United States Patent [19]

Voss et al.

[11] **3,920,528**

[45] **Nov. 18, 1975**

[54] **BRIGHT ACID ZINC PLATING METHOD AND ELECTROLYTE**

[75] Inventors: **Gunter Voss; Helga Hoffmann,** both of Berlin, Germany

[73] Assignee: **Schering AG,** Berlin, Germany

[22] Filed: **Oct. 25, 1973**

[21] Appl. No.: **409,694**

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

[51] **Int. Cl.²** **C25D 3/22**

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

[56] **References Cited**

UNITED STATES PATENTS

3,766,024	10/1973	Yamagishi et al.	204/55 R
3,769,184	10/1973	Rushmere	204/55 R
3,778,359	12/1973	Popescu	204/55 R

Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Joseph F. Padlon

[57] **ABSTRACT**

Bright zinc electrodeposits are obtained at high current densities from aqueous, acid electrolytes containing zinc ions, inert alkali metal salts of strong mineral acids for improving conductivity, and a brightener which includes a small amount of an acid having a carboxyl group or a sulfo group attached directly or through a lower alkylene, vinyl, carbonyl, or phenylene group to the heterocyclic ring of pyridine, quinoline, isoquinoline, pyrrol, piperidine, pyrrolidine, or pyrrolidone. The electrolytes are free from significant amounts of complexing agents that would impede precipitation of the zinc ions at weakly alkaline pH so that the electrolytes do not present a waste disposal problem.

9 Claims, No Drawings

BRIGHT ACID ZINC PLATING METHOD AND ELECTROLYTE

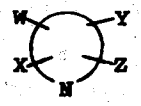
This invention relates to the electrodeposition of zinc, and particularly to a method of plating bright zinc coatings on conductive substrates from acid electrolytes and to electrolytes for use in the method.

Acid zinc baths are much less toxic than conventional alkaline zinc plating electrolytes and preferred for this reason where the disposal of waste electrolyte presents an environmental problem. However, the known acid zinc plating baths do not produce bright electrodeposits unless they contain complexing agents for zinc. Such complexing agents impede the removal of zinc ions from waste electrolyte by precipitation in the weakly alkaline pH range, and high concentrations of ammonium salts which may replace stronger complexing agents, are themselves toxic to aquatic life and are not readily removed from waste electrolyte.

It is an object of the invention to permit the production of bright zinc electrodeposits from electrolytes which can be released safely into sewers or streams after precipitation of their zinc content as zinc hydroxide in a simple manner.

Another important object of the invention is the provision of zinc plating baths from which bright zinc can be deposited at high current densities with good adhesion to all common conductive substrates.

With these objects and others in view, the invention provides an acid zinc plating electrolyte of the type including a source of zinc ions, an inert salt for improving the conductivity of the electrolyte, and a brightener. According to the invention, the brightener comprises an effective amount, normally between 0.01 and 10 grams per liter, of a brightening agent of the formula



wherein



is the heterocyclic ring of pyridine, quinoline, isoquinoline, pyrrol, piperidine, pyrrolidine, or pyrrolidone,

W is —COOH, —SO_3H, —$(CH_2)_n$COOH, —C_2H_3COOH, —CO—COOH, or —C_6H_4—COOH,

n is 1, 2, or 3,

X is hydrogen, carboxyl, lower alkyl, or vinyl,

Y is hydrogen, hydroxyl, methyl, or methoxy, and

Z is hydrogen or methyl.

While electrolytes containing only the heterocyclic acids mentioned above produce zinc electrodeposits of good brightness, particularly in concentrations of 0.1 to 1.0 g per liter, even greater brightness and a good levelling effect can be achieved by the use of a secondary brightener, conventional in itself, such as a compound having a carbonyl group directly attached to an aromatic ring, as exemplified by acetophenone, benzalacetone, benzoylacetone, 3-acetylcoumarin, 3-acetylpyridine, and m-hydroxybenzaldehyde.

The secondary brighteners are employed in concentrations which are preferably determined experimentally for each primary brightening agent of the invention. Usually, the concentration of the secondary brightener is between 0.01 to 2.0 g/liter, and the ratio of the primary brightening agent to the secondary brightener is between 1:1 and 10:1.

The preferred source of zinc ions is zinc chloride in a concentration of 30 to 150 g/liter which furnishes 15 to 75 g/liter zinc ions. Boric acid or other weak acids in small amounts have been found to contribute to the performance of the electrolytes of the invention, but not to be critically necessary.

Wetting agents are preferably employed as is conventional in this art, and should be non-foaming, but are otherwise not critical as to their specific properties or chemical composition. Their concentration is also non-critical, but normally between 0.1 and 30 g/liters, a concentration of 1 to 10 g/liter wetting agent being preferred under most conditions.

The electrolytes of the invention are operated at pH values between 3 and 7, and preferably between 4.5 and 5.5, and at ambient temperature (15° to 35°C), a temperature of 20° to 30°C being readily maintained in all but tropical climates without heat exchanges. The electrolyte is preferably agitated although cathode rod agitation is also effective. Bright deposits can be obtained over most of the cathode current density range between 0.1 and 20 amps/dm^2.

The electrolytes of the invention are suitable for plating in tanks with stationary cathodes, in plating conveyors, and for barrel plating of small objects in bulk.

Adhesion to conventionally prepared metallic and other substrates is good, and the electrolytes are particularly useful for plating on cast iron.

The following Examples are further illustrative of the invention.

EXAMPLE 1

Ductile zinc electrodeposits of uniform, good brightness were obtained at ambient temperature (15° – 35°C) over a current density range from 0.04 to 10 amps/dm^2 from an agitated electrolyte of the following composition:

Zinc chloride	70	g/liter
Potassium chloride	210	"
Boric acid	20	"
Potassium benzoate	2.0	"
Wetting agent	3.0	"
Pyridine-3-acetic acid	0.4	"

The wetting agent employed was a mixture of anionic surfactants mainly consisting of hydroxyalkyl sulfates and amphoteric, ethoxylated surfactants. The pH value of the electrolyte was kept at 5.0.

Brightness was maintained over all practical deposit thickness values.

EXAMPLE 2

Mirror-bright zinc electrodeposits were obtained at ambient temperature at cathode current densities of 0.1 to 8 amps/dm² from an electrolyte consisting of:

Zinc chloride	70 g/liter
Potassium chloride	210 "
Boric acid	20 "
Benzoyl acetone	0.2 "
Wetting agent (as in Ex. 1)	4.0 "
Pyridine-3-sulfonic acid	0.3 "
pH 5.3	

EXAMPLE 3

Reasonably bright zinc electrodeposits were obtained at current densities of 0 to 3 amps/dm² from an electrolyte of the following composition:

Zinc chloride	34 g/liter
Potassium chloride	149 "
Boric acid	20 "
Potassium benzoate	8 "
Wetting agent (as in Ex. 1)	4.0 "
Benzalacetone	0.2 "
pH 5.5	

When 0.1 g/liter pyridine-3-carboxylic acid was added to the electrolyte, brightness was improved substantially, and the fully bright range was extended to 8 amps/dm² without loss of brightness at very low cathode current densities.

EXAMPLE 4

Fully bright zinc electrodeposits were formed at current densities up to at least 15 amps/dm² from an electrolyte consisting of:

Zinc chloride	100 g/liter
Potassium chloride	210 "
Boric acid	20 "
Potassium 2,4-dihydroxybenzoate	6.0 "
Wetting agent (as in Ex. 1)	4.0 "
Benzalacetone	0.2 "
Pyridine-3-carboxylic acid	0.2 "
pH 5.0	

Brightness was not impaired when the zinc deposit was made several thousandths of an inch thick.

EXAMPLE 5

An electrolyte of the composition:

Zinc chloride	90 g/liter
Potassium chloride	350 "
Boric acid	20 "
Potassium salicylate	7.5 "
Wetting agent (as in Ex. 1)	4.0 "
Benzoylacetone	0.3 "
pH 5.3	

produced bright zinc electrodeposits at ambient temperatures at cathode current densities of no more than 5 amps/dm².

When 0.4 g/liter pyridine-3-carboxylic acid was added, the fully bright range was extended to a current density limit of at least 15 amps/dm² with exceptionally good throwing power.

EXAMPLE 6

Bright zinc electrodeposits were formed at current densities up to about 5 amps/dm² from an electrolyte of the following composition at ambient temperature:

Zinc chloride	70 g/liter
Potassium chloride	210 "
Boric acid	20 "
Wetting agent (as in Ex. 1)	5.0 "
3-Acetylpyridine	0.5 "
pH 5.0	

When the current density was raised to 5.5 amps/dm², zinc was deposited as a greyish-black powder which adhered poorly to a properly prepared steel cathode.

When 0.4 g/liter pyridine-3-sulfonic acid was added to the electrolyte, fully bright zinc electrodeposits showing excellent adhesion were produced at cathode current densities of 15 amps/dm² and even more, producing a zinc coating at a growth rate of 4 microns per minute.

Pyridine-3-acetic acid, pyridine-3-sulfonic acid, and pyridine-3-carboxylic acid were employed in the six Examples for illustration of best modes of carrying out this invention, and are preferred brighteners of the invention at this time because they are readily available at low cost. However, substantially identical results were obtained by equal weights of any one or mixtures of the following acids:

Pyridine-2,6-dicarboxylic acid
Pyridine-3,4-dicarboxylic acid
Pyridine-3,5-dicarboxylic acid
Pyridine-4-carboxylic acid
Pyridine-3-propionic acid
Pyridine-2,3-dicarboxylic acid
4-Hydroxy-pyridine-2,6-dicarboxylic acid
2-Methylpyridine-5-carboxylic acid
4-Methylpyridine-3-carboxylic acid
4-Ethylpyridine-3-carboxylic acid
2,4-Dimethylnicotinic acid
2,6-Dimethylnicotinic acid
2,3,4-Trimethylpyridine-5-carboxylic acid
2-Vinylnicotinic acid
β-3-Pyridylacrylic acid
2-β-Pyridyl-benzoic acid
Pyridine-3-carbonylacetic acid
α-6-Methyl-pyridyl(3) -acrylic acid
6-Hydroxynicotinic acid
4-Hydroxy-2,6-dimethyl-nicotinic acid
4-Hydroxypyridine-3-carboxylic acid
Quinoline-3-carboxylic acid
Quinoline-4-carboxylic acid
Piperidine-2-carboxylic acid
Piperidine-4-carboxylic acid
L-Pyrrolidone-2-carboxylic acid
L-Pyrrolidine-2-carboxylic acid
Isoquinoline-4-carboxylic acid
Pyrrol-α-carboxylic acid

The preferred conventional brighteners which enhance the effect of the compounds of this invention are aromatic carbonyl compounds, but not necessarily benzol acetone, benzalacetone, or acetyl pyridine exemplified above. Acetophenone, 3-acetylcoumarin, and m-hydroxybenzaldehyde are equally effective and merely representative of this class of compounds.

Zinc chloride may be replaced by other water soluble zinc salts which furnish the necessary concentration of

zinc ions, such as zinc sulfate, zinc acetate, or zinc fluorborate, a zinc ion concentration of 15 to 75 g/liter being generally effective.

Similarly, potassium chloride may be replaced by other neutral and inert alkali metal salts of strong mineral acids such as potassium sulfate and the corresponding sodium salts for improving the conductivity of the electrolyte, as is common practice. The necessary concentrations range from about 50 g/liter to saturation at the operating temperature, an upper limit of 250 g/liter being generally set by practical considerations.

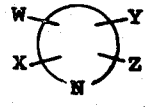
Boric acid in the electrolyte may be replaced or supplemented by equally small amounts of carboxylic acids such as acetic acid, benzoic acid, or salicylic acid, and may be omitted if desired.

The chemical nature of the wetting agent or agents employed is not critical. As is known in this art, it is desirable to reduce the surface tension of the electrolyte and to prevent the adhesion of hydrogen bubbles to the cathode surface. The wetting agent should not cause formation of foam on the electrolyte since the foam may trap hydrogen and oxygen and cause accidents.

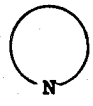
It should be understood, therefore, that the foregoing disclosure relates only to preferred embodiments of the invention, and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of the disclosure which do not constitute departures from the spirit and scope of the invention set forth in the appended claims.

What is claimed is:

1. In an acid zinc electroplating electrolyte including a source of zinc ions, an inert salt for improving the conductivity of the electrolyte, and a brightener, the improvement in the brightener which consists essentially of an effective amount of a brightening agent of the formula



wherein



is the heterocyclic ring of pyridine, quinoline, isoquinoline, pyrrol, piperidine, pyrrolidine, or pyrrolidone,

W is $-COOH$, $-SO_3H$, $-(CH_2)_nCOOH$, $-C_2H_3COOH$, $-CO-COOH$, or $-C_6H_4-COOH$,

n is 1, 2, or 3,

X is hydrogen, carboxyl, lower alkyl, or vinyl,

Y is hydrogen, hydroxyl, methyl, or methoxy, and

Z is hydrogen or methyl the electrolyte being substantially free from complexing agents capable of impeding precipitation of said zinc ions from said electrolyte when the electrolyte is made weakly alkaline.

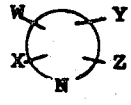
2. In an electrolyte as set forth in claim **1**, said brightener further comprising an effective amount of a secondary brightener selected from the group consisting of acetophenone, benzalacetone, benzoylacetone, 3-acetyl-coumarin, 3-acetylpyridine, and m-hydroxybenzaldehyde.

3. In an electrolyte as set forth in claim **2**, the amount of said secondary brightener being between 0.01 and 2.0 grams per liter.

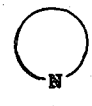
4. In an electrolyte as set forth in claim **1**, the amount of said brightening agent being between 0.01 and 10 grams per liter.

5. In an electrolyte as set forth in claim **1**, the amount of said brightening agent being between 0.1 and 1.0 gram per liter.

6. A method of producing a bright electrodeposit of zinc on a conductive substrate which comprises making said substrate the cathode in an aqueous electrolyte at pH 3.0 to 7.0 and a temperature of 15° to 35°C, said electolyte containing 15 to 75 grams per liter zinc ions, at least 50 grams per liter of an inert alkali metal salt of a strong mineral acid, and an effective amount of a brightening agent of the formula



wherein



is the heterocyclic ring of pyridine, quinoline, isoquinoline, pyrrol, piperidine, pyrrolidine, or pyrrolidone,

W is $-COOH$, $-SO_3H$, $-(CH_2)_nCOOH$, $-C_2H_3COOH$, $-CO-COOH$, or $-C_6H_4-COOH$,

n is 1, 2, or 3,

X is hydrogen, carboxyl, lower alkyl, or vinyl,

Y is hydrogen, hydroxyl, methyl, or methoxy, and

Z is hydrogen or methyl

the electrolyte being substantially free from complexing agents capable of impeding precipitation of said zinc ions from said electrolyte when the electrolyte is made weakly alkaline.

7. A method as set forth in claim **6**, wherein the concentration of said brightening agent is between 0.01 and 10 grams per liter.

8. A method as set forth in claim **7**, wherein said electrolyte further contains an amount of a secondary brightener sufficient to enhance the brightening effect of said brightening agent, said secondary brightener being a member of the group consisting of acetophenone, benzalacetone, benzolyacetone, 3-acetyl-coumarin, 3-acetylpyridine, and m-hydroxybenzaldehyde.

9. A method as set forth in claim **8**, wherein the amount of said secondary brightener in said electrolyte is between 0.01 and 2.0 grams per liter, and the weight ratio of said brightening agent to said secondary brightener is between 1:1 and 10:1.

* * * * *