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Creutz

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[54] **NON-CYANIDE ZINC PLATING**

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[*] Notice: The portion of the term of this patent subsequent to July 24, 1990, has been disclaimed.

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[21] Appl. No.: **385,940**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 263,580, June 16, 1972, abandoned, which is a continuation of Ser. No. 20,855, March 18, 1970, abandoned.

[52] **U.S. Cl.** ..... **204/55 R**

[51] **Int. Cl.²** **C25D 3/22**

[58] **Field of Search** ..... 204/55 R, 55 Y, 43 Z, 44

[56] **References Cited**

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[57] **ABSTRACT**

A non-cyanide zinc electroplating bath which contains a linear polyether and a bath soluble heterocyclic nitrogen compound to improve the quality of the zinc electrodeposits obtained. Additionally, the electroplating baths may also contain an organic chelating agent. With this bath, zinc electrodeposits having improved brightness and leveling are produced even from baths having a relatively low zinc content, over a relatively wide pH and current density range. These baths have further been found to be useful in both barrel and rack plating processes.

9 Claims, No Drawings

NON-CYANIDE ZINC PLATING

CROSS REFERENCE TO RELATED CASES

This application is a continuation-in-part of application Ser. No. 263,580 filed June 16, 1972, which in turn is a continuation of application Ser. No. 20,855 filed Mar. 18, 1970 and both now abandoned.

This invention relates to an improved composition and process for the production of bright zinc electrodeposits, and more particularly, relates to compositions and processes for forming bright zinc electrodeposits from non-cyanide zinc electroplating baths.

Heretofore, various processes have been utilized for the electrodeposition of zinc to provide both corrosion resistant and decorative coatings, particularly on ferrous metals, such as iron and steel. In general, the zinc electroplating baths have been either acid zinc baths, which are generally operated in a pH range of from about 3 to 5, and alkaline zinc baths, which are generally operated in a pH within the range of from about 10 to 14. Although the acid zinc plating baths are more inexpensive to operate, because of their relatively poor throwing power, their use has been largely restricted to the plating of relatively simple shapes, such as steel strip, pipe, wire and the like, in which the plating is carried out over a relatively narrow current density range. Additionally, because of the corrosive nature of the acid zinc baths, corrosion resistant linings such as rubber, lead, ceramics, synthetic resins and the like, must be used in the plating tanks. For these reasons, the acid zinc plating baths have not been widely used.

The alkaline zinc plating baths have commonly been of two types, the cyanide-free baths, which contain sodium zincate, and the more conventional bright zinc baths which contain sodium cyanide. The sodium zincate baths, however, have a relatively low efficiency and often produce soft-spongy electrodeposits. Moreover, even with various additives, the zinc deposits produced are not as bright as those obtained from cyanide baths and, hence, there has been limited commercial use of such baths.

With the alkaline cyanide zinc plating baths, however, generally acceptable electrodeposits are obtained, the baths are stable, and relatively easy to control and the cyanide-containing solution is not corrosive to ferrous metal plating tanks. Accordingly, such baths have been widely used commercially. Notwithstanding this widespread commercial acceptance, however, in recent years there has been an increasing awareness that these plating baths containing sodium cyanide constitute both a health hazard to operating personnel and a source of industrial pollution. Accordingly, and particularly because of the increased expense encountered in the installation and operation of the special processing equipment to overcome the waste disposal problem, significant numbers of platers have discontinued the use of zinc and switched to other metals as substitutes.

It is, therefore, an object of the present invention to provide an improved bright zinc plating bath which is free of cyanide.

Another object of the present invention is to provide a cyanide-free bright zinc plating bath which has excellent throwing power and which will produce a smooth, bright, adherent zinc deposit over a relatively wide operating range of pH and current densities.

A further object of the present invention is to provide an improved process for the electrodeposition of a smooth, bright, adherent zinc deposit from a cyanide-free zinc plating bath.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes an aqueous, cyanide-free zinc electroplating bath, which bath contains as brightening additives, a linear polyether and a heterocyclic nitrogen compound. These baths, either as such, or when further containing an organic chelating agent have been found to produce bright, lustrous zinc electrodeposits over a wide range of operating conditions.

More specifically, the baths of the present invention are aqueous, cyanide-free zinc electroplating baths, having a pH of from about 3.5 to 9.6 and containing a linear polyether and a bath-soluble heterocyclic nitrogen compound, in amounts sufficient to produce a zinc electrodeposit having improved brightness. These baths are aqueous solutions of a zinc salt, such as zinc sulfate, zinc chloride, zinc fluoroborate, or the like. Additionally, the bath may also contain ammonium chloride, which has been found to improve the bath conductivity and throwing power. Desirably, these baths contain the zinc in an amount within the range of about 5 to 75 grams per liter, with an amount of zinc within the range of about 10 to 30 grams per liter being preferred. Additionally, where ammonium chloride is included in the bath, it is desirably present in amounts within the range of about 20 to 300 grams per liter, with amounts within the range of about 100 to 200 grams per liter being preferred. Moreover, compounds such as ammonium hydroxide, and hydrochloric acid may also be included in the zinc plating baths in amounts which will provide the desired pH of the bath. Accordingly, the specific amounts used will vary, depending upon the specific make-up of the particular zinc plating bath which is being used.

As brightening additives, it has been found that the cyanide-free zinc electroplating baths of the present invention must contain at least a water soluble non-ionic wetting agent and a heterocyclic nitrogen compound. Desirably, the water soluble non-ionic wetting agent is a polyether compound and is present in the bath in an amount within the range of about 0.2 to 20 grams per liter, with an amount within the range of about 0.5 to 5 grams per liter being preferred. The polyether compounds which have been found to be suitable for use in the plating baths of the present invention are linear, mono or difunctional polyethers which are substantially free of side chains which terminate in a functional group, such as an OH group. Suitable linear polyethers of this type include the difunctional polyethers, such as the polyglycols, exemplary of which are the polyethylene glycols, polypropylene glycols, mixed polymers of polyethylene and polypropylene glycol, and the like, as well as the monofunctional linear polyethers, such as the ethoxylated alkyl phenols, ethoxylated fatty alcohols, and the like. Typically, these linear polyether compounds will have a molecular weight within the range of about 500 to 1,000,000. In the case of the monofunctional linear polyethers such as the ethoxylated alkyl phenols, these may contain up to about 18 carbon atoms in the alkyl group and up to about 50 moles of ethylene oxide. Of the various linear poly-

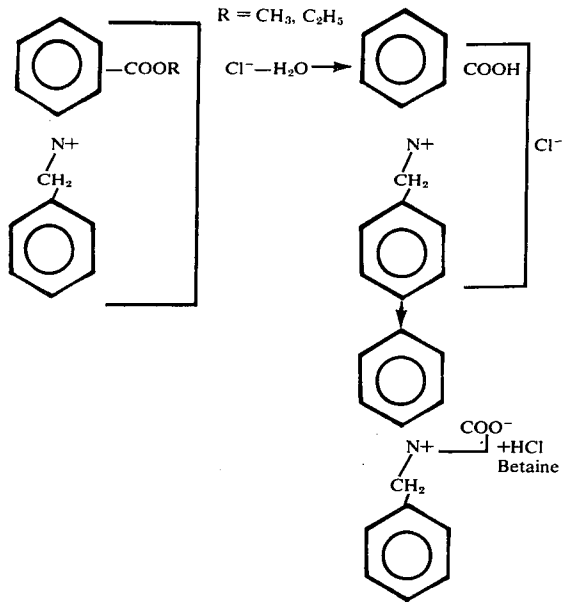
ethers which are suitable for use in the present electroplating bath, the polyethylene glycols having a molecular weight of from about 1000 to 100,000 and the condensation products of nonyl phenol with about 30 moles of ethylene oxide, have been found to be preferred. It is to be appreciated, however, that these materials are merely exemplary of the linear polyethers which may be used and are not to be taken as a limitation on these materials.

More specifically, it has recently been found that particularly advantageous results are obtained when there is combined with the isopropyl ester of benzyl chloride nicotinate either one or both of water soluble non-ionic wetting agents of the polyether class, identified as acetylenic glycol 2, 3, 7, 9-tetramethyl 5-decyne-4, 7 diol-ethoxylated and monyl phenoxy poly (ethyleneoxy)-ethanol. The structural formula of the first mentioned polyether will be set forth later in connection with certain working Examples.

These polyethers, which have a molecular weight between about 200 and 20,000, synergestically work very well with the propyl or isopropyl ester of benzyl nicotinic acid quaternary to produce zinc plated parts with uniform fully bright electrodeposits. This is quite in contrast to the teachings of the prior art which disclose that certain quaternaries and betaines of nicotinic acid and derivatives thereof are useful additives in alkaline zinc plating baths, and more specifically, alkaline cyanide zinc plating baths. One would presume that these nicotinic compounds would have a beneficial effect in neutral or slightly acidic baths; however, it has been demonstrated that this is not the case. Betaines of nicotinic acid quaternaries have been found not to function as good brighteners except in very low current density areas, but with respect to medium to high current density areas, deleterious effects were clearly discernible.

To be more specific, further tests have been conducted which clearly demonstrate the superiority of the propyl or isopropyl esters of benzyl chloride nicotinate over the methyl or ethyl nicotinates when combined with an effective polyether. While the methyl and ethyl compounds when first added to a neutral or slightly acidic zinc plating bath with a polyether provided acceptably bright zinc electrodeposits, it has been found that after a relatively short period of bath operation the effectiveness of the plating operation deteriorated. As an example, after 150 to 200 A-hours/gallon were passed through a plating solution containing a polyether and either a methyl or ethyl nicotinate, burning of the cathode occurred at rather high current densities. Even further, it has been found that the combination of the methyl or ethyl nicotinates and an effective polyether at 30 ASF initially produced a uniformly bright electrodeposit; however, after a period there was noticeable dulling or burning.

While various theories might be advanced, it would appear that the deteriorating performance of a plating bath of the character described in the preceding paragraph is due to the fact that the ester converts back to the carboxylic group which then forms a betaine generally in accordance with the following equation:



The heterocyclic nitrogen compound additives, which are used in conjunction with the polyether materials, are desirably present in the present zinc electroplating bath in amounts within the range of about 2 milligrams to 10 grams per liter, with amounts within the range of about 10 to 100 milligrams per liter being preferred. These additive materials are bath-soluble quaternary nitrogen compounds which contain at least one substituting group selected from carboxylic esters, carboxamide, substituted carboxamides, carboxy and nitrile groups and; preferably, are quaternaries or betaines of various pyridines. Exemplary of such materials which are suitable are the bath soluble pyridine quaternary compounds which contain at least one substituting group selected from carboxylic esters, carboxamide, substituted carboxamides, carboxy and nitrile groups which have been quaternarized with agents such as benzyl chloride, alkyl bromide, methyl or ethyl chloroacetate, and the like. Heterocyclic nitrogen compounds of this general class are disclosed in U.S. Pat. No. 3,318,787. Although in this patent these compounds are disclosed as producing smooth, bright zinc deposits when added to alkaline cyanide zinc electroplating baths, surprisingly it has been found that when used alone in the non-cyanide zinc electroplating baths of the present invention, they have little effect. It is only when the propyl is isopropyl esters of benzyl chloride nicotinate are used in combination with the linear polyether materials that fully bright and commercially acceptable zinc electrodeposits are obtained from the non-cyanide baths.

In addition to the linear polyether material and the heterocyclic nitrogen compounds, in many instances it has also been found desirable upon occasion to include in the plating baths an organic chelating or sequestering agent to help prevent the formation of zinc hydroxide. An exemplary condition when chelating agents might be employed would be when the pH of the bath was too high for the zinc ions to remian in solution. These chelating agents are used in amounts sufficient

to chelate the zinc in the bath and, hence, the specific amounts used will vary in each instance, depending upon the composition of the bath. Typically, however, they are present in amounts up to about 250 grams per liter, with amounts within the range of about 10 to 150 grams per liter being preferred. Exemplary of the various suitable chelating agents which may be used are ethylene diamine tetraacetic acid, nitrilotriacetic acid, ethylene diamine tetraethanol, citric acid, ethylene diamine diacetic acid, and the like, including the various salts of these compounds.

In formulating the zinc electroplating baths of the present invention, the various additive materials may be added separately to the bath in amounts which will provide the desired concentration of these components in the bath. Preferably, however, an aqueous concentrate composition is utilized which contain all of the desired additive material in the proper ratio and proportion to each other so as to provide the desired concentration of these materials in the bath. Thus, a suitable additive concentrate composition for use in formulating the zinc electroplating baths of the present invention may contain the following components in the amounts indicated:

Component	Amount
Linear polyether	5.0 to 20 grams per liter
Heterocyclic nitrogen compound	5.0 to 150 mg/l
Organic chelating agent	0 to 250 grams/liter

Concentrate compositions of this type may be added to the plating baths in amounts which will provide the desired amount of the concentrate components in the bath.

In utilizing the plating baths of the present invention, the baths may be operated at temperatures up to about 60 degrees centigrade, with temperatures in the range of about 15 to 30 degrees centigrade being preferred. The pH of the plating baths during operation may be within the range of about 3.5 to 9.6, with pHs from about 5 to 8 being preferred. Desirably, the average cathode current densities used will be within the range of about 5 to 100 amps per square foot, with the average current densities of from about 10 to 50 amps per square foot being preferred. Thus, it is to be appreciated that the plating baths of the present invention may be used in various plating operations, including both barrel plating and rack plating processes.

In order that those in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, parts and percent are by weight and temperatures are in degrees centigrade. It is to be appreciated, however, that these are merely exemplary of the present invention and are not to be taken as a limitation thereof.

EXAMPLE 1

A cyanide-free zinc electroplating bath was formulated containing the following components in the amounts indicated:

Components	Amounts
Zinc chloride	50 grams per liter
Ammonium chloride	200 grams per liter
Tetraethanol ethylene diamine	50 grams per liter
Ammonium hydroxide (29% by weight)	25 milliliters per liter
Polyethylene glycol (molecular weight 4000)	40 grams per liter
Ethyl nicotinate-benzyl chloride quaternary	50 milligrams per liter

Using this plating bath, at a pH of 8.0 a bent, J-shaped steel cathode was plated for 20 minutes at a current density of 30 amps per square foot and a uniform full bright zinc electrodeposit was obtained.

EXAMPLE 2

A cyanide-free electroplating bath was formulated containing the following components in the amounts indicated:

Components	Amounts
Zinc chloride	30 grams per liter
Ammonium chloride	220 grams per liter
Ammonium hydroxide (29% by weight)	80 milliliters per liter
Polyethylene glycol (molecular weight 100,000)	10 milliliters per liter
Isopropyl nicotinate-benzyl chloride quaternary	30 milligrams per liter

With this bath, at a pH of 8.2, and an average current density of 20 amps/square foot, uniform full bright zinc electrodeposits were obtained, as in Example 1.

EXAMPLE 3

A generic plating formulation which has given particularly good results may be defined as follows:

Components	Range	Preferred
Zinc chloride	5g–200 g/l	30–120 g/l
Ammonium chloride	50–300 g/l (saturation)	100–250 g/l
Benzyl chloride-isopropyl nicotinate	10–100 mg/l	15–50 mg/l
Polyether	2–50 g/l	5–10 g/l

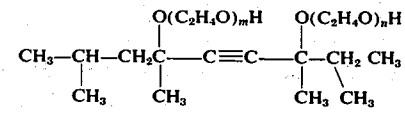
The pH range is 3 to 9, with 4 to 6 preferred.

EXAMPLE 4

A more specific formulation is as follows:

Zinc chloride	40 g/l
Ammonium chloride	200 g/l
Benzyl chloride quaternary of isopropyl nicotinate	30 mg/l
Polyether	5 cc/l

In the above composition the polyether was acetylenic glycol 2,3,7,9-tetramethyl 5-decyne-4, 7 diolethoxylated, having the formula:



and wherein *m* and *n* are integers of from 4 to 10.

The bath of Example 4 was operated at a pH of 4.6, and when steel cathodes were plated at 30 ASF for 15 minutes at room temperature, the plating quality was excellent.

EXAMPLE 5

A further specific formulation which was tested is as follows:

Zinc chloride	50 g/l
Ammonium chloride	250 g/l
Benzyl chloride quaternary of isopropyl nicotinate	50 mg/l
Polyether	5 g/l

In the above composition the polyether was monyl phenoxy(ethyleneoxy)-ethanol. The pH of the bath was 5.0, and when steel cathodes were plated at 40 ASF for 10 minutes at room temperature, the plating quality was excellent.

EXAMPLE 6

An additional specific formulation within the scope of this invention is:

$ZnSO_4.H_2O$	10 g/l
$ZnCl_2$	25 g/l
NH_4Cl	225 g/l
Benzyl chloride quaternary of isopropyl nicotinate	50 mg/l
Polyether A	2 g/l
Polyether B	2 cc/l

In the composition of Example 6, polyether A was the same as the polyether of Example 5 and polyether B was the same as the polyether of Example 4. With the pH of the bath of Example 6 at 5.2, steel cathodes were plated at 25 ASF for 20 minutes at room temperature and good plating quality was obtained.

EXAMPLE 7

Another specific bath formulation tested was as follows:

Zinc chloride	50 g/l
Ammonium chloride	270 g/l
Benzyl chloride quaternary of isopropyl nicotinate	40 mg/l
Polyether A	2.5 g/l
Polyether B	2.5 g/l

In the composition of the Example just above, Polyethers A and B were the same as in Example 6. With the pH of the bath in Example 6 at 3.9, steel cathodes were plated at 25 ASF for 10 minutes at room temperature and good plating resulted.

EXAMPLE 8

An additional specific bath formulation tested was as follows:

Zinc chloride	60 g/l
Benzyl chloride quaternary of propyl nicotinate	150 mg/l
Polyether A	3.0 g/l
Polyether B	6.0 g/l

In the composition of the Example just above, Polyethers A and B were the same as in Example 6. The pH of the bath in Example 8 was 4.6 and steel cathodes were plated at 30 ASF for 15 minutes with a bath temperature of 76°F and good plating resulted.

Various changes and modifications in the formulations and process of this invention has been disclosed herein, and these and other variations may of course be practiced without departing from the spirit of the invention or the scope of the subjoined claims.

We claim:

1. An aqueous, cyanide-free zinc electroplating bath having a pH of from about 3.5 to 9.6 and including as brightening agents a linear polyether having a molecular weight within the range of about 500 to 1,000,000 and a heterocyclic nitrogen compound in the form of the propyl or isopropyl ester of benzyl chloride nicotinate, said polyether and nitrogen compound being soluble in the bath and further being present in combined amounts sufficient to produce a zinc electrodeposit of improved brightness.

2. An electroplating bath as defined in claim **1**, wherein the linear polyether is present in an amount within the range of about 2 to 50 grams per liter and the heterocyclic nitrogen compound is present in an amount within the range of about 10 to 100 milligrams per liter.

3. An electroplating bath as defined in claim **2**, wherein zinc chloride is the source of zinc in the bath.

4. An electroplating bath as defined in claim **2**, in which there is also present in the bath between about 5 to 200 g/l of zinc chloride and 50 to 300 g/l of ammonium chloride.

5. An electroplating bath as defined in claim **1**, in which the polyether is selected from the group consisting of acetylenic glycol 2, 3, 7, 9-tetramethyl 5-decyne-4, 7 diol-ethoxylated and monyl phenoxy poly (ethyleneoxy) -ethanol.

6. An electroplating bath as defined in claim **1**, in which the polyether is present in the bath in an amount of between about 5 to 10 g/l, the nicotinate is present in an amount of between about 15 to 50 mg/l, and in which there is also present in the bath about 5 to 200 grams/liter zinc chloride and about 50 to 300 grams/liter of ammonium chloride.

7. An electroplating bath as defined in claim **1**, in which there is also present in the bath about 0 to 250 grams/liter of a chelating agent selected from the group consisting of ethylene-diamine tetraacetic acid, nitrilotriacetic acid, ethylene diamine tetraethanol, citric acid and ethylene diamine diacetic acid.

8. An electroplating bath as defined in claim **1**, in which the polyether is acetylenic glycol 2,3,7, 9-tetramethyl 5-decyne-4, 7 diol-ethoxylated.

9. A method of depositing a smooth, adherent bright zinc deposit, which comprises electrodepositing zinc from an aqueous cyanide-free zinc electroplating bath of the character defined in claim **1**.

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