United States Patent

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[54] METHOD FOR OBTAINING A BRIGHT ZINC COATING BY ELECTRODEPOSITION AND THE BATH USED THEREFOR

16 Claims, No Drawings

[52] **U.S. Cl.** **204/55**
[51] **Int. Cl.** **C23b 5/10,** C23b 5/46
[50] **Field of Search** 204/55, 55.1, 50, 50.1, 43, 44, 114; 106/1

[56] **References Cited**

UNITED STATES PATENTS

2,734,026	2/1956	Chester	204/44
2,315,802	4/1943	Lind et al.	204/49
3,088,884	5/1963	Passal	204/55
3,317,412	5/1967	Dahlmann	204/55
3,472,743	10/1969	Rushmere	204/55

FOREIGN PATENTS

1,109,479	6/1961	Germany	204/55

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Attorneys—Wayne C. Jaeschke, Martin Goldwasser and Daniel S. Ortiz

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ABSTRACT: A brightening composition and a process for electrodepositing of zinc is described herein. The brightening composition is the reaction product of an aromatic aldehyde and an amine of the formula H_2NR wherein R is a saturated aliphatic hydroxyl radical having from one to four carbon atoms. In particular, bright deposits are achieved when an amide or substituted amide is intermixed with the reaction product of the aromatic aldehyde and the amine.

METHOD FOR OBTAINING A BRIGHT ZINC COATING BY ELECTRODEPOSITION AND THE BATH USED THEREFOR

BACKGROUND OF THE INVENTION

In the art of electroplating, it is a practice to charge a cell with an electrolyte having the particular metals to be plated dissolved therein. The cells are equipped with anodes usually at each end thereof, with the material to be plated serving as the cathode. Thus, current flows therebetween to deposit the metal to be plated. Conventional solutions for the electrodeposition of zinc can be classified into two categories. The first category is the acid zinc baths, such as those containing zinc sulphate, zinc chloride, zinc fluoborate and the like. The second category is the alkaline zinc baths that contain zinc oxide, with and without sodium cyanide, and sodium hydroxide. The electrodeposit from both of these baths is generally dull without brightening agents. These agents are seldom suitable for baths of both categories.

The electrodeposition of zinc from alkaline cyanide zinc solutions is widely used to produce coatings which protect iron or steel by sacrificial cathodic action. To improve this bath, brightening agents are used. These agents impart to the electrodeposit metal a lustrous appearance. A wide variety of brightening agents have been successfully used; however, most have not been completely satisfactory. Some work well for still plating while others are only successfully used in barrel plating. In addition, some brightener compositions are not stable in the plating bath. Other compositions, while yielding bright deposits, are not suitable for accepting a chromate or phosphate protective film. Illustrative of these systems may be found in the following U.S. Pat. Nos. 2,740,754; 2,989,449; 3,088,884; 3,296,105; 3,317,412 and 3,318,767.

The conventional baths for obtaining bright zinc coatings have a cyanide content from about 10 to about 14 oz./gal. The removal of the poisonous cyanide waste from the rinse water effluent as required by governmental regulations is excessively expensive. Therefore, it is desirable to operate the zinc electroplating bath at a low cyanide content to minimize effluent treatment expenses. Moreover, the conventional zinc cyanide baths have a short downtime life. For example, after a bath containing additives of the prior art is allowed to stand overnight without plating, about one-half of the initial charge of the additive must be added to restore the deposit to its original degree of brilliance.

BRIEF DESCRIPTION OF THE INVENTION

It has been discovered that certain water-soluble reaction products of an aromatic aldehyde with aliphatic amines form complex chemical structures and provide bright deposits in zinc cyanide electrolytes with excellent downtime life. These complexes are formed by adding predetermined amounts of aromatic aldehyde with alkanolamines to provide the structures of this invention. In particular, excellent brilliance is provided to the zinc deposits by employing with the amine aldehyde complexes a water-soluble amide or substituted amide compound.

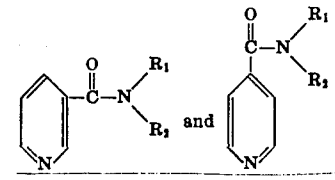
DETAILED DESCRIPTION OF THE INVENTION

In the practice of the present invention, a brightener compound is prepared by reacting an aromatic aldehyde with an amine having the formula H_2NR wherein R is a saturated aliphatic hydroxyl radical wherein the aliphatic moiety can have from one to four carbon atoms. The reaction of the two components is preferably carried out in the presence of water. Thus, the aromatic aldehydes can be selected from a group consisting of anisic aldehyde, salicyclic aldehyde, tolyl aldehyde vanillin or other aromatic aldehydes conventionally used in cyanide baths. The aromatic aldehydes can be first emulsified with the water to form an aromatic aldehyde water emulsion. Thereafter, the alkanolamine is added thereto in an amount of at least a stoichiometric quantity to react with the aromatic aldehyde. Preferably, up to about 60 percent excess of the amine can be used. The reaction product of the aromatic aldehyde and the alkanolamine has shown to be an excellent brightening composition when used in a cyanide bath.

In its preferred form, the reaction product of the aromatic aldehyde and alkanolamines is manufactured by first adding the aromatic aldehyde to heated water to form an emulsion. The water temperature is then reduced and the alkanolamine is added which reacts exothermically with the aromatic aldehyde.

After the brightening composition has been manufactured, it is then added to a conventional cyanide bath consisting of sodium cyanide, sodium hydroxide and zinc. It has been found in practice that when metals are plated with the zinc solution contained in the brighteners of the present invention, a full bright and brilliant coating is obtained. Thus, the aldehyde amine composition can be present in an amount ranging between about 0.02 to about 0.3 grams per liter of the bath solution.

Furthermore, it has been discovered that even a brighter and more brilliant zinc deposit can be obtained when a water-soluble amide or substituted amide compound is dissolved within the brightening solution. These compounds may be selected from the group consisting of:



wherein R_1 and R_2 can each be selected from a group consisting of hydrogen, saturated aliphatic radicals having from one to six carbon atoms, saturated hydroxyl substituted aliphatic radicals having from one to six carbon atoms, and any mixtures thereof. Specific examples of the amide compounds within the scope of the above identified formulas are nicotinamide, N-hexylnicotinamide, N,N-diethylnicotinamide, N-ethylnicotinamide, N,N-di(2-hydroxylpropyl) nicotinamide, isonipecotamide, N-methylisonipecotamide and N-ethylolisonipecotamide and mixtures thereof. The amide composition can be present in an amount ranging between about 0.0015 to about 0.14 grams per liter of the bath solution.

It has been particularly noted that when the amide or substituted amide component is incorporated within the brightener solution, considerably less amount of sodium cyanide can be employed within the bath solution. It is preferred that from about 1 to about 10 grams of the brightener be added per liter of bath solution.

In order to illustrate the merits of the present invention, the following examples are provided.

Example 1

A brightener was prepared from the following formula:

Salicylaldehyde	200 g.
Vanillin	10 g.
Gelatin	200 g.
Polyvinyl alcohol	30 g.
2-aminoethanol	200 g.
Water	3,310 g.

1.5 ml. of the above brightener was added to 1 liter of a standard cyanide zinc bath which had the following analysis:

Sodium cyanide	105 g./l.
Sodium hydroxide	86 g./l.
Zinc	37 g./l.

A bent panel was plated in this solution using rod agitation at 1 amp. for 10 minutes. The panel was full bright but not brilliant.

Example 2

0.04 g. of N-methylnicotinamide was added to the bath of example 1. A bent panel was plated in this solution using rod agitation at 1 amp. for 10 minutes. The panel was full bright and brilliant.

Example 3

The bath from example 2 was allowed to stand for 4 weeks without plating. After this period of standing, a bent panel was plated using the same plating conditions as in example 2. The brilliancy of the resulting plated panel was almost the equivalent of that in example 2.

Example 4

A brightener was prepared from the following formula:

Anisic aldehyde	200 g.
Vanillin	5 g.
Gelatin	200 g.
Polyvinyl alcohol	30 g.
3-amino-n-propanol	200 g.
Water	3,315 g.

1.5 ml. of this brightener was added to 1 liter of a standard cyanide zinc bath. A bent panel plated from this solution using rod agitation at 1.5 amps. was bright except for the extreme low current density areas.

Example 5

0.04 g. of N(2-hydroxyethyl)isonipecotamide was added to the bath of example 4. Ten ¼-inch hex nuts were plated in this solution in a small barrel at 1.5 amps. for 20 minutes. The nuts were bright. No trouble was experienced chromating the nuts under the normal chromating cycle.

Example 6

0.05 g. of N-ethylnicotinamide was added to the solution of example 5, and 10 more hex nuts were plated similarly to example 5. The nuts appeared to be slightly brighter than those in example 5.

Example 7

A brightener was prepared containing the following ingredients:

Nicotinamide	2%
Salicylaldehyde	5%
Vanillin	1.5%
Gelatin	6%
2-aminopropanol	5%
Water	80.5%

Ten ml, of the above brightener was added to 1 gallon of a low-cyanide zinc bath which had the following analysis:

Zinc	9 g./l.
Sodium cyanide	11.5 g./l.
Sodium hydroxide	79 g./l.

Forty ¼×20 1-inch hexhead bolts were plated in a small laboratory plating barrel. The barrel was plated at 5 amps. for one-half hour. The plated zinc deposit on the bolts was bright and leveled. Five of these bolts were chromated in an iridescent chromate. No difficulty was found in obtaining the normal chromate film on the bolts provided that they were rinsed thoroughly.

Example 8

Plating tests were continued on the bath of example 7. The brightener level was kept high enough so that full bright deposits were obtained. The barrel tests were continued until a definite addition pattern was established. A consumption rate was calculated from these tests. The addition rate established was 426 X cc. of the brightener/1,000 amp. hr.

Example 9

A brightener was prepared with the following ingredients:

Salicylaldehyde	3%
Anisic aldehyde	2%
Vanillin	1.5%
Gelatine	5%
Polyvinyl alcohol	0.75%
2-aminoethanol	5%
Water	80.75%
Nicotinamide	2%

When the 2-aminoethanol was added to the water emulsion of anisic aldehyde and salicylaldehyde, considerable heat was evolved indicating that a reaction between the aldehydes and the 2-aminoethanol took place.

Example 10

A standard cyanide zinc solution had the following analysis:

Sodium hydroxide	47 g./l.
Sodium cyanide	52.5 g./l.
Zinc	16.5 g./l.

This bath had been previously brightened with a standard anisic aldehyde-bisulfite-containing brightener. Barrel loads of parts were plated from this bath until the brightener was obviously depleted. An addition of 1 cc./gallon of the brightener of example 9 was made. After this addition, barrel loads of parts were plated. The zinc deposit was full bright after this addition. No difficulty was experienced in chromating these plated parts with a blue white clear chromate. The barrel test continued. An addition rate of 1.1 liters/10,000 amp. hr. was sufficient to produce full bright deposits of zinc.

Example 11

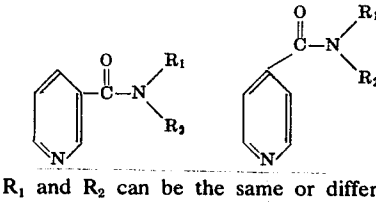
Barrel tests continued on the bath of example 10. The sodium cyanide content of this bath was allowed to drop and the sodium hydroxide was increased while plating every day until the bath had the following analysis:

Sodium hydroxide	78 g./l.
Sodium cyanide	13.2 g./l.
Zinc	7.5 g./l.

Full bright deposits were obtained from this bath during this transition period by the periodic addition of the brightener of example 9. At the end of this test full bright zinc plated deposits were still obtained. No difficulty was experienced in chromating the parts at any time. The consumption rate of the low cyanide bath was calculated to be 2 liters/10,000 amp. hr.

What is claimed is:

1. In an aqueous, alkaline zinc cyanide plating bath, the improvement which comprises the presence in said bath of a brightener composition which comprises a combination of: (1) the reaction product of at least one aromatic aldehyde with at least a stoichiometric quantity of at least one alkanolamine having the formula H_2NR wherein R is a saturated aliphatic hydroxyl radical containing from one to four carbon atoms and (2) at least one water-soluble amide or substituted amide corresponding to the formula:



wherein R_1 and R_2 can be the same or different and are selected from the group consisting of hydrogen, saturated aliphatic radicals containing from one to six carbon atoms and

saturated hydroxyl substituted aliphatic radicals containing from one to six carbon atoms; said reaction produce being present in said bath in a concentration from about 0.02 to 0.3 grams per liter and said amide or substituted amide being present in a concentration of from about 0.0015 to 0.14 grams per liter.

2. The bath of claim 1, wherein said aromatic aldehyde is at least one member selected from the group consisting of anisic aldehyde, vanillin, salicylic aldehyde and tolyl aldehyde.

3. The bath of claim 2, wherein said aromatic aldehyde is vanillin.

4. The bath of claim 1, wherein said amide or substituted amide is at least one member selected from the group consisting of:

nicotinamide, N-hexylnicotinamide,
N,N-diethylnicotinamide, N-ethylolnicotinamide,
N-N-di(2-hydroxypropyl)nicotinamide, isonipecotamide,
N-methylisonipecotamide, and N-ethylolisonipecotamide.

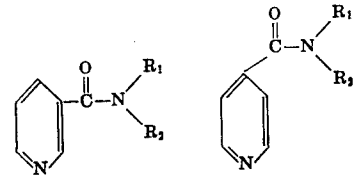
5. The bath of claim 4, wherein said amide or substituted amide is nicotinamide.

6. The bath of claim 1, wherein polyvinyl alcohol is also present therein.

7. The bath of claim 1, wherein gelatine is also present therein.

8. The bath of claim 1, wherein both polyvinyl alcohol and gelatine are also present therein.

9. In the process of electrodepositing zinc from an aqueous, alkaline zinc cyanide plating bath, the improvement which comprises adding to the bath a brightener composition which comprises a combination of: (1) the reaction product of at least one aromatic aldehyde with at least a stoichiometric quantity of at least one alkanolamide having the formula H_2NR wherein R is a saturated aliphatic hydroxyl radical containing from one to four carbon atoms and (2) at least one water-soluble amide or substituted amide corresponding to the formula:



wherein R_1 and R_2 can be the same or different and are selected from the group consisting of hydrogen, saturated aliphatic radicals containing from one to six carbon atoms and saturated hydroxyl substituted aliphatic radicals containing from one to six carbon atoms; said reaction product being present in said bath in a concentration of from about 0.02 to 0.3 grams per liter and said amide or substituted amide being present in a concentration of from about 0.0015 to 0.14 grams per liter.

10. The process of claim 9, wherein said aromatic aldehyde is at least one member selected from the group consisting of anisic aldehyde, vanillin, salicylic aldehyde and tolyl aldehyde.

11. The process of claim 10, wherein said aromatic aldehyde is vanillin.

12. The process of claim 9, wherein said amide or substituted amide is at least one member selected from the group consisting of:

nicotinamide, N-hexylnicotinamide,
N,N-di(2-hydroxypropyl)nicotinamide, isonipecotamide,
N,N-di(2hydroxypropyl)nicotinamide, isonipecotamide,
N-methylisonipecotamide, and N-ethylolisonipecotamide.

13. The process of claim 9, wherein said amide or substituted amide is nicotinamide.

14. The process of claim 9, wherein polyvinyl alcohol is also present in said bath.

15. The process of claim 9, wherein gelatine is also present in said bath.

16. The process of claim 9, wherein both polyvinyl alcohol and gelatine are also present in said bath

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,620,938 Dated November 16, 1971

Inventor(s) James A. Von Pless and Richard P. Cope, Jr.

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

Column 3, Example 7, line 55, after "ml" the comma should be a --period--.

Column 4, line 2, after "426" delete the X.

Column 5, line 2, the word "produce" should read --product--; line 3, after the word "concentration" insert --of--.

Column 6, Claim 12, line 6, delete "N,N-di(2hydroxypropyl)-nicotinamide, isonipecotamide" and insert --N,N-diethylnicotinamide, N-ethyl-olnicotinamide--.

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents