

United States Patent [19]
Passal

[11] 3,755,096
[45] Aug. 28, 1973

[54] BRIGHT ACID TIN PLATING

[75] Inventor: Frank Passal, Detroit, Mich.
[73] Assignee: M & T Chemicals Inc., Greenwich,
Conn.
[22] Filed: July 1, 1971
[21] Appl. No.: 159,035

[52] U.S. Cl. 204/54 R, 204/DIG. 2
[51] Int. Cl. C23b 5/14, C23b 5/46
[58] Field of Search 204/54 R, 54 L

[56] References Cited

UNITED STATES PATENTS

3,471,379 10/1969 Schoot et al. 204/54 R
3,642,590 2/1972 Engelsman et al. 204/54 R
3,669,854 6/1972 Harbulak 204/DIG. 2
3,483,100 12/1969 Engelsman et al. 204/54 R
3,616,306 10/1971 Conoby et al. 204/54 R

FOREIGN PATENTS OR APPLICATIONS

1,242,427 6/1967 Germany 204/54 R

Primary Examiner—F. C. Edmundson
Attorney—Kenneth G. Wheless et al.

[57]

ABSTRACT

This invention relates to the electrodeposition of tin; acid tin plating compositions, acid tin plating baths; to processes for the electrodeposition of bright tin in the presence of glacial acrylic acid, at least one non-ionic alkoxylated wetting agent, and as a novel brightener, the reaction product of hexan-2,5-dione and a compound selected from the group consisting of homocyclic aromatic aldehydes and 5-membered ring heterocyclic aldehydes, wherein the aldehyde group is bonded directly to the aromatic ring, conjugated aromatic ring or 5-membered ring heterocyclic group, said ring or group being otherwise inertly substituted or unsubstituted; to said novel brighteners; and a method of producing said novel brighteners.

19 Claims, No Drawings

BRIGHT ACID TIN PLATING

BRIEF DESCRIPTION

This invention relates to the electrodeposition of tin in acid tin plating compositions, acid tin plating baths, and to processes for the electrodeposition of bright tin in the presence of specific novel brighteners. More specifically this invention provides an acid solution for electrodepositing bright tin containing stannous ions; sulfate ions; glacial acrylic acid; at least one non-ionic alkoxylated wetting agent; and as a brightener, the reaction product of hexan-2,5-dione and a compound selected from the group consisting of homocyclic aromatic aldehydes and 5-membered ring heterocyclic aldehydes, wherein the aldehyde group is bonded directly to the aromatic ring, conjugated aromatic ring or 5-membered ring heterocyclic group, said ring or group being otherwise inertly substituted or unsubstituted.

During the last 10 to 15 years there has occurred an increasing interest and commercial importance for the electroplating of bright tin from acidic electrolytes. The deposits have achieved increasing numbers of applications in the electronics and other fields to provide improved appearance of plated articles, improved solderability characteristics and improved resistance to staining in use. A number of organic additive systems have been developed in the prior art attempting to achieve these and other advantages but none have been completely satisfactory. Some of the shortcomings have been inadequate and non-uniform degrees of luster, too narrow a bright plate cathode current density range, and difficulty in controlling the bath compositions to give consistent operational characteristics under commercial plating conditions for both barrel and rack plating purposes. Other shortcomings have been limited solubility characteristics of some of the brightening additives resulting in tarry precipitates which adversely affect the electrodeposits and uncertainty in composition and reproducibility of such additives during their manufacture usually resulting in complicated mixtures of unknown reaction products.

It is an object of this invention to provide a new bright acid tin plating additive system which would utilize as primary brightener a compound which would be a single chemical entity and which would result in substantial improvement in process performance over those systems of the prior art.

It is also an object of this invention to provide improved baths or solutions for obtaining tin deposits having enhanced brightness characteristics. In addition, it is another object of this invention to provide a novel primary brightener for bright acid tin plating baths.

DETAILED DESCRIPTION

This invention is an acid solution for electrodepositing bright, well-leveled tin comprising:

a. 10 grams per liter to 100 grams per liter of stannous sulfate;

b. 20 grams per liter to 200 grams per liter of sulfuric acid;

c. 0.025 grams per liter to 0.5 gram per liter of glacial acrylic acid;

d. 1 gram per liter to 50 grams per liter of a non-ionic water soluble alkoxylated wetting agent, and;

e. as a primary brightener, 0.005 gram per liter to 1.0 gram per liter of the reaction product of hexan-2,5-

dione and a member selected from the group consisting of:

1. A - CHO wherein A is selected from the group consisting of 5-membered, heterocyclic rings and 6-membered homocyclic rings; and
2. condensed aromatic rings exhibiting at least one aldehyde substituent.

According to another of its aspects this invention relates to a process of producing bright, highly leveled, 10 tin electrodeposits which comprises passing current from an anode to a metal cathode through an aqueous acidic bath composition containing at least one stannous compound providing bivalent tin ions for electrodeplating tin; glacial acrylic acid; at least one non-ionic 15 water soluble alkoxylated wetting agent; and the reaction product of hexan-2,5-dione and a member selected from the group consisting of 5-membered heterocyclic ring aldehydes, 6-membered homocyclic ring aldehydes and condensed aromatic rings bearing aldehyde 20 groups.

This invention has been found applicable to a wide variety of conventional acid tin baths such as, for example, baths containing a bivalent tin salt, such as stannous sulfate and an acid, such as sulfuric acid. Furthermore, the compositions and methods herein are applicable to both barrel and rack electroplating processes. The concentrations of tin and free acid may be varied generally within the limits conventional in this art. For example, baths with a tin content of 10 to 100 grams 30 per liter and a free acid concentration of 20 to 200 grams per liter may be utilized with the additives of the invention herein.

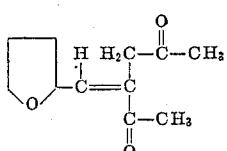
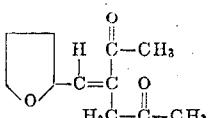
The preparation of the reaction product of hexan-2,5-dione and an aldehyde selected from the group 35 consisting of 5-membered ring heterocyclic aldehydes, 6-membered homocyclic ring or condensed aromatic ring is effected by reacting hexan-2,5-dione in a mole ratio of 1:1 or 2:1 of aldehyde to hexan-2,5-dione. The reaction is catalyzed by a catalytic amount of alkali. 40 Water, present in an amount of 0.3 liter per mole of aldehyde results in an optimum yield. Greater quantities of water result in decreased yields. Organic solvents such as ethylene glycol, monoethyl ether or dioxane may be employed. An acid such as acetic acid should be employed to neutralize the excess caustic after the reaction has reached completion.

The reaction temperature should be maintained within the range between -5° C and 50° C, preferably between 0° C and 25° C.

Thus, according to another of its aspects this invention resides in a method for producing a primary brightener for acid tin plating baths, the steps which comprise reacting as reactants hexan-2,5-dione and an aldehyde selected from the group consisting of 5-membered ring heterocyclic aldehydes, 6-membered ring homocyclic aldehydes, and condensed aromatic ring aldehydes, in a molar ratio of about 1:1 to about 1:2, in the presence of a catalytic amount of alkali, at a temperature between -5° C and 50° C, subsequently adding an acid to the reaction mixture and separating the reaction product.

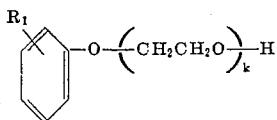
When a typical aldehyde, furfuraldehyde, is reacted in a unimolar ratio with hexan-2,5-dione, the reaction product is predominantly a single chemical entity with but two major peaks in the vapor phase chromatogram representing the cis and trans forms of the product. The structure of the active ingredient was characterized by

NMR spectra to be the following written in the form of the two possible optical isomers:



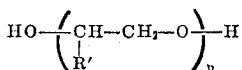
The cooperating additives employed in cooperation with the primary brightener are non-ionic alkoxylated wetting agents and glacial acrylic acid. The wetting agent serves to transform the loosely adherent, spotty, sometimes dendritically crystalline tin deposit from an additive-free bath into a dense, continuous, adherent, microcrystalline deposit. The acrylic acid seems to function by increasing the hydrogen overvoltage at the cathode and thereby favoring the increase of cathode current efficiency for the deposition of tin.

Non-ionic alkoxylated wetting agents operable in the practice of this invention include aromatic polyethers and aliphatic polyethers. Preferably the wetting agent is a polyalkoxylated alkyl phenol. Typical polyalkoxylated alkyl phenols include polyethoxylated alkyl phenols having the formula:



wherein R_1 represents an alkyl group of from 8 to 16 carbon atoms (preferably 9 carbon atoms) and k is an integer of from 2 to 50 (preferably from about 10 to 30).

Other polyethers which may be employed in amounts of about 1.0 - 50 grams per liter (preferably about 2-10 grams per liter) include aliphatic polyethers characterized by the following general formula:



wherein R' represents hydrogen or methyl and p is an integer of from about 7 to 50 (preferably from about 20 to 40).

Still other polyethers which may be employed in amounts of 1.0 to 50 grams per liter (preferably about 2 - 10 grams per liter) include nitrogen-containing aliphatic polyethers characterized by the following general formula:



wherein R represents a mixture of isomers having 12 - 22 carbon atoms, with 12 - 15 preferred, and having a tertiary alkyl structure and $n = 15$.

The preferred operating conditions, such as pH, temperature, and current density may vary depending upon the particular bath composition and the nature of the article receiving the layer of bright acid in tin electrodeposits. In general, good, bright acid tin electrodeposits may be obtained within a specific range of operating conditions.

The bright acid tin electroplating processes using the compositions of the invention may be carried out at 10 temperatures of about 10° C - 60° C (preferably 15° C - 20° C) either with or without agitation. The temperature of the plating solution is usually the ambient temperature, say 35° C or below, with lower temperatures giving optimum results, such as 15 - 20° C. In some operations, where substantial cell currents are used, resulting in a temperature elevation tendency, suitable cooling must be provided such as by circulating cool water through immersed cooling coils, by means of refrigeration machines, etc. Using average current densities of 0.5 - 5.0 amperes per square decimeter (ASD), bright tin electrodeposits having average thicknesses of 0.25 - 25 microns may be obtained using plating times which may average 0.1 - 100 minutes.

If necessary, vigorous and uniform agitation of the plating bath composition may be provided either by mechanical movement of the article being plated or by solution agitation during the electrodeposition. Such agitation may permit the use of high plating current densities on the article being plated.

In the plating of bright tin the parts may be plated on racks, i.e. on fixtures holding single or multiple parts which may all be the same or which may be different in size, geometrical configuration, etc. Parts may also be plated in bulk in rotating barrels and in this type of plating, usually used for plating of smaller parts which lend themselves to tumbling action, the barrel loads usually consist of the same part although mixed loads are sometimes plated. Because of the number, size, and shape complexity of parts it is important that the plating bath be so formulated as to provide the widest possible bright plate current density range. It is also important that the limiting currents density, i.e., the current density at which the deposit ceases to be sound in structure and appearances, be as high as possible to allow for the wide variations in cathode current density which may be encountered due to the size and shape complexity of parts.

Particularly brilliant, well leveled deposits are attained using the following representative bath composition:

| | |
|---|------------------|
| $SnSO_4$ | 30 g/l |
| Conc. H_2SO_4 (S.G. 1.84) | 10.5 % by volume |
| Furfural-Acetylacetone reaction product | 0.05 g/l |
| *Tergitol Non-Ionic NP-35 | 4 g/l |
| Glacial Acrylic Acid | 0.2 ml/l |

*The reaction product of 1 mole of nonylphenol and 15 moles of ethylene oxide as sold by Union Carbide Chemical Corp.

The primary brightener additive may be used in the form of a stock solution in an organic solvent such as Cellosolve (ethylene glycol mono-ethyl ether), i.e., for example, 25 grams per liter in which form it would then be added at a concentration of 20 ml/l or 2 percent by volume. The non-ionic alkoxylated wetting agent such as Tergitol Non-Ionic NP-35 may be added as a concentrated aqueous stock solution, say 100 grams per liter, in which form it would be added at a concentration of 40 ml/l or 4 percent by volume.

The following examples are submitted for the purpose of illustration only, so that those skilled in the art of bright tin plating may better understand the operation of the invention. These examples are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1 - Synthesis of Acid Tin Brightener

To a 500 milliliter Erlenmeyer flask containing 75 milliliters of water was added 20 milliliters (0.25 mole) of furfuraldehyde and 30 milliliters (0.25 mole) of hexan-2,5-dione. While the mixture was stirred magnetically, a solution of 10 grams (0.25 mole) of sodium hydroxide in 30 milliliters of water was slowly added through an addition funnel. The addition of the sodium hydroxide solution was controlled to maintain a temperature within the range of 22° C to 29° C. The stirring was continued for 2 hours.

Thereafter, the solution was acidified with 20 milliliters (0.33 mole) of glacial acetic acid and the mixture was transferred to a separatory funnel whereupon the mixture separated into two layers. The lower organic layer yielded 49 grams of brown liquid product. A solution of 25 grams per liter of the product was prepared in ethylene glycol monoethyl ether to be used as the primary brightener stock solution.

EXAMPLE 2

An acidic bright tin electroplating bath composition containing the following components was prepared and evaluated during four weeks of electrolysis:

TABLE I

| Component | Amount |
|--|-----------------|
| SnSO ₄ | 30 g/l |
| Conc. H ₂ SO ₄ (S.G. 1.84) | 10.5% by volume |
| Furfural-hexan-2,5-dione reaction product | 0.05 g/l |
| Polyethoxylated nonyl phenol having an average of 15 oxyethylene groups (Sold as Tergitol Non-Ionic NP-35 by Union Carbide Chemical Corp.) | 4 g/l |
| Glacial acrylic acid | 0.2 ml/l |

The life test plating conditions were essentially as follows:

| | |
|-----------------|--|
| Solution volume | 4 liters |
| Anode | slab tin (99.99% pure) |
| Cathode | 2.54 cm × 20.3 cm × 0.0456 cm brass strip polished on one side (facing anode) and having at bottom a 2.54 cm horizontal length and 2.54 cm × 2.54 cm 45° internal angle bend facing cathode. |
| Temperature | ambient room |
| Agitation | moving cathode rod parallel to anode and at about 10 cm from anode. |
| Current | 1 to 3 amperes per a total immersed area of 90 sq. cm. |

It is necessary to maintain the anode area at a reasonable value compared to the cathode area, i.e. at least 2:1 anode to cathode area ratio. This life test was operated for many weeks and the baths operated satisfactorily to obtain brilliant, well leveled deposits with periodic replenishment of the furfural-hexan-2,5-dione reaction product and with very infrequent replenishment additions of glacial acrylic acid.

EXAMPLE 3

A life test the same as that set forth in Example 2 was run except that the reaction product of benzaldehyde and hexan-2,5-dione was used as a brightening additive rather than the reaction product of furfuraldehyde and hexan-2,5-dione. The deposits from this system were

somewhat less brilliant and less uniform than those of Example 2 but were excellent deposits. Practically no replenishment additions of the surfactant were necessary and the rate of consumption of the other additives was very low.

EXAMPLE 4 - Synthesis of Acid Tin Brightener with Cooling

20 milliliters of furfural (0.25 mole) and 30 milliliters of hexan-2,5-dione (0.25 mole) were added to 75 milliliters of water. The suspension obtained was cooled with an ice-salt bath to a temperature of 0° C. 10 grams of sodium hydroxide (0.25 mole) were dissolved in 30 milliliters of water. The sodium hydroxide solution was thereafter added to the aldehyde suspension drop by drop with cooling and stirring. After the addition of the sodium hydroxide solution, during which a maximum temperature of 17° C was reached, the stirring was continued for another 3 hours. Thereafter, the solution was acidified with 20 milliliters of glacial acetic acid. The bottom layer of product was extracted with three 150 milliliter portions of chloroform. The chloroform extract was then dried over anhydrous magnesium sulfate and filtered. Thereafter, the low boiling components were removed under aspirator vacuum, keeping the bath at a temperature of between about 70°-80° C. 45 grams of reaction product were obtained. The product was a yellow brown liquid, appearing slightly viscous.

EXAMPLE 5

A life test the same as set forth in Example 2 was run except that in place of Tergitol Non-Ionic NP-35 there were used 4 grams per liter of Priminox R-15 a nitrogen-containing aliphatic polyether sold by Rohm and Haas characterized by the following general formula:



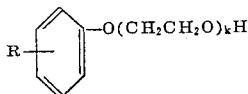
wherein R represents a mixture of isomers having 12-14 carbon atoms with a tertiary alkyl structure and n is equal to 15. The deposits from this system were somewhat less brilliant than those of Example 2 and showed a somewhat lower degree of leveling but were still excellent deposits. With Priminox R-15 the system responded to a periodic current interruption cycle, typically plating for 10 seconds and not plating for 2 seconds, to substantially increase deposit luster and increase the limiting current density. Again periodic replenishment of the furfural-hexan-2,5-dione reaction product and of acrylic acid was made to maintain optimum deposit luster.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are closely within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process of producing bright highly leveled tin electrodeposits which comprises passing current from an anode to a metal cathode through an acidic bath composition containing:
 - a. 10 grams per liter to 100 grams per liter of stannous sulfate;
 - b. 20 grams per liter to 200 grams per liter of sulfuric acid;
 - c. 0.025 gram per liter to 0.5 gram per liter of glacial acrylic acid;

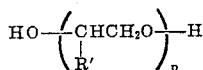
d. 1 gram per liter to 50 grams per liter of a non-ionic water soluble alkoxylated wetting agent selected from the group consisting of:



wherein R is an alkyl group of 8-16 carbon atoms and K is an integer 2-50;



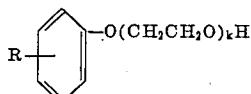
wherein R is a mixture of isomers exhibiting 12 to 22 carbon atoms and having a tertiary alkyl structure and n is 15;



wherein R' is hydrogen or a methyl group and p is an integer of about 7-60;

e. as a primary brightener, 0.005 gram per liter to 1.0 gram per liter of the reaction product of hexan-2,5-dione and a member selected from the group consisting of furfuraldehyde and benzaldehyde.

2. The process of claim 1 wherein the non-ionic water soluble alkoxylated wetting agent is of the formula:



30

35

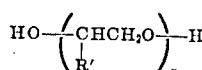
wherein R is an alkyl group of 8-16 carbon atoms and k is an integer 2-50.

3. The process of claim 1 wherein the non-ionic water soluble alkoxylated wetting agent is of the formula:



wherein R is a mixture of isomers exhibiting 12 to 22 carbon atoms and having a tertiary alkyl structure and n is 15.

4. The process of claim 1 wherein the non-ionic water soluble alkoxylated wetting agent is of the formula:



50

wherein R' is hydrogen or a methyl group and p is an integer of about 7-60.

5. The process of claim 1 wherein said 5-membered heterocyclic ring aldehyde is furfuraldehyde.

6. The process of claim 1 wherein said 6-membered homocyclic ring aldehyde is benzaldehyde.

7. The process of claim 1 wherein said stannous compound is present in an amount of 10 grams per liter to 100 grams per liter.

8. The process of claim 1 wherein said glacial acrylic acid is present in an amount of 0.025 gram per liter to 0.5 gram per liter.

9. The process of claim 1 wherein said water soluble alkoxylated wetting agent is present in an amount of 1 gram per liter to 50 grams per liter.

10. The process of claim 1 wherein said reaction product of hexan-2,5-dione and a member selected from the group consisting of 5-membered heterocyclic ring aldehydes, 6-membered homocyclic ring aldehydes and condensed aromatic rings bearing aldehyde groups is present in an amount of 0.005 gram per liter to 1.0 gram per liter.

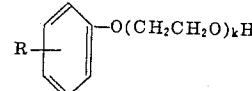
11. A composition for providing bright highly leveled tin electrodeposits which comprises a bath composition containing:

a. 10 grams per liter to 100 grams per liter of stannous sulfate;

b. 20 grams per liter to 200 grams per liter of sulfuric acid;

c. 0.025 grams per liter to 0.5 gram per liter of glacial acrylic acid;

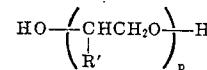
d. 1 gram per liter to 50 grams per liter of a non-ionic water soluble alkoxylated wetting agent selected from the group consisting of:



wherein R is an alkyl group of 8-16 carbon atoms and K is an integer 2-50;



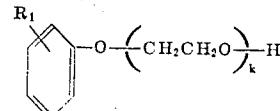
wherein R is a mixture of isomers exhibiting 12 to 22 carbon atoms and having a tertiary alkyl structure and n is 15;



wherein R' is hydrogen or a methyl group and p is an integer of about 7-60;

e. as a primary brightener, 0.005 gram per liter to 1.0 gram per liter of the reaction product of hexan-2,5-dione and a member selected from the group consisting of furfuraldehyde and benzaldehyde.

12. A composition as claimed in claim 11 wherein the non-ionic water soluble alkoxylated wetting agent is of the formula:



55

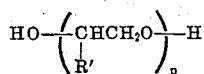
wherein R is an alkyl group of 8-16 carbon atoms and k is an integer 2-50.

13. A composition as claimed in claim 11 wherein the non-ionic water soluble alkoxylated wetting agent is of the formula:



wherein R is a mixture of isomers exhibiting 12 to 22 carbon atoms and having a tertiary alkyl structure and n is 15.

14. A composition as claimed in claim 11 wherein the water soluble alkoxylated wetting agent is of the formula:



wherein R' is hydrogen or a methyl group and p is an integer of about 7-60.

15. The composition of claim 11 wherein the brightener is the reaction product of hexan-2,5-dione and furfuraldehyde.

16. The composition of claim 11 wherein the brightener is the reaction product of hexan-2,5-dione and

benzaldehyde.

17. The composition of claim 11 wherein said glacial acrylic acid is present in an amount of 0.025 gram per liter to 0.5 gram per liter.

18. The composition of claim 11 wherein said non-ionic water soluble alkoxylated wetting agent is present in an amount of 1 gram per liter to 50 grams per liter.

19. The composition of claim 11 wherein said brightener is present in an amount of 0.005 gram per liter to 1.0 gram per liter.

* * * * *

15

20

25

30

35

40

45

50

55

60

65