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ACID ZINC ELECTROPLATING

John Derek Rushmere, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del.

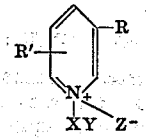
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Int. Cl. C23b 5/12, 5/46

U.S. Cl. 204—55 R 12 Claims

ABSTRACT OF THE DISCLOSURE

Acid zinc electroplating baths at pH 2.5 to 5.5 are provided which use as additives compounds with the general formula:



wherein

R is —$CONH_2$, —CN, —$CONHNH_2$, —COOH or —COOR" where R" is an alkyl group of 1 to 4 carbon atoms,

R' is hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms,

X is an alkyl group of 1 to 8 carbon atoms,

Y is —COOH, —COO^-, —SO_3H, —SO_3^- or —$CONH_2$, and

Z^- is a halide ion or is absent when Y is —COO^- or —SO_3^-.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to acid zinc electroplating baths and processes and, more particularly, to such baths and processes for depositing bright zinc plates.

Prior Art

Heretofore, bright decorative zinc plates have been customarily obtained from alkaline cyanide zinc baths or alkaline zincate baths, whereas acid zinc baths have been used where the appearance of the deposited zinc is not especially important as in the coating of steel strip or conduit. With increasing industry emphasis on pollution control and the diminution of cyanide plating baths, the art in acid zinc plating is being increasingly directed to additives useful for improving the appearance of the zinc deposit over a wide current density range.

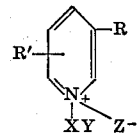
Numerous patents concerned with bright zinc deposits obtained from acid zinc baths have issued over the years. Many of these have been directed to the use of sulfur and nitrogen compounds such as thioureas, pyridine (U.S. Pat. 2,355,505 issued to John L. Bray and Robert E. Howard on Aug. 8, 1944), sulfonated heterocyclics (U.S. Pat. 2,543,545 issued to Charles L. Faust and Arthur E. Bearse on Feb. 27, 1951), alkylamines or polyamines as additives to improve brightness; a recent patent U.S. 3,537,959 issued to Joachim Korpiun and Hans J. Steeg is directed to the use of primary amines and naphthalene sulfonic acid-formaldehyde condensation products for this purpose.

Quaternary nitrogen compound additives useful in alkaline zinc electroplating are described in U.S. Pat. 3,318,787 issued to Gustav Rindt, and Donald H. Becking on May 9, 1967, and U.S. Pat. 3,411,996 issued to John D. Rushmere on Nov. 19, 1968.

SUMMARY OF THE INVENTION

According to the present invention there is provided an aqueous acid zinc electroplating bath comprising an

aqueous solution of a zinc salt maintained at a pH in the range of about 2.5 to 5.5 and having dissolved therein in an amount effective to give a bright zinc deposit a pyridinium compound of the general formula:



wherein

R is —$CONH_2$, —CN, —$CONHNH_2$, —COOH or —COOR" where R" is an alkyl group of 1 to 4 carbon atoms,

R' is hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms,

X is an alkyl group of 1 to 8 carbon atoms,

Y is —COOH, —COO^-, —SO_3H, —SO_3^- or —$CONH_2$, and

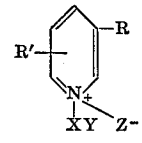
Z^- is a halide ion or is absent when Y is —COO^- or —SO_3^-.

Also provided is a process of electroplating bright zinc using the above acid zinc electroplating bath.

DETAILED DESCRIPTION OF THE INVENTION

Generally, the invention pertains to the electro-deposition of zinc from acid zinc plating baths known to those skilled in the art. These baths can be formed by the dissolution of zinc oxide in an excess of a common non-complexing acid such as sulfuric, sulfamic, fluoboric or hydrochloric with the pH of the bath adjusted to between about 2.5 and 5.5, preferably between 3.5 and 4.5, by the addition of aqueous ammonia. Alternatively, the baths can be formed by the dissolution of commercial zinc and ammonium salts, such as the sulfates, acetates, chlorides, fluoborates or sulfamates, in water with subsequent adjustment of pH to the normal range by means of aqueuos ammonia, an alkali metal base or acid as required. Mixtures of zinc salts can be used if desired. Temperature of operation is usually at ambient temperatures, but can be between 15° C. and 45° C. Other metal salts such as sodium sulfamate or potassium sulfate may be added to enhance electrical conductivity.

Zinc electrodeposits obtained from such acid baths are typically coarse and dull gray in appearance and have little commercial value, especially in the decorative plating of screws, chains and other items of hardware. It has now been found that when certain quaternized pyridine compounds are added singly or in combination to an acid zinc electroplating bath of the type described above in amounts from 0.2 to 20 grams per liter, preferably 2 to 8 grams per liter, the resultant zinc electroplate is smooth and bright, and of commercially acceptable quality. Excellent throwing power is also usually obtained from baths using these compounds as is demonstrated by uniform plating between the threads and in the head recesses of ordinary wood screws. The quaternized pyridine compounds useful in the present invention have the general formula:



wherein

R is —$CONH_2$, —CN, —$CONHNH_2$, —COOH or —COOR" where R" is an alkyl group of 1 to 4 carbon atoms,

R' is hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms,

X is an alkyl group of 1 to 8 carbon atoms,
Y is —COOH, —COO^-, —SO_3H, —SO_3^- or —$CONH_2$ and
Z^- is a halide ion or is absent when Y is —COO^- or —SO_3^-.

Preferred compounds are where R is —$CONH_2$ or —CN, R' is hydrogen, X is alkyl of 1 to 4 carbon atoms, Y is —SO_3H, —SO_3^- or —$CONH_2$ and Z^- is chloride ion or is absent when Y is SO_3^-. Particularly preferred compounds are 1-(3-propanesulfonate) 3-cyano pyridinium betaine and 1-(2-acetamido) 3-amido pyridinium chloride. Other compounds which have been found useful in the plating of zinc from acid baths are:

1. 1-(3-propane sulfonate) 3-amido pyridinium betaine
2. 1-(2-diethylacetic acid) 3-amido pyridinium bromide
3. 1-(2-isobutyric acid) 3-amido pyridinium chloride
4. 1-(3-propane sulfonate) 3-carbomethoxy pyridinium betaine
5. 1-(2-proprionic acid) 3-amido pyridinium chloride
6. 1-(2-octanoic acid) 3-amido pyridinium bromide
7. 1-(2-acetamido) 3-hydrazido pyridinium chloride
8. 1-(2-acetic acid) 3-carboxy pyridinium chloride

Further compounds within the general formula useful in the invention are:

9. 1-(2-acetamido) 3-amido 4-bromo pyridinium chloride
10. 1-(3-pyropanesulfonate) 3-cyano 5-methyl pyridinium betaine
11. 1-(2-isobutyric acid) 3-amido 6-chloro pyridinium chloride
12. 1-(2-propionic acid) 3-amido 6-ethyl pyridinium chloride.

The compounds within the scope of the invention are not all equally effective under all conditions. Thus, some are preferred for still or automatic rack plating, whereas others are more effective for barrel plating or other plating operations. However, the compounds described have been found capable of improving the quality of zinc plate deposited from acid zinc baths.

It should be understood that the quaternized pyridine compounds described have been used both in the form of betaines which undergo no further ionization in solution and in the form of normal salts which undergo ionization on dissolution in the plating bath. Thus, where appropriate, the betaine and normal salt forms are essentially the same compounds. For instance, 1-(3-propanesulfonate) 3-cyano pyridinium betaine is equivalent in the bath to 1-(3-propanesulfonic acid) 3-cyano pyridinium chloride.

In the examples which follows, the following plating bath was used unless otherwise indicated.

$ZnSO_4$—140 g./l.
$(NH_4)_2SO_4$—30 g./l.
pH—3.5
Temp.—25° C.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated:

EXAMPLE 1

To a Hull Cell containing 267 ml. of the acid zinc sulfate plating bath was added 1 g. of 1-(2-acetamido), 3-amido pyridinium chloride prepared by precipitation from a refluxing ethanolic solution of nicotinamide and 2-chloroacetamide. A steel panel was then plated at 2 amps. for 5 minutes to obtain a deposit of smooth bright zinc over the C.D. range 1–65 amp./ft.^{2}

EXAMPLE 2

One g. of 1-(3-propane sulfonate), 3-cyano pyridinium betaine prepared by precipitation from a refluxing acetone solution of 3-cyano pyridine and propane sultone was added to 250 ml. of acid zinc sulfate plating bath and the whole transferred to a mini-plating barrel. Thirty g. of #6 x ½" steel wood screws were then barrel plated at 1.5 amps. for 20 minutes. The zinc-plated screws were bright and lustrous and required no bright dip. They were, however, treated with a standard chromate conversion dip to give a blue white product of excellent appearance.

EXAMPLE 3

To 250 ml. of acid zinc sulfate plating bath was added 1 g. of (2-diethylacetic acid), 3-amido pyridinium bromide prepared by precipitation from refluxing acetone containing nicotinamide and 2-bromodiethylacetic acid. Using this solution, 30 g. of #6 x ½" steel screws were barrel plated at 1.5 amps. for 30 minutes. A shiny bright product was obtained which required no bright dip.

A second 30 g. batch of screws were plated from this solution at low current density, namely 0.5 amp. for 30 minutes. Again a shiny bright product was obtained which required no bright dip.

EXAMPLE 4

Ten ml. of a 10 percent solution of the disodium salt of 1-(2-acetic acid) 3-carboxy pyridinium chloride, prepared by refluxing together in aqueous solution equimolar amounts of sodium nicotinate and sodium chloroacetate at pH 6, was added to 250 ml. of acid zinc sulfate plating bath. Thirty g. of # x ½" wood screws were zinc plated for 20 minutes at 1.5 amps. to give a smooth, semi-bright zinc-plated product. The screws were then treated with a chromate conversion dip to give a commercially acceptable product.

EXAMPLE 5

To 1.2 l. of acid zinc sulfate bath was added 2 g. of 1-(2-diethylacetic acid) 3-amido pyridinium bromide plus 2 g. of 1-(2-acetamido) 3-amido pyridinium chloride. A steel Hull Cell panel, bent in the form of a rectangular Z was then zinc plated at 2 amps. for 10 minutes. Each minute the work was removed from the bath for 2–5 seconds to simulate conveyance on an automatic rack plater, and also help detach gas bubbles which might otherwise cause pitting. At the end of the plating period, the shape was bright and shiny with even coverage into the recesses.

EXAMPLE 6

An acid zinc-plating bath was prepared containing:

$ZnSO_4$—70 g./l.
$Zn(SO_3NH_2)_2$—110 g./l.
$(NH_4)_2SO_4$—15 g./l.
pH—2.7

To 150 ml. of this bath was added 0.4 g. of 1-(3-propane sulfonate) 3-cyano pyridinium betaine and the bath then used to zinc plate 30. g. of #6 x ½" wood screws at 1.5 amps. for 20 minutes in a mini-barrel. After plating and a brief dip in 0.1 percent nitric acid, the screws were smooth, semi-bright and of acceptable commercial quality.

EXAMPLE 7

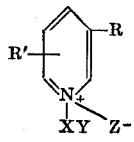
The bath of Example 6 was diluted with water to give 250 m. of a bath now containing:

$ZnSO_4$—42 g./l.
$Zn(SO_3NH_2)_2$—66 g./l.
$(NH_4)_2SO_4$—9 g./l.
pH—3.4

With no further addition of additives this bath gave zinc deposits that were dull and of unacceptable quality. However after the addition of a further 0.4 g. of 1-(3-propane sulfonate) 3-cyanopyridinium betaine and 0.5 g. of 1-(2-diethylacetic acid) 3-amido pyridinium bromide, 30 g. of #6 x ½" wood screws plated at 1.5 amps. for 10 minutes gave a shiny bright product. The screws took an excellent chromate conversion coating.

What is claimed is:

1. An aqueous acid zinc electroplating bath comprising an aqueous solution of a zinc salt maintained at a pH in the range of about 2.5 to 5.5 and having dissolved therein in an amount effective to give a bright zinc deposit a pyridinium compound of the general formula:



wherein

R is $-CONH_2$, $-CN$, $-CONHNH_2$, $-COOH$ or $-COOR''$ where R'' is an alkyl group of 1 to 4 carbon atoms,

R' is hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms,

X is an alkyl group of 1 to 8 carbon atoms,

Y is $-COOH$, $-COO^-$, $-SO_3H$, $-SO_3^-$ or $-CONH_2$, and

Z^- is a halide ion or is absent when Y is $-COO^-$ or $-SO_3^-$.

2. The acid electroplating bath of Claim 1 wherein the pyridinium compound is added to give a bath concentration within the range of about 0.2 to 20 grams per liter.

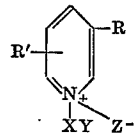
3. The acid electroplating bath of Claim 2 wherein the pyridinium compound is selected from the group consisting of 1-(3-propanesulfonate) 3 cyano pyridinium betaine and 1-(2-acetamido) 3-amido pyridinium chloride.

4. The acid electroplating bath of Claim 2 wherein the pH of the bath is within the range of about 3.5 to 4.5.

5. The acid electroplating bath of Claim 4 wherein the pyridinium compound is added to give a bath concentration within the range of about 2 to 8 grams per liter.

6. The acid electroplating bath of Claim 5 wherein the pyridinium compound is selected from the group consisting of 1-(3-propanesulfonate) 3-cyano pyridinium betaine and 1-(2-acetamido) 3-amido pyridinium chloride.

7. In a process of electroplating bright zinc from an aqueous acid zinc electroplating bath having a zinc salt dissolved therein the improvement comprising maintaining said bath at a pH in the range of about 2.5 to 5.5 and adding thereto in an amount effective to give a bright zinc deposit a pyridinium compound of the general formula:



wherein

R is $-CONH_2$, $-CN$, $-CONHNH_2$, $-COOH$ or $-COOR''$ where R'' is an alkyl group of 1 to 4 carbon atoms,

R' is hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms,

X is an alkyl group of 1 to 8 carbon atoms,

Y is $-COOH$, $-COO^-$, $-SO_3H$, $-SO_3^-$ or $-CONH_2$, and

Z^- is a halide ion or is absent when Y is $-COO^-$ or $-SO_3^-$.

8. The process of Claim 7 wherein pyridinium compound is added to give a bath concentration within the range of about 0.2 to 20 grams per liter.

9. The process of Claim 8 wherein the pyridinium compound is selected from the group consisting of 1-(3-propanesulfonate) 3-cyano pyridinium betaine and 1-(2-acetamido) 3-amido pyridinium chloride.

10. The process of Claim 8 wherein the pH of the bath is within the range of about 3.5 to 4.5 and the pyridinium compound is added to give a bath concentration within the range of about 2 to 8 grams per liter.

11. The process of Claim 10 wherein the pyridinium compound is selected from the group consisting of 1-(3-propanesulfonate) 3-cyano pyridinium betaine and 1-(2-acetamido) 3-amido pyridinium chloride.

References Cited

UNITED STATES PATENTS

2,543,545	2/1951	Faust et al.	204—55 R
2,813,065	11/1957	Du Rose	204—45
3,203,878	8/1965	Willmund et al.	204—52
3,318,787	5/1967	Rindt et al.	204—55 Y
3,594,291	7/1971	Todt et al.	204—55 R

FOREIGN PATENTS

805,316	12/1958	Great Britain.
1,202,525	8/1970	Great Britain.

FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

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