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3,806,431

ZINC ELECTROPLATING BATH HAVING LOW CYANIDE CONTENT

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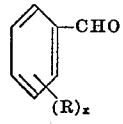
Int. Cl. C23b 5/10, 5/46
U.S. Cl. 204—55 Y 3 Claims

ABSTRACT OF THE DISCLOSURE

A bath for electroplating zinc containing in aqueous solution a zinc salt, an alkali metal cyanide, an alkali metal hydroxide, an aldehyde-alkanolamine condensation product, a water soluble polyvinyl alcohol and optionally salts of metals of Groups VII–B or VIII of the Periodic Table of Elements and further tricrotonylene tetramine and trithione (3-thio-3H-1,2-dithiole), said bath having a low cyanide content, yields highly brilliant zinc coatings with very good throwing power and metal distribution. Preferred aldehyde-alkanolamine condensation products are condensation products of a mono-alkanolamine with an aromatic aldehyde of the general formula



wherein R is hydroxyl and/or lower alkoxy having from 1 to 4 carbon atoms and x is zero, one, or two.

BACKGROUND OF THE INVENTION

The invention relates to a zinc electroplating bath having a low cyanide content.

It is known to use cyanide containing electroplating baths for depositing zinc on, e.g., iron. The zinc deposits obtained with the known baths may have good throwing power, brilliance and a good metal distribution. In order to obtain zinc deposits of high brilliance the addition of brighteners to the electroplating baths is required. As brighteners for this purpose aldehyde-alkanolamine condensation products, water soluble polyvinyl alcohol and salts of metals of Group VII–B or Group VIII of the Periodic Table are known. Since the problem of water pollution and the costly measures of freeing waste water from poisonous substances gain growing importance the use of cyanide containing electroplating baths recently has decreased considerably. At present increasingly weak acid or alkaline zinc electroplating baths with no cyanide or having a low cyanide content are used which, however, usually do not provide the brilliance of cyanide containing zinc electroplating baths.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a zinc electroplating bath having a low cyanide content but the properties of a good cyanide containing zinc electroplating bath with respect to brilliance, throwing power, and metal distribution. The cyanide content of the bath of the invention may be lowered from the normal content of 80 g. to 150 g./l. to a level of from 10 g. to 25 g./l. without adversely affecting the zinc deposit obtained.

It is a further object of the present invention to provide an alkaline zinc electroplating bath comprising in aqueous solution a zinc salt, one or more aldehyde-alkanolamine condensation products, water soluble polyvinyl alcohol and optionally salts of a metal of Groups VII–B or VIII of the Periodic Table of Elements and, in addition, tricrotonylene tetramine and trithione (3-thio-3H-1,2-dithiole).

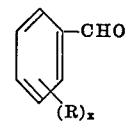
If desired other additives, such as additional brighteners may be used.

Further objects of the invention may be taken from the following specification.

DESCRIPTION OF THE INVENTION

The zinc electroplating bath according to the invention preferably contains 0.1 g. to 1.0 g./l. of tricrotonylene tetramine. Most preferred is an amount of 0.1 g. to 0.5 g. of tricrotonylene tetramine per liter of the zinc bath. The preferred amounts of trithione in the zinc bath are 0.01 g. to 0.05 g./l., in particular 0.01 g. to 0.02 g./l.

Preferred aldehyde-alkanolamine condensation products (Schiff's bases) are condensation products of a lower mono-alkanolamine, such as mono-ethanolamine and of an aldehyde of the formula



wherein R is hydroxyl and/or lower alkoxy having 1 to 4 carbon atoms, in particular methoxy, and x is zero, one, or two. Preferred aldehydes are salicylaldehyde, anisaldehyde, vanillin, or veratraldehyde. Further, unsaturated aromatic aldehydes, such as cinnamic aldehyde, or formaldehyde can also be used.

The amount of the aldehyde-alkanolamine condensation product is preferably between 0.2 g. and 2 g./l. of the bath, in particular between 0.3 g. and 1 g./l., as the salt of a metal of Group VII–B or Group VIII of the Periodic Table, a salt of manganese, cobalt or nickel is preferred. Said salt is used in amounts between 0.01 g. and 0.1 g./l. preferably between 0.01 g. and 0.05 g./l. Polyvinyl alcohol is preferably used in an amount between 0.01 g. and 0.5 g./l., in particular between 0.1 g. and 0.5 g./l. of the bath.

The invention is further illustrated by the following examples.

EXAMPLE I

Zinc deposits on iron having a smooth surface and excellent brightness as well as throwing power and metal distribution were obtained by using a bath of the following composition:

7–15 g./l. of zinc (calculated as zinc oxide),
10–25 g./l. of sodium cyanide,
80–100 g./l. of sodium hydroxide,
1.0 g./l. of the condensation product of mono-ethanolamine and veratraldehyde,
0.2–0.4 g./l. of tricrotonylene tetramine,
0.01–0.05 g./l. of trithione,
0.2–0.4 g./l. of polyvinyl alcohol (water soluble), and
0.02 g./l. of manganese sulfate.

Temperature: Between 15° C. and 35° C., current density: 0.3 to 5.0 amps/dm.^{2}.

EXAMPLE II

Smooth and bright zinc coatings on iron having excellent throwing power and metal distribution were obtained by using an electroplating bath of the following composition:

7–15 g./l. of zinc (calculated as zinc oxide),
10–25 g./l. of sodium cyanide,
80–100 g./l. of sodium hydroxide,
0.5 g./l. of the condensation product of mono-ethanolamine and formaldehyde,
0.5 g./l. of a condensation product of mono-ethanolamine and vanillin,
0.2–0.4 g./l. of tricrotonylene tetramine,
0.01–0.05 g./l. of trithione,

0.04 g./l. of nickel sulfate, and
0.2–0.4 g./l. of polyvinyl alcohol (water soluble).

Temperature: Between 15° C. and 35° C., current density: 0.3–5.0 amps/dm.^{2}.

EXAMPLE III

Smooth and bright zinc coatings on iron having good throwing power and metal distribution were obtained by using an electroplating bath of the following composition:

7–15 g./l. of zinc (calculated as zinc oxide),
10–25 g./l. of sodium cyanide,
80–100 g./l. of sodium hydroxide,
0.5 g./l. of condensation product of mono-ethanolamine and anisaldehyde,
0.2–0.4 g./l. of tricrotonylene tetramine,
0.2–0.4 g./l. of manganese sulfate,
0.2–0.4 g./l. of polyvinyl alcohol (water soluble).

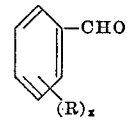
Temperature: Between 15° C. and 35° C., current density: 0.3–5.0 amps./dm.^{2}.

What is claimed is:

1. A zinc electroplating bath comprising, in aqueous solution,

a zinc salt in an amount equivalent to between about 7 g./l. and about 15 g./l. of zinc oxide,
between about 10 g./l. and about 25 g./l. of an alkali metal cyanide,
between about 80 g./l. and about 100 g./l. of an alkali metal hydroxide,
between about 0.2 g./l. and about 2.0 g./l. of a condensation product of an aldehyde with an alkanolamine,
between about 0.1 g./l. and about 1.0 g./l. of tricrotonylene tetramine,
between about 0.1 g./l. and about 0.05 g./l. of trithione,
between about 0.01 g./l. and about 0.1 g./l. of a salt of a metal selected from the group consisting of metals of Groups VII–B and VIII of the Periodic Table, and
between about 0.01 g./l. and about 0.5 g./l. of a water soluble polyvinyl alcohol.

2. The zinc electroplating bath of claim **1** in which the condensation product of an aldehyde with an alkanolamine is the condensation product of a lower mono-alkanolamine and an aromatic aldehyde of the formula



in which

R is a member selected from the group consisting of hydroxyl and lower alkoxy with 1 to 4 carbon atoms, and x is one of the numerals 0, 1, and 2.

3. A zinc electroplating bath comprising, in aqueous solutions,

a zinc salt in an amount equivalent to between about 7 g./l. and about 15 g./l. of zinc oxide,
between about 10 g./l. and about 25 g./l. of an alkali metal cyanide,
between about 80 g./l. and about 100 g./l. of an alkali metal hydroxide,
about 0.5 g./l. of a condensation product of an aldehyde with an alkanolamine,
between about 0.2 g./l. and about 0.4 g./l. of tricrotonylene tetramine,
between about 0.01 g./l. and about 0.05 g./l. of trithione, and
between about 0.2 g./l. and about 0.4 g./l. of a water soluble polyvinyl alcohol.

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GERALD L. KAPLAN, Primary Examiner

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,806,431 Dated April 23, 1974

Inventor(s) REINHARD KOCH

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

Column 3, line 34: "0.1 g./l." should read -- 0.01 g./l. --.

Column 4, line 14: "solutions" should read -- solution --.

Signed and sealed this 10th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

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Commissioner of Patents

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,806,431 **Dated** April 23, 1974

Inventor(s) REINHARD KOCH

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

Column 1, between the 6th and 7th line of the Heading, there is to be inserted a new line reading as follows:

-- Claims priority: Application Germany, May 10, 1971, No. P 21 23 108.3. --

Signed and sealed this 12th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patent