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[54] **ZINC ELECTROPLATING BATHS**

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[51] **Int. Cl.**..... **C23b 5/10,** C23b 5/46, C23b 5/12

[58] **Field of Search**..... 204/55 R, 55 Y, 43, 204/44; 260/611 A, 347.8, 346.1 R

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[57] **ABSTRACT**

A process for obtaining brighteners for galvanic baths, particularly electrolytic zinc-plating baths, whereby at least one aromatic aldehyde or ketone is made to react under heat with at least one acetylenic alcohol in the presence of hydrochloric acid acting as a catalyzer, the pieces treated in the galvanic bath comprising the brightener having a very brilliant and ductile surface state.

10 Claims, No Drawings

ZINC ELECTROPLATING BATHS

The invention relates to a process for obtaining brighteners for galvanic zinc-plating baths, the brighteners obtained in accordance with the process and the zincing electrolytes, acid or neutral, containing these brighteners.

It is well-known that, in the present state of the technique, the majority of industrial galvanic zinc-plating baths are made basically from cyanides in order to obtain the qualities of zinc deposits required by industry. These baths have the disadvantage of being very toxic and produce residuary waters that are expensive to disintoxicate.

In addition, these baths continually deteriorate through the carbonation of their basic ingredients.

Known electrolytic zinc-plating baths having a base of zinc salts other than cyanide, such as sulfate, chloride, zinc fluoborate, etc., have disadvantages which make their industrial exploitation difficult or restricted, mainly because of their low penetration power, the insufficient brightness, or the lack of ductility of the zinc deposits obtained in these baths, and the difficulty in maintaining them.

The object of this invention is to remedy these disadvantages and, for this purpose, it relates to a process for obtaining brighteners for acid or neutral galvanic zinc-plating baths, and the brighteners which, added in small amounts (0.05 to 5 g./liter) to the aforementioned zinc-plating baths, enable very bright and uniform zinc deposits to be obtained, with a good power of penetration and having high ductility and very low (or non-existent) hydrogen absorption.

In accordance with the invention, the products of the condensation of aromatic aldehydes and ketones with acetylenic alcohols, in the presence of hydrochloric acid as catalyzer, that is to say the acetals of aromatic aldehydes and ketones with acetylenic alcohols, are used as brighteners in acid or neutral zinc-plating baths.

The addition of these products to the zinc-plating baths is accompanied by the addition of a category of products called "addition agents" which are non-ionic or anionic wetting agents intended mainly to ensure dispersion of the brighteners in the zinc-plating electrolyte.

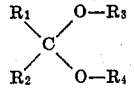
Electrolytic zinc-plating baths are made from a base of zinc salts, conductor salts, buffer salts and complexing salts, known in the technique, and contain as adjuvant, in accordance with this invention:

A. one or more brighteners selected from among the acetals defined hereinabove, in an amount of from 0.05 to 5 g./liter, and

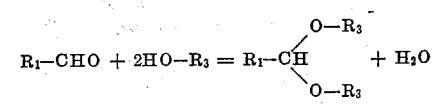
B. one or more addition agents selected from among the non-ionic or anionic wetting agents made from ethylene oxide, in an amount of from 0.5 to 50 g./liter.

Baths made with these products are chemically stable, give a high yield, are easy to maintain and have a low cost price.

The role of the brighteners used in accordance with the invention is to ensure the brilliance, the evenness and the penetration power of the zinc deposits obtained. They may be represented by the general formula:



in which R_1 is a benzene or heterocyclic nucleus (furan group) or substituted if need be, R_2 is an atom of hydrogen, a methyl or oxymethyl group or a benzene nucleus, and R_3 and R_4 are radicals coming from the action of the acetylenic alcohols in accordance with the plan:



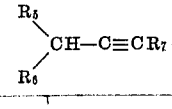
The radical R_3 may be identical to or different from R_4, depending on whether one or more alcohol is made to react.

Among the acetylenic alcohols used to advantage to prepare brighteners in accordance with the invention may be cited, as non-limiting examples:

TABLE 1

1. 2 - propyne-1-01 HC ≡ CCH_2OH
2. 3-butyne-1-01 HC ≡ $CCH_2\ CH_2\ OH$
3. 2-methyl-3-butyne-2-01 HC ≡ CC (OH) $(CH_3)_2$
4. 1-pentyne-3-01 HC ≡ CCH (OH) $CH_2\ CH_3$
5. 3-methyl-1-pentyne-3-01 HC ≡ CC (CH_3) (OH) $CH_2\ CH_3$
6. 2-butyne-1.4-dihydric alcohol $HOCH_2C$ ≡ CCH_2OH
7. 3-hexyne-2.5-dihydric alcohol CH_3CH (OH) C ≡ C CH (OH) CH_3
8. 2.5-dimethyl-3-hexyne-2.5-dihydric alcohol $(CH_3)_2$ C(OH)C ≡ CC (OH)$(CH_3)_2$

and, in general, the compounds of the general formula:

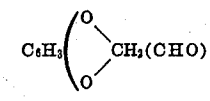


in which R_5 is a radical hydroxyl, hydroxymethyl, hydroxyethyl or hydroxyethoxyethyl, R_6 is a hydrogen or a radical methyl and R_7 is a hydrogen or a radical methyl, hydroxymethyl, hydroxyethyl, methoxymethyl or hydroxyethoxyethyl.

Among the aromatic aldehydes and ketones used to advantage to prepare brighteners in accordance with the invention may be cited:

TABLE 2

1. benzaldehyde C_6H_5 — CHO
2. methylbenzaldehyde $CH_3—C_6H_4—CHO$
3. cuminic aldehyde p-$(CH)_2CH—C_6H_4—CHO$
4. phenyl acetaldehyde $C_6H_5—CH_2—CHO$
5. cinnamaldehyde $C_6H_5—CH=CH—CHO$
6. ortho-hydroxybenzaldehyde C_6H_4 (OH) (CHO)
7. p-methoxybenzaldehyde C_6H_4 (OCH_3) (CHO)
8. piperonal



9. furfuraldehyde $C_4H_3O—CHO$

10. acetophenone C_6H_5 CO CH_3
11. p-methoxyacetophone CH_3O (C_6H_4) $COCH_3$
12. p-methylacetophenone $CH_3(C_6H_4)$ $COCH_3$
13. benzophenone $(C_6H_4)_2$ CO

In accordance with a preferred method in this invention, the products in category A, the brighteners, are prepared by making one mole of aromatic aldehyde react with two moles of acetylenic alcohol, using hydrochloric acid as catalyzer in the proportion of 1 % of the total mixture. The products are put into a reactor equipped with a system for agitation, reflux and heating, and the mixture is heated to 85° – 95°C for 2 – 3 hours. After cooling, the product is washed with water and the dark-colored, insoluble liquid, which is the brightener proper, is separated by decantation.

To facilitate implementation of the brightener, it may be mixed with varying proportions (preferably 1/1) of an aliphatic alcohol or glycol, such as ethylic alcohol, isopropylic alcohol ethyl-glycol, etc.

As an example, the condensation product of the benzaldehyde with the 2-methyl-3-butyne-2-01 is prepared by heating for 3 hours at 90°C, under agitation and reflux, a mixture of 106 g. of benzaldehyde, 168 g. of 2-methyl-3-butyne-2-ol, and 3 g. of hydrochloric acid. After cooling to the ambient temperature of the dark-colored liquid obtained, an equal volume of water is added, the mixture is well stirred and left to decant into a separating funnel. The aqueous phase is eliminated and the product is diluted in the proportion 1/1 with ethyl-glycol. This solution may be used as a brightener in accordance with this invention. The brightener is added to the zinc-plating bath after all the other products have been added, in particular the addition agents, and the electrolyte is stirred for several minutes to ensure that the brightener is well dispersed.

The role of the compounds in category B, the additional agents, is to effect a stable dispersion in the electrolyte of the brighteners, which are insoluble in water. At the same time, the addition agent improves the quality of the zinc deposits by making them more uniform and by preventing the formation of pores or pits.

The addition agents are non-ionic wetting agents with a predominantly hydrophilic chain, or anionic wetting agents, both types of wetting agents being manufactured by the various condensations of ethylene oxide. Some examples of types of wetting agents usable in association with brighteners in accordance with this invention are:

polyoxyethyl alkylphenols, with a minimum of 15 moles of ethylene oxide (for example, nonyl phenoxypoly (ethylenoxy) ethanol with 20 moles of ethylene oxide):

fatty polyoxyethyl alcohols with a minimum of 10 moles of ethylene oxide (for example, fatty polyoxyethyl tallow alcohols with 12 moles of ethylene oxide);

ether sulfates or fatty alcohols with a minimum of 5 moles of ethylene oxide (for example, sodium lauryl-ether sulfate with 6 moles of ethylene oxide).

All these wetting agents are commercially available under different trade-marks.

The bright zinc-plating baths in accordance with this invention must contain at least one brightener from category A and at least one addition agent from category B.

The basic electrolyte is made up of a zinc salt, such as chloride, sulfate, fluoborate or zinc oxide (or a mixture of these salts), one or more zinc ion complexing agents, such as ammonium chloride or the polyhydroxycarboxylic compounds, and buffer substances such as boric acid and appropriate acids or bases (hydrochloric acid or ammonia) to obtain the bath's optimal pH, which is from 4 to 5 for acid baths and from 7 to 7.5 for neutral baths.

A preferred base composition in this invention is that wherein the zinc salt is chloride or zinc oxide which is in the presence of an excess of ammonium chloride and, possibly, ammonia, so as to obtain the formation of the probable formula complexes: Zn $(NH_4)_3$ Cl_2 or Zn $(NH_4)_2$ Cl_4.

The following examples illustrate the typical compositions and conditions to achieve the objects of this invention, but are not restricted to the specified products, their concentration and the conditions indicated:

EXAMPLE 1

Zinc chloride $ZnCl_2$: 70 g./liter
Ammonium chloride NH_4Cl: 260 g./liter
Citric acid $C_6H_8O_7$: 5 g./liter
Nonyl phenoxypoly (ethylene oxide) ethanol with 20 moles of ethylene oxide: 10 g./liter
Product of the condensation of the benzaldehyde with the 2-butyne-1.4 dihydric alcohol: 0.6 g./liter

pH = 4.2 – 4.5; temperature 20° – 30°C; voltage 1 – 3 volts; cathode current density 1–4 A/cm²; anodes pure zinc (99.99 %).

Steel parts, previously cleaned and pickled, are treated in this bath under cathodic agitation. Very bright, uniform zinc deposits are obtained, light-colored and with excellent power of penetration, which easily become passive in blue- or iris-tinged iridiscent passivization solutions in accordance with common techniques.

EXAMPLE 2

Zinc chloride $ZnCl_2$: 60 g./liter
Ammonium chloride NH_4Cl: 270 g./liter
Nonyl phenoxypoly (ethylene oxide) ethanol with 30 moles of ethylene oxide: 8 g./liter
Fatty polyoxyethyl tallow alcohol with 12 moles of ethylene oxide: 4 g./liter
Product of the condensation of the benzaldehyde with the 2-propyne-1-ol: 1 g./liter

Working conditions are the same as in Example 1.

EXAMPLE 3

Zinc oxide ZnO: 30 g./liter
Ammonium chloride NH_4Cl: 170 g./liter
Citric acid $C_6H_8O_7$: 60 g./liter
Tartaric acid $C_4H_6O_6$: 5 g./liter
Ammonia NH_4OH: to bring the pH back to 7.3
Nonyl phenoxypoly (ethylene oxide) ethanol with 20 moles of ethylene oxide: 10 g./liter
Product of the condensation of the benzaldehyde with the 2-propyne-1-01: 0.4 g./liter
Product of the condensation of the p-methoxybenzaldehyde with the 2-butyne-1.4 dihydric alcohol: 0.2 g./liter

pH = 7.2 – 7.5; temperature 25° – 35°C; cathode current density 1–4 A/cm².

The deposits are bright and very ductile.

EXAMPLE 4

Zinc chloride $ZnCl_2$: 70 g./liter
Ammonium chloride NH_4Cl: 260 g./liter

Boric acid H_3BO_3: 10 g./liter

Fatty polyoxyethyl alcohols with 11 moles of ethylene oxide: 8 g./liter

Sodium lauryl-ether-sulfate with 6 moles of ethylene oxide: 2 g./liter

Product of the condensation of the O-hydroxybenzaldehyde with the 2-methyl-3-butyne-2-ol: 0.5 g./liter

Product of the condensation of the acetophenone with the 2-propyne-1-ol: 0.1 g./liter

pH = 4.5; temperature 25°C; cathode current density 2–4 A/cm².

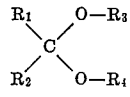
The bright zinc-plating baths forming the object of this invention may be used industrially in zinc-plating installations by assembling or in casks. These baths may with advantage replace cyanide baths and enable new effects to be obtained through the greater brilliance of the objects treated in these electrolytes.

It should be understood that the invention is not restricted to the embodiments hereinabove described; other variations may be foreseen which in no way exceed the scope of the invention.

What is claimed is:

1. An aqueous zinc electroplating bath comprising, as a brightening agent for said bath, the combination of:

a. about 0.05–5 grams per liter of a compound having the formula:



wherein R_1 is selected from the group consisting of phenyl, methyl phenyl, isopropyl phenyl, phenyl methyl, phenyl vinyl, hydroxy phenyl, methoxy phenyl, methylene dioxy phenyl, and furyl radicals; R_2 is selected from the group consisting of the methyl radical and hydrogen; and R_3 and R_4, which may be the same or different, are each selected from the group consisting of alkyne, methyl substituted alkyne, and hydroxy substituted alkyne radicals; and

b. an addition agent selected from the group consisting of nonionic and anionic wetting agents in an amount effective to reduce surface tension.

2. The electroplating bath of claim **1** wherein said bath includes a plurality of said compounds in a total concentration of about 0.05–5 grams per liter.

3. The electroplating bath of claim **1** wherein said bath includes a plurality of said addition agents in a total concentration of about 0.5–5 grams per liter.

4. The electroplating bath of claim **1** wherein R_1 is phenyl and R_2 is hydrogen.

5. The electroplating bath of claim **1** wherein R_1 is methoxyphenyl and R_2 is hydrogen.

6. The electroplating bath of claim **1** wherein R_1 is hydroxyphenyl and R_2 is hydrogen.

7. The electroplating bath of claim **1** wherein R_1 is phenyl and R_2 is methyl.

8. The electroplating bath of claim **1** wherein R_3 and R_4 are hydroxybutyne radicals.

9. The electroplating bath of claim **1** wherein R_3 and R_4 are propyne radicals.

10. The electroplating bath of claim **1** wherein R_3 and R_4 are methyl butyne radicals.

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