ABSTRACT OF THE DISCLOSURE

Mirror bright zinc electrodeposits are formed from acid zinc plating solutions containing as brighteners N-polyvinylpyrrolidone-(2) and a ketone of the formula

\[ R_1-\left(\text{CH}=-\text{CH}\right)_n-\text{CO}=-R_2 \]

wherein R1 is phenyl, mono- or dihydroxyphenyl or trihydroxyphenyl methylenedioxymethyl, mono-, di- or tri- lower-alkylphenyl, mono- or di- or tri-lower-alkoxyphenyl, furyl, thiienyl, coumaryl, or pyridyl, and R2 may be lower alkyl, lower alkenyl, lower-alkyl-carbonyl-lower-alkylene, cyano-lower-alkylene, lower-alkoxy-carbonyllower-alkylene, or \(-\left(\text{CH}=-\text{CH}\right)_n-\text{C}_6\text{H}_5\) n being 1 or 0.

This invention relates to the electrodeposition of bright zinc, and particularly to bright zinc plating from acid electrolytes.

A wide variety of bright zinc plating solutions of the cyanide type is available. The cyanide baths are relatively unstable because of the decomposition of cyanide to carbonate, and the cyanide drag-out into rinsing baths presents a serious disposal problem. The deposits formed from known acid zinc plating baths free from organic complexing agents are at best smooth, but not bright, and complex forming organic components in acid zinc plating solutions, such as EDTA present a disposal and pollution problem as difficult to solve as that caused by cyanide. Zinc and other heavy metals cannot be precipitated from the rinse water and other wastes bearing EDTA by means of alkaline reagents. Bright coatings can be produced from baths containing EDTA (ethylenediamine-tetra-acetic acid) only if other heavy metals, particularly iron, copper, and nickel, are carefully and initially removed.

The object of the invention is the provision of a brightener system for acid zinc plating solutions which permits the zinc dragged out into rinsing baths to be precipitated by an alkaline reagent because of the absence of complex forming compounds, is insensitive to substantial amounts of other heavy metal, provides bright and ducile deposits over a wide range of cathode current densities, and is stable under the operating conditions usual for the electrodeposition of dull coatings from acid electrolytes including agitation by means of compressed air.

Such a brightener system has been found in the combination of N-polyvinylpyrrolidone-(2) with a secondary brightener of the formula

\[ R_1-\left(\text{CH}=-\text{CH}\right)_n-\text{CO}=-R_2 \]

wherein R1 is

[Diagram]

R3 is lower alkyl, lower alkenyl, lower-alkyl-carbonyl-lower-alkylene, cyano-lower-alkylene, lower-alkoxy-carbonyl-lower-alkylene, or \(-\left(\text{CH}=-\text{CH}\right)_n-\text{C}_6\text{H}_5\) n being 1 or 0.

R3, R4 and R5 each are hydrogen, hydroxy, lower alkyl, or lower alkoxy, and R3 and R4 together represent the methylendioxymethylene group, and n is 1 or 0.

The concentration of polyvinylpyrrolidone-(2) in the electrolytes of the invention may be between 0.5 to 100 g/l, and that of the secondary brightener between 0.01 and 0.5 g/l, with best results usually being obtained at respective concentrations of 2-10 g/l and 0.05-0.3 g/l. For reasons not fully understood at this time, the two brighteners synergistically cooperate, the brightness of the electrodeposited obtained by their simultaneous presence being far superior to the sum of their individual effects. Neither of them alone can produce the mirror brightness available from the combination.

The brighteners of the invention are known compounds, and may be prepared from readily available starting materials by known methods. The solution polymerization of vinyl pyrrolidone in the presence of azosobutyronitrile has been described in German Pat. No. 922,378.

The degree of polymerization of the polyvinylpyrrolidone is not critical, acceptable results being obtained with products whose degree of polymerization is between 5 and 1000. Most consistently satisfactory results are achieved with a polymer having an average molecular weight of about 10,000 to 30,000, and a corresponding intrinsic viscosity of about 17 to 25.

Representative secondary brighteners of the invention are listed below:

- Acetophenone
- Ethinylphenylketone
- Propiophenone
- Benzalacetone
- 2-Hydroxybenzalacetone
- 3-Methoxybenzalacetone
- 2,3-Dimethyl-benzalacetone
- Piperonylidenebenzalacetone
The aqueous electrolyte which may be improved by the use of the brighteners may typically contain zinc sulfate and ammonium chloride, and optionally boric acid within the following ranges:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>G./l</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>100–600</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>10–100</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0–40</td>
</tr>
</tbody>
</table>

The zinc sulfate may be replaced as a source of zinc ions partly or entirely by other zinc salts such as the chloride, acetate, fluoroborate, and sulfamate. Ammonium chloride has the primary function of improving the conductivity of the electrolyte, and may therefore be replaced by other conductive salts such as sodium chloride, sodium sulfate, sodium acetate, aluminum sulfate, and many others, as is well known in itself according to the art.

If so desired, other known brighteners may be employed in conjunction with those of this invention, known thiazol derivatives being particularly suited for this purpose. Warming agents and other conventional adjuvants may be added to perform their known functions.

The electrolytes of the invention may be operated over a wide range of plating conditions, particularly a pH value of 3 to 6, a temperature of 10° to 45° C., most conveniently at 20° to 30° C., and at cathode current densities from 0.1 to 10.0 amperes per dm². For highest brightness, cathode rod agitation or aeration is necessary. Still baths produce coatings which are not truly mirror bright, particularly at relatively high current densities. The electrolytes of the invention are particularly useful for barrel plating, both in oblique barrels containing the electrolyte and in horizontal barrels immersed in a tank. Racked objects have been handled successfully on conveyors, with highest brightness being achieved with air agitation. Such zinc plates of the invention are completely free from haze.

The brighteners of the invention undergo neither chemical nor electrolytic decomposition in the acid zinc plating solutions and can be used for a long time without additions other than those needed to make up for drag-out losses. They are relatively insensitive to contamination with heavy metals other than zinc, particularly to iron contamination. The electrolytes of the invention are not impaired if steel parts are accidentally immersed in the bath without current as may occur if a rack drops into the electrolyte from a conveyor.

A few zinc plating solutions of the invention and the operating conditions under which they were operated successfully to produce fully bright zinc plates are listed in the following examples.

**Example 1**

Zinc sulfate (ZnSO₄·7H₂O): 145 g./l.
Ammonium chloride: 55 g./l.
Boric acid: 20 g./l.
Polyvinylpyrrolidone: 5 g./l.
Benzoylecetone: 0.1 g./l.
Current density: 0.1–5.0 amperes/dm²
Air agitation
EXAMPLE 2
Zinc sulfate (ZnSO₄·7H₂O): 290 g/l.
Ammonium chloride: 25 g/l.
Polyvinylpyrrolidone-(2): 5 g/l.
Propiophenone: 0.1 g/l.
Nonylphenol-ethylhexylsulfate addition compound: 0.04 g/l.

pH: 4.5
Temperature: 30°C.
Current density: 0.1-6.0 amps/dm²
Cathode rod agitation

EXAMPLE 3
Zinc chloride (ZnCl₂): 70 g/l.
Ammonium sulfate: 130 g/l.
Sodium chloride: 10 g/l.
Polyvinylpyrrolidone-(2): 3 g/l.
Benzalacetone: 0.1 g/l.
Ethyl benzylacetate: 0.1 g/l.
Sodium ethylhexylsulfate: 0.5 g/l.

pH: 5.0
Temperature: 25°C.
Current density: 0.1-5.0 amps/dm²
Air agitation

EXAMPLE 4
Zinc sulfate (ZnSO₄·7H₂O): 145 g/l.
Ammonium chloride: 53 g/l.
Boric acid: 20 g/l.
Polyvinylpyrrolidone-(2): 3 g/l.
1-(2-Furyl)-1'-buten-3-one: 0.1 g/l.
Nonylphenol-ethylhexylsulfate: 0.4 g/l.

pH: 4.2
Temperature: 25°C.
Current density: 0.1-5 amps/dm²
Cathode rod agitation

EXAMPLE 5
Zinc sulfate (ZnSO₄·7H₂O): 290 g/l.
Ammonium chloride: 25 g/l.
Polyvinylpyrrolidone-(2): 5 g/l.
3-Acetylpyridine: 3 g/l.
Fatty alcohol polyglycol ether: 0.2 g/l.

pH: 4.8
Temperature: 30°C.
Current density: 0.1-7.5 A/dm²
Cathode rod agitation

EXAMPLE 6
Zinc sulfate (ZnSO₄·7H₂O): 145 g/l.
Ammonium chloride: 53 g/l.
Polyvinylpyrrolidone-(2): 2.5 g/l.
1-(2-Furyl)-1'-buten-3-one: 0.2 g/l.
Sodium dodecylbenzene-sulfate: 0.1 g/l.

pH: 5.0
Temperature: 25°C.
Current density: 0.1-5 amps/dm²
Cathode rod agitation

EXAMPLE 7
Zinc sulfate (ZnSO₄·7H₂O): 145 g/l.
Ammonium chloride: 53 g/l.
Boric acid: 20 g/l.
Polyvinylpyrrolidone-(2): 3 g/l.
3-methoxy-benzalacetone: 0.15 g/l.

pH: 5.5
Temperature: 25°C.
Current density: 0.1-5.0 A/dm²
Air agitation

EXAMPLE 8
Zinc sulfate (ZnSO₄·7H₂O): 290 g/l.
Ammonium chloride: 25 g/l.

EXAMPLE 9
Zinc chloride (ZnCl₂): 70 g/l.
Ammonium sulfate: 130 g/l.
Sodium chloride: 10 g/l.
Polyvinylpyrrolidone-(2): 3 g/l.
Piperonylideneacetone: 0.2 g/l.

pH: 4.2
Temperature: 25°C.
Current density: 0.1-5 amps/dm²
Air agitation

EXAMPLE 10
Zinc sulfate (ZnSO₄·7H₂O): 145 g/l.
Ammonium chloride: 53 g/l.
Boric acid: 20 g/l.
Polyvinylpyrrolidone-(2): 3 g/l.
Piperonylidenebenzalacetone: 0.1 g/l.
Nonylphenol-ethylhexylsulfate: 0.4 g/l.

pH: 4.5
Temperature: 25°C.
Current density: 0.1-5 amps/dm²
Cathode rod agitation

EXAMPLE 11
Zinc sulfate (ZnSO₄·7H₂O): 145 g/l.
Ammonium chloride: 53 g/l.
Polyvinylpyrrolidone-(2): 2.5 g/l.
2-thiencylaceton: 0.2 g/l.
Sodium dodecylbenzene-sulfate: 0.25 g/l.

pH: 4.8
Temperature: 30°C.
Current density: 0.1-5 amps/dm²
Cathode rod agitation

EXAMPLE 12
Zinc sulfate (ZnSO₄·7H₂O): 290 g/l.
Ammonium chloride: 25 g/l.
Polyvinylpyrrolidone-(2): 5 g/l.
A-acetylcoumarin: 0.4 g/l.

pH: 4.8
Temperature: 30°C.
Current density: 0.1-5 amps/dm²
Cathode rod agitation

What is claimed:
1. In an aqueous acid plating electrolyte for the deposition of zinc electrodeposits in the abundance of organic compounds forming complex ions with heavy metals, the electrolyte containing a source of zinc ions, the improvement which comprises having present in said electrolyte:
(a) 0.5 to 100 grams per liter N-polyvinylpyrrolidone-(2) dispersed in said electrolyte as a primary brightener; and
(b) 0.01 to 0.5 gram per liter of a secondary brightener dispersed in said electrolyte, said secondary brightener being a compound of the formula

\[ R_1-(CH═CH)\text{a}-CO-R_2 \]

wherein \( R_1 \) is

70

75

\( R_2 \) is lower alkyl, lower alkenyl, lower alkyl-carbonyl-
7. In an electrolyte as set forth in claim 1, R₃ being hydrogen, hydroxy, lower alkyl, or lower alkoxy, and R₂ and R₄ together represent the methylenedioxy group, and n is 1 or 0.

2. In an electrolyte as set forth in claim 1, the concentration of said N-polyvinylpyrrolidone-(2) being between 2 and 10 grams per liter, and the concentration of said secondary brighteners between 0.05 and 0.3 gram per liter.

3. In an electrolyte as set forth in claim 1, R₂ being methyl or ethyl.

4. In an electrolyte as set forth in claim 3, R₃ being ethenyl.

5. In an electrolyte as set forth in claim 1, R₂ being —CH₂—CO—CH₃.

6. In an electrolyte as set forth in claim 1, R₂ being

7. In an electrolyte as set forth in claim 1, the pH being 3 to 6.

8. A method of forming bright zinc electrodeposits which comprises making an object the cathode in the electrolyte as set forth in claim 1.

References Cited
UNITED STATES PATENTS

2,853,444 9/1958 Pye et al. --------- 204—55X
3,005,759 10/1961 Safranek et al. --------- 204—55
3,285,840 11/1966 Lindemann --------- 204—55

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