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ALKALINE ZINC PLATING BATHS

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This invention relates to the electrodeposition of zinc from alkali cyanide baths, and more particularly to a new type of addition agent for such baths.

We have found that certain bath-soluble condensation polymers prepared from an aliphatic alkylenepolyamine (such as ethylenediamine, propylenediamine and higher members of this series; diethylenetriamine, triethylenetetramine, tetraethylenepentamine and so on; dipropylenetriamine; N-hydroxyethyl ethylenediamine, NN'-dihydroxyethyl ethylenediamine, 1,3-diamino-2-propanol) as one reactant, and furfural, furfural sodium bisulphite, formaldehyde, and/or formaldehyde sodium bisulphite as the other reactants exert a strong brightening action on the electrodeposits, when added in relatively small amounts to a cyanide zinc plating bath.

EXPERIMENTAL

The composition of the aqueous plating solutions used in our experiments was:

	Oz./gal.
Zinc cyanide	8 to 12
Sodium cyanide	4 to 9
Sodium hydroxide	8 to 12

Before use, the solutions were treated with zinc dust to eliminate metallic impurities. Our experiments were performed at room temperature.

The usual bright dips can be applied to the zinc plates obtained, but in many cases this is not necessary.

1 mol. diethylenetriamine reacted with 1 mol. furfural gave products of little brightening efficiency; with 2 mols. furfural, products of higher brightening efficiency were obtained, but they possessed a high tendency to provoke the formation of deep streaks on the electroplate.

When the reaction product of 1 mol. diethylenetriamine with 1 mol. furfural was further condensed with 2 to 3 mols. formaldehyde, products of high brightening efficiency resulted. Paraformaldehyde can be used instead of aqueous formaldehyde.

We obtained considerably better addition agents by using the furfural-sodium bisulphite addition compound instead of furfural itself. Also partial or entire substitution of N-hydroxyethyl ethylenediamine, NN'-dihydroxyethyl ethylenediamine or 1,3-diamino-2 propanol for diethylenetriamine (or triethylenetetramine) gave improved results.

Example 1

To 103.2 g. (1 mol.) diethylenetriamine, 96.1 g. (1 mol.) furfural were added under stirring, and

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the reaction product was heated to 110° C. Then, after cooling to room temperature, 216 g. (2.66 mols.) formaldehyde (37%) were added and the reaction product heated for 10 minutes in a water bath to 90° C. The final product was diluted to 1 liter. A cyanide zinc plating bath containing per liter 10 to 25 ml. of this brightener solution gave large areas of brilliancy in the Hull cell, the optimum of brilliancy occurring at higher current densities with increasing brightener concentration.

Lower and higher amounts of formaldehyde than those indicated above gave less potent brighteners. Too long and too high heating of these condensation products increased their brightening efficiency but provoked blistering of the electrodeposits over a steel base.

Example 2

To 90.1 g. (1 mol.) 1,3-diaminopropanol, 96.1 g. (1 mol.) furfural were added under stirring. The reaction product was then heated for a short time to 85° C., cooled, and 121.6 g. (1.5 mols.) formaldehyde (37%) were added under stirring and the product again shortly heated to 85° C. This dark brown syrupy reaction product was diluted with water to make 1 liter; 20 to 30 ml. of this solution, when added to 1 liter zinc bath, produced bright zinc deposits over a wide current density range.

Example 3

26 g. (0.25 mol.) hydroxyethy ethylenediamine and 100 g. (0.5 mol.) furfural-sodium bisulphite (powdered) were mixed. Strong heat evolution occurred and a dark brown resin resulted which was dissolved in water to make 250 ml. 24 ml. of this solution, when added to 1 liter zinc bath, gave brilliant electrodeposits in the high current density range.

Example 4

To 36.6 g. (0.25 mol.) triethylenetetramine were added under stirring 20 g. (0.25 mol.) formaldehyde and then 100 g. (0.5 mol.) furfural-sodium bisulphite. The reaction product was heated to around 105° C., where gas evolution and volume increase occurred. The resulting dark colored resin was dissolved to 250 ml. Only 5 ml. of this solution, when added to 1 liter zinc bath, caused the formation of brilliant but pitted zinc electrodeposits.

When the reaction product was heated only to 70° C. and dissolved to 250 ml., larger brightener additions were required (14 ml./liter), but

pit-free bright zinc deposits were obtained over a wide current density range (approximately 20 to 50 amps./sq.ft.) in the Hull cell.

Examples 5 to 19

A great number of reaction products of triethylenetetramine, alone or mixed with N-hydroxyethyl ethylenediamine (or sometimes with NN'-dihydroxyethyl ethylenediamine), with furfural-sodium bisulphite (concentrated aqueous solution) and formaldehyde were prepared. The addition agents prepared from triethylenetetramine gave somewhat better results than those prepared from diethylenetriamine or tetraethylenepentamine.

The following table gives the concentration of the reactants in mols. The procedure was as follows:

To the polyamine or the polyamine mixture, aqueous formaldehyde (37%) (if indicated in the table) was slowly added under stirring and cooling. Then a solution of 1 mol. furfural and 1 mol. sodium bisulphite (0.5 mol. sodium metabisulphite) in 200 ml. of water, aged for at least half an hour, was added under stirring and, if required, cooling. Then the final formaldehyde (if indicated in the table) was added and the reaction product heated for about 15 minutes at slight boiling. When larger quantities were prepared, external heating was not necessary as the reactions are strongly exothermic.

Example	Triethylenetetramine	N-Hydroxyethyl ethylenediamine	1st Reaction Step: Formaldehyde	1st or 2nd Reaction Step: Furfural-sodium bisulphite	2nd or 3rd Reaction Step: Formaldehyde
5	1.0			1.0	2.0
6	1.0			2.0	2.0
7	1.0		0.5	1.0	2.0
8	1.0		0.5	2.0	2.0
9	1.0		1.0	2.0	1.0
10	0.5	0.5	1.0	2.0	
11	0.5	0.5	0.5	2.0	1.0
12	0.5	0.5	1.0	2.0	1.0
13	0.5	0.5		2.0	
14	0.5	0.5		2.0	1.0
15	0.5	0.5		2.0	2.0
16	0.5	0.5	1.0	1.33	
17	0.5	0.5	1.0	2.66	
18	0.5	0.5	0.5	2.0	
19	0.25	0.75	1.0	2.0	

Above reaction products were diluted to 1 liter, and 10 to 15 ml. of these solutions, equivalent to about 2.5 to 9.5 grams of reaction products, were added to 1 liter plating bath. They all exert a strong brightening action over a wide current density range (approximately 10 to 50 amps./sq. ft.). Brighteners #10 and #14 seemed to be the best suitable for still zinc plating. Brighteners #15 and #19 were less good than the average.

These addition agents were very stable in the aqueous stock solution, but less so in the zinc plating bath, to which they have to be added periodically in order to maintain a high degree of brightness of the electrodeposits.

However, all these addition agents of high brightening power have a tendency to produce blistering of the zinc deposit on steel in the low current density range, if the plating time is about 10 to 15 minutes and the plated parts are soaked in almost boiling water. This blistering tendency is especially pronounced in older baths replenished several times with brightener.

We have discovered the surprising fact that addition of very small amounts of the higher molecular polyamines suppresses this tendency to blistering. This anti-blistering action increases with increasing molecular weight of the polyamine. Thus a polyethylene polyamine of an average molecular weight of 650 is more effective than tetraethylenepentamine, and the latter more than triethylenetetramine. The very small amount of 0.1 g./liter of said polyethylene polyamine was sufficient to suppress this blistering tendency. However, an excess of these higher polyamines reduces the brightness of the electrodeposits considerably.

Complete elimination of this blistering tendency was also obtained by introducing formaldehyde-sodium bisulphite in the brightener molecule.

Example 20

To a mixture of triethylenetetramine 366 g. (2.5 mols.) and N-hydroxyethyl ethylenediamine 260 g. (2.5 mols.) were slowly added, with stirring, formaldehyde (37%) 375 ml. (approximately 5 mols.). Then an aldehyde-sodium bisulphite solution was prepared as follows: To 2300 ml. of water were added 375 ml. formaldehyde (5 mols.), then, with stirring, 1500 g. of sodium metabisulphite 95% (corresponding to 15 mols. sodium bisulphite) and finally 961 g. furfural (10 mols.).

After about half an hour of aging, this mixed aldehyde-bisulphite solution was added to the polyamine-formaldehyde reaction product with stirring and the final mixture heated to boiling, where it was kept for about 10 minutes.

The reaction product was finally diluted to 5 liters. On addition of 10 ml./liter of this brightener stock solution, equivalent to about 6.5 g./liter of reaction product to a standard zinc bath, uniform bright and blister-free zinc electrodeposits were obtained over a wide current density range (20 to 70 and more amps./sq. ft.) and the bath could be easily maintained in good performance by periodic additions of brightener.

We claim:

1. An aqueous alkaline cyanide zinc plating bath containing, in amounts of substantially 2.5 to 9.5 g./liter, as a brightening agent a condensation polymer of an aliphatic alkylenepolyamine with furfural-sodium bisulphite and formaldehyde, 0 to 50% of the latter in the form of its sodium bisulphite compounds.

2. An aqueous alkaline cyanide zinc plating bath containing, in amounts of substantially 6.5 g./liter, as a brightening agent a condensation polymer of triethylenetetramine, N-hydroxyethyl ethylenediamine, formaldehyde, furfural-sodium bisulphite and formaldehyde-sodium bisulphite.

3. An aqueous alkaline cyanide zinc plating bath containing, in amounts of substantially 6.5 g./liter, as a brightening agent a condensation polymer of 1 mol. triethylenetetramine, 1 mol. N-hydroxyethyl ethylenediamine, 2 mols. formaldehyde, 4 mols. furfural-sodium bisulphite and 2 mols. formaldehyde-sodium bisulphite.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,384,300	Harford	Sept. 4, 1945
2,495,629	Chester et al.	Jan. 24, 1950
2,589,209	Kardos	Mar. 18, 1952