alkaline non-cyanide or cyanide zinc electrodepositing baths herein in amount within the range of 0.1–10 g./l., the melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction product in amount within the range of 0.1–10 g./l., and the formaldehyde acyclic amine-epihalohydrin reaction product in amount within the range of 0.1–10 g./l.

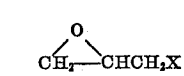
The bath-soluble reaction product or condensation polymer of formaldehyde, the acyclic amine having two or more functional groups and the epihalohydrin can be prepared by reacting the formaldehyde, acyclic amine, and the epihalohydrin, in the presence of an aqueous diluent, usually water, at a temperature of from room temperature to refluxing temperature of the reaction mixture. The time of reaction to yield the condensation polymer is dependent on the temperature employed for the reacting, with room temperature reacting requiring considerably longer times, which is a matter of days, than reflux temperature reacting which requires only minutes to yield the condensation polymer. The reaction time is that sufficient to yield the condensation polymer, and will range from about 5 minutes to several days depending on the reaction temperature as previously mentioned. In carrying out the condensation reaction, all reactant compounds can be present simultaneously in the reactant mixture, or one or two of the reactants can be added, preferably slowly, to the other reactant compound or compounds herein either simultaneously or successively, and with the particular sequence in which the reactant compound or compounds herein are added to the other reactant or reactants not being critical. In accordance with a preferred embodiment hereinafter disclosed in detail however, an aqueous solution of formaldehyde is first slowly added to the acyclic primary amine and the epihalohydrin is added to the reaction product mixture of elevated temperature substantially immediately after the addition of all the aldehyde.

The aqueous diluent such as water utilized in the preparation of the condensation polymer of formaldehyde, the acyclic amine having two or more functional groups and the epihalohydrin 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 reaction during formation of the polymer. The amount of water utilized can be varied over a wide range and is not especially critical except that the amount of water should be at least equimolar with respect to epihalohydrin. The water is not believed to be an inert diluent with respect to 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 brightener additive compositions of this invention comprise a mixture of the melamine-formaldehyde reaction product or the melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction product, the soluble condensation polymer obtained by the condensation reaction of the acyclic amine having two or more functional groups with the formaldehyde and epihalohydrin, and a liquid diluent or carrier, usually an aqueous liquid diluent or solvent such as water. However any liquid diluent or carrier that is compatible with such reaction product and polymer 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 proportions of the constituents of the brightener additives herein are not critical and can be varied over broad ranges, for instance 0.1%–10% of the melamine-formaldehyde reaction product of melamine-formaldehyde-epihalohydrin or melamine-formaldehyde-glycerol chlorohydrin reaction product, and 1% 60% of the formaldehyde-acyclic amine-epihalohydrin reaction product.

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.

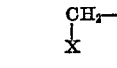
The epihalohydrin reactant for forming the soluble melamine-formaldehyde-epihalohydrin reaction product herein and for forming the reaction product of formaldehyde, the acyclic amine having two or more functional groups and the epihalohydrin will usually be of the formula:



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

When glycerol chlorohydrin is utilized as reactant in place of the epihalohydrin in preparation of the melamine-

formaldehyde-glycerol chlorohydrin reaction product, the glycerol chlorohydrin will usually be of the formula:



wherein at least one but not more than two X's are hydroxy and the remaining non-hydroxyl 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 for forming the soluble condensation polymer of formaldehyde, the acyclic amine and the epihalohydrin 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. Exemplary of the amine reactant are monoethanolamine, diethanolamine, triethylenetriamine, tetraethylenepentamine, triethanolamine, ethylenediamine and diethylenetriamine. The functional groups in the amines enumerated immediately supra include the —NH_2, —OH, and —NH groups. By "functional group" as used herein in referring to the amine reactant having at least two functional groups is meant a group or radical capable of reacting with another reactant, group or radical in the reaction mixture, such as by an addition reaction or a condensation reaction, under the reaction conditions of the invention. It is essential that the acyclic amine reactant have two or more functional groups so as to be capable of forming the relatively large polymer molecules.

The source of zinc ions in the aqueous alkaline electrodepositing baths herein can be zinc cyanide, $Zn(CN)_2$, and/or an alkali metal zincate such as sodium zincate, Na_2ZnO_2, or potassium zincate, K_2ZnO_2, in the cyanide baths, and an alkali metal zincate such as sodium zincate or potassium zincate in the non-cyanide baths herein. The cyanide and non-cyanide alkaline baths also contain an alkaline material, usually an alkali metal hydroxide, e.g. sodium or potassium hydroxide, with the zinc-containing compound dissolved in the aqueous alkaline solution. An alkali metal carbonate, e.g. sodium or potassium carbonate may also be a constituent of the cyanide and non-cyanide alkaline baths herein.

The electrodepositing of the bright or semi-bright zinc in accordance with the invention is carried out by passing a DC electrical current from 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" content used herein with reference to the alkaline zinc cyanide electrodepositing bath means such a bath with a total cyanide content of up to 2.0 oz./gal. The terms "full cyanide" content or "high cyanide" content used herein in referring to the alkaline zinc electrodepositing bath means such a bath with a total cyanide content of 10.0 oz./gal. or higher.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The melamine and formaldehyde are preferably reacted together in a mole ratio within the molar ratio range of about 1.5–4:1 of formaldehyde to melamine respectively. An especially preferred mole ratio of the reactants is about 3:1 of the formaldehyde to melamine respectively.

The reaction temperature for preparation of the melamine-formaldehyde reaction product is preferably in the range of about 95° C. to about 100° C.

The melamine-formaldehyde reactoin product is preferably added to the alkaline non-cyanide or cyanide zinc electroplating baths in amount within the range of about 0.01–1.0 ml./l. the melamine-formaldehyde-epihalohydrin reaction product is preferably added thereto in amount within the range of about 0.1–10 ml./l., the melamine-formaldehyde-glycerol chlorohydrin reaction product preferably in amount within the range of about 0.1–10 ml./l., and the formaldehyde-acrylic amine-epihalohydrin reaction product preferably within the range of about 0.1–10 ml./l.

Preferably the formaldehyde is added to the melamine in the preparation of the melamine-formaldehyde reaction product. 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° 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 formaldehyde aqueous solution is preferably added 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 of Formalin per minute. The reaction mixture is milky or opaque in appearance at the outset of the reaction and subsequently becomes clear which is indicative that the melamine has reacted with the formaldehyde.

The reaction is preferably carried out in the presence of a liquid aqueous diluent, usually water.

In the preparation of the melamine-formaldehyde-epihalohydrin or -glycerol chlorohydrin reaction product, the melamine-formaldehyde reaction product is formed first preferably by the same procedure and reaction conditions as are disclosed previously herein. The epihalohydrin, e.g. epichlorohydrin, or glycerol chlorohydrin is added to the preformed melamine-formaldehyde reaction product preferably at a slow or gradual addition rate which is sufficient to render the exothermic reaction between the melamine-formaldehyde reaction product and the epichalohydrin or glycerol chlorohydrin self sustaining. The slow rate of addition of the epihalohydrin or glycerol chlorohydrin to the melamine-formaldehyde reaction product is about 3–5 pounds of the epihalohydrin or glycerol chlorohydrin per minute. The preferred method of addition of the epihalohydrin or glycerol chlorohydrin to the reaction product is dropwise addition. The reaction mixture is preferably mixed or stirred during the addition of the epihalohydrin or glycerol chlorohydrin, and the epihalohydrin or glycerol chlorohydrin is added to the melamine-formaldehyde reaction product preferably over a period of about 25–35 minutes and reacted therewith at a temperature of the reaction mixture in the range of about 100° C. to about 105° C. After the addition of all epihalohydrin is completed, the reaction mixture is preferably mixed or stirred for an additonal 25–35 mnutes at a temperature within the range set forth immediately above. The resulting melamine-formaldehyde-epihalohydrin or -glycerol chlorohydrin reaction product is dark brown in color, and the formation of such reaction product is indicated when the reaction changes to a dark brown color from a yellow color.

The formaldehyde and melamine are preferably reacted together in a mole ratio within the molar ratio range of about 1.5–4:1 of formaldehyde to melamine respectively, and the epihalohydrin is preferably reacted in a mole ratio in the molar ratio range of about 1.5–3.5:1 of the

epihalohydrin (calculated as epichlorohydrin) to melamine respectively. The glycerol chlorohydrin is preferably reacted in a mole ratio in the molar ratio range of about 1.5–3.5:1 of the glycerol chlorohydrin to melamine respectively.

The following examples further illustrate the invention:

EXAMPLE 1

One-hundred and twenty-six (126) lbs. of melamine was charged to a reactor. 200 lbs. of aqueous formaldehyde solution (37% formaldehyde concentration) was then added to the melamine over a period of about 60 minutes. The reaction mixture was stirred and heated gently during the addition of the formaldehyde aqueous solution. After the addition of all of the formaldehyde aqueous solution, the liquid reaction mixture was mixed for an additional 30 minutes at a temperature of about 50° C. to 80° C. The resultant melamine-formaldehyde reaction product-containing solution was effective as a semi-brightener additive for alkaline non-cyanide zinc electroplating baths, and with improved semi-brightness of the zinc electrodeposit when utilized as additive in such baths in combination with a formaldehyde-ethanolamine-epichlorohydrin reaction product.

EXAMPLE 2

A melamine-formaldehyde reaction product was prepared by the same procedure and reaction conditions as set forth in Example 1 herein. 78 lbs. of epichlorohydrin was then added to the resulting melamine-formaldehyde reaction product-containing solution with stirring and at a slow rate of about 4 lbs. of the epichlorohydrin per minute. The epichlorohydrin reacted exothermically with the melamine-formaldehyde reaction product. The rate of addition of the epichlorohydrin was sufficient to maintain the exothermic reaction between the epichlorohydrin and the melamine-formaldehyde reaction product in a state of reflux. After the addition of all the epichlorohydrin was completed, the reaction mixture was stirred for an additional 35 minutes. The resultant melamine-formaldehyde-epichlorohydrin reaction product-containing solution was effective as a semi-brightener additive for alkaline non-cyanide zinc electroplating baths and with improved semi-brightness as additive when utilized in the baths in combination with a formaldehyde-ethanolamine-epichlorohydrin reaction product.

EXAMPLE 3

A melamine-formaldehyde-epifluorohydrin reaction product is prepared by the same procedure and reaction conditions as set forth in Example 2 herein, except that 76 lbs. of epifluorohydrin is utilized in this Example 3 instead of the epichlorohydrin of Example 2. The resultant melamine-formaldehyde-epifluorohydrin reaction product is effective as a semi-brightener additive for alkaline non-cyanide zinc electroplating baths, and with improved semi-brightness of the zinc electrodeposit when utilized in the baths as additive in combination with a formaldehyde - ethanolamine - epichlorohydrin reaction product.

EXAMPLE 4

A melamine-formaldehyde glycerol chlorohydrin reaction product is prepared by the same procedure and reaction conditions as in Example 2 herein, except that 110 lbs. of glycerol chlorohydrin is utilized as reactant in this Example 4 instead of the epichlorohydrin of Example 2. The resultant melamine-formaldehyde-glycerol chlorohydrin reaction product is effective as a semi-brightener additive for alkaline noncyanide zinc electroplating baths, and with improved semi-brightness of the zinc electrodeposit when utilized in the bath in combination with a formaldehyde-ethanolamine-epichlorohydrin reaction product.

EXAMPLE 5

A melamine-formaldehyde-epibromohydrin reaction product is prepared by the same procedure and reaction conditions as set forth in Example 2 herein, except that 78 lbs. of epibromohydrin is utilized in this Example 5 instead of the epichlorohydrin of Example 2. The resultant melamine-formaldehyde-epibromohydrin reaction product is effective as a semi-brightener additive for alkaline cyanide or non-cyanide zinc electroplating baths, and with improved semi-brightness of the zinc electrodeposit when utilized in the bath in combination with a formaldehyde-ethanolamine-epichlorohydrin reaction product.

Tests were carried out in a Hull cell to compare the melamine-formaldehyde and melamine-formaldehyde-epihalohydrin reaction products of this invention with the prior 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 baths containing the melamine-formaldehyde reaction product as additive also contained formaldehyde - ethanolamine-epichlorohydrin reaction product as brightener additive in the weight ratio of about 1:10 respectively. The baths containing the melamine-formaldehyde-epichlorohydrin reaction product also containing formaldehyde-ethanolamine-epichlorohydrin reaction product in the weight ratio of about 1:10 respectively. The electrodeposits obtained on the Hul test panels from the baths containing the melamine-formaldehyde reaction product plus the formaldehyde-ethanolamine-epichlorohydrin reaciton product and from the baths containing the melamine-formaldehyde-epichlorohydrin reaction product plus the formaldehyde-ethanolamine-epichlorohydrin reaction product plus were semi-bright zinc deposits which were of considerably increased brightness over the zinc electrodeposits deposited on the test panels from the bath containing solely the prior formaldehyde - ethanolamine-epichlorohydrin reaction product.

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, sufficient to yield a semi-bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of melamine with formaldehyde, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

2. The bath of claim **1** also containing an effective amount, sufficient to impart semi-brightness to the zinc electrodeposit, of a bath-soluble reaction product of formaldehyde, an acyclic aliphatic amine having at least two functional groups separated by at least one different group, and an epihalohydrin wherein the halogen is chloro, bromo or fluoro.

3. An alkaline zinc electrodepositing bath comprising an alkaline solution containing a source of zinc ions and an effective amount, sufficient to yield a semi-bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of melamine with formaldehyde and an epichalohydrin or glycerol chlorohydrin, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

4. The bath of claim **3** also containing an effective amount, sufficient to impart semi-brightness to the zinc electrodeposit, of a bath-soluble reaction product of formaldehyde, an acyclic aliphatic amine having at least two functional groups separated by at least one different

group, and an epihalohydrin wherein the halogen is chloro, bromo or fluoro.

5. The bath of claim 2 wherein the melamine and formaldehyde are reacted at a reaction temperature in the range of from room temperature to reflux temperature of the reaction mixture.

6. The bath of claim 5 wherein the melamine and formaldehyde are reacted together in a mole ratio within the molar ratio range of about 1.5–4:1 of formaldehyde to melamine respectively.

7. The bath of claim 6 wherein the reaction temperature is in the range of from about 95° C. to about 100° C. of the reaction mixture.

8. The bath of claim 7 wherein the reaction product is obtained by slowly adding the formaldehyde to the melamine, the formaldehyde exothermically reacting with the melamine whereby the temperature of the reaction mixture is increased to a temperature in the range of about 95° C. to about 100° C., the formaldehyde and melamine being reacted together for a period sufficient to obtain the melamine-formaldehyde reaction product.

9. The bath of claim 4 wherein the melamine and formaldehyde are reacted together at a reaction temperature in the range of from about room temperature to reflux temperature of the reaction mixture to form a melamine-formaldehyde reaction product, and the epihalohydrin or glycerol chlorohydrin is reacted with the melamine-formaldehyde reaction product at a reaction temperature in the range of from room temperature to reflux temperature of the reaction mixture.

10. The bath of claim 9 wherein the melamine and formaldehyde are reacted together in a mole ratio within the molar ratio range of about 1.5–4:1 of formaldehyde to melamine respectively, and the epihalohydrin or glycerol chlorohydrin is reacted in a mole ratio in the molar ratio range of about 1.5–3.5:1 of the epihalohydrin or glycerol chlorohydrin to the melamine respectively.

11. The bath of claim 10 wherein the melamine and formaldehyde are reacted together at a reaction temperature in the range of from about 95° C. to about 100° C., and the epihalohydrin or glycerol chlorohydrin is reacted with the melamine-formaldehyde reaction product at a reaction temperature in the range of about 100° C. to about 105° C. of the reaction mixture.

12. The bath of claim 10 wherein the reaction product is obtained by slowly adding the epihalohydrin or glycerol chlorohydrin to the melamine-formaldehyde reaction product, the epihalohydrin or glycerol chlorohydrin exothermically reacting with the melamine-formaldehyde reaction product whereby the temperature of the reaction mixture is increased to a temperature in the range of from about 100° C. to about 105° C., the epihalohydrin or glycerol chlorohydrin and the melamine-formaldehyde reaction product being reacted together for a period sufficient to obtain the reaction product.

13. The bath of claim 12 wherein the epihalohydrin or the glycerol chlorohydrin is added dropwise to the melamine-formaldehyde reaction product in an aqueous reaction mixture.

14. A method for the electrodeposition of semi-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 semi-bright zinc electrodeposit, of a bath-soluble reaction product obtained by the reaction of melamine with formaldehyde, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

15. The method of claim 14 wherein the electrodepositing bath also contains an effective amount of a bath-soluble reaction product of formaldehyde, an acyclic aliphatic amine having at least two functional groups separated by at least one different group, and an epihalohydrin wherein the halogen is chloro, bromo or fluoro.

16. The method of claim 14 wherein the bath-soluble reaction product in the electrodepositing bath is obtained by the reaction of melamine with formaldehyde and an epihalohydrin wherein the halogen is chloro, bromo or fluoro or glycerol chlorohydrin, the amount of melamine reacted being insufficient to result in formation of an insoluble gel.

17. The method of claim 16 wherein the electrodepositing bath contains as an additional constituent an effective amount of a bath-soluble reaction product obtained by the reaction of formaldehyde, an acyclic aliphatic amine having at least two functional groups separated by at least one different group, and an epihalohydrin wherein the halogen is chloro, bromo and fluoro.

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FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—DIG. 2

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,745,099 Dated July 10, 1973

Inventor(s) Paul J. Szilagyi and Juan Hajdu

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

Column 4, line 54, "of" should read -- or --. Column 6, line 6, "reactoin" should read -- reaction --; line 9, a comma should be inserted after "1."; line 14, "-acrylic" should read -- acyclic --; line 33, "of" should read -- or --. Column 8, line 29, "containing" should read -- contained --; line 32, "Hul" should read -- Hull --; line 34, "reaciton" should read -- reaction --.

Signed and sealed this 12th day of February 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents