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[56]

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[54] **ELECTRODEPOSITION OF BRIGHT ACID TIN  
AND ELECTROLYTES THEREFOR**  
28 Claims, No Drawings

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**ABSTRACT:** Improved baths or solutions are provided for the electroplating of tin, and containing as the primary brightener therefor the reaction product of furfural with crotonaldehyde in the presence of a catalytic amount of an alkali. In addition, this invention is concerned with brightening additive compositions for tin-electroplating baths, and with methods for preparing such additive compositions and for electroplating bright tin deposits.

# ELECTRODEPOSITION OF BRIGHT ACID TIN AND ELECTROLYTES THEREFOR

Generally speaking, this invention relates to electrolytic tin plating. More particularly, this invention relates to new and improved baths and methods for electroplating of bright acid tin deposits, to brightening additive compositions for tin-electroplating baths and to methods for the preparation of such additive compositions.

Bright acid tin deposits are being used increasingly for such applications as printed circuits for the various components of devices used in the electronics industry, parts used to establish electrical contacts, and for such purposes as tools and implements for handling packaging in the food products industry. In printed circuit applications, for example, it is most important that the deposits be bright because such bright deposits provide added protection to the circuits for later handling in that they protect the circuits much better from finger staining. In addition, the bright deposits, for reasons which are not completely understood, solder easier in later handling and/or connection of the circuits when they are incorporated into various devices being used.

Further, as will be understood, bright tin deposits utilized in the electronics industry for printed circuits, and in other applications involve mass production techniques in which literally thousands of the same object may be produced in a single production run. Thus, it is most important that baths for such tin deposits provide consistency and ease of operation because mass production techniques require the processes providing the products thereof to be economically feasible.

In plating bright tin, different well-known procedures may be utilized including rack plating in which items to be plated are suspended on insulated fixtures (or racks), and barrel plating. In rack plating, a single item may be plated or a plurality of that item, or there may be different parts to be plated of a variety of sizes and configurations. Further, parts may be bulk plated, in which generally smaller parts, usually all the same and which lend themselves to a tumbling action, are disposed in a rotating barrel.

In electroplating, because of the size, number, and shape complexity of the parts being plated, it is important that the bath be formulated in a manner to provide the widest possible bright plate current density range. Furthermore, it is important that the limiting current density (the current density at which the deposit ceases to be sound in structure and appearance) 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 the parts being plated.

Commercially used bright acid tin-plating solutions in the past generally have contained as brighteners such materials as tar and tar fractions obtained in the destructive distillation of wood. Such electrolytes are difficult to control, and it is not readily possible to produce bright tin plates of consistent quality from them over extended periods of time. Furthermore, tin deposits obtained by many of the prior art baths suffered from the fact that the resultant tin deposits did not have the required brightness to be esthetically acceptable for certain purposes and/or to provide such protection as a non-finger-staining deposit for electronic circuitry. In addition, many of the prior art baths may suffer from certain operational problems such as extreme sensitivity to agitation and the degree of agitation leading to striated deposits.

By contrast, and quite unexpectedly, it has now been found, in accordance with this invention, that by incorporating in otherwise conventional acid tin baths, as one of the cooperating additives thereof, the product obtained from the reaction of furfural and crotonaldehyde, hereinafter referred to as primary brightener, that tin deposits are obtained of enhanced brightness and in a fully reproducible manner. Furthermore, cooperating brightening additives and baths incorporating them, in accordance herewith, provide enhanced bright deposits simultaneously with less cost, ease of operation and consistency of results. In addition, the primary brightener of this invention cooperates with known materials of the prior

art, such as secondary brighteners, and wetting agents, as well known, which improve brightness and/or widen the effective operating bright plate cathode current density range in which the desired brightness for the deposits is obtained. With such an arrangement, therefore, much less control is necessary over extended periods of time thus making the arrangements and baths in accordance herewith especially appropriate for mass production techniques.

A further feature of this invention provides a method for bright tin electroplating in which an otherwise conventional acid tin-electroplating bath is utilized incorporating the primary brightener in accordance herewith simultaneously with application of a current interruption procedure in which current is applied with the periodic momentary interruption thereof. This is carried out in a specific predetermined cycle to provide deposits of even greater continuity and luster than is achieved with the new primary brightener here utilizing the usual steady current application procedures.

The cooperating additives which may be employed in cooperation with the primary brightener, in accordance herewith, may include nonionic-alkoxylated wetting agents, and formaldehyde as the secondary brightener, as well known. 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. Formaldehyde acts as a cathode depolarizer when used in cooperation with the wetting agent and other additives in the bath to help increase cathode current efficiency. When the formaldehyde is used only with the wetting agent, and in the absence of the primary brightener in accordance with this invention, an unsatisfactory deposit is obtained.

Accordingly, it is one 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 primary brightener for otherwise conventional bright acid tin-plating baths.

It is a further object of this invention to provide methods for preparing such additive compositions and methods for electroplating bright tin deposits in which the primary brightener additive, in accordance herewith, is utilized in combination with already known secondary brighteners to provide enhanced brightness characteristics over a much wider cathode current density range and in a manner whereby the baths require relatively little control and improved ease of operation. Additionally, methods are provided for bright tin electroplating utilizing the improved baths, in accordance herewith, simultaneously with an improved application of current in a specific cycle of periodic current interruption.

With the foregoing and additional objects in view, this invention will be described in more detail and other objects and advantages will be apparent from the following description and the appended claims.

Before describing this invention in more detail, it may be well to note that 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 tin sulfate or tin fluoroborate and an acid, such as sulfuric acid or fluoboric acid. Furthermore, the compositions and methods herein are applicable to other 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, a tin content of 10 to 100 g./l. and a free acid concentration of 20 to 200 g./l. are typical of the sulfate, fluoborate, and aromatic sulfonate solutions known in themselves, which may be utilized with the brightener of the invention herein. Sulfuric, fluoboric and aromatic sulfonic acids may be present simultaneously in the electrolytes in a manner not novel in itself.

Such process variables as the configuration of the object which is made the cathode during the plating process, the desired rate of depositions, etc., will determine, in many cases the exact composition of the plating bath, as well known.

Furthermore, known antioxidants used in acid tin-plating solutions may be utilized when employed in the tin-plating solutions of the invention in small amounts. The temperature of the plating solution is generally ambient, and preferably held below 35° C. and within the range of between about 15°–20° C. for optimum plating performance.

In considering generally the conditions for achieving the most enhanced results in connection herewith, which conditions are more specifically set forth below, one may note that satisfactory tin deposits are realized by introducing into an otherwise conventional acid tin plating bath an amount of the primary brightener, in accordance herewith, in substantially the same amount as the amount of an already known primary brightener formulation which would be introduced for the same purpose. In formulating the baths in accordance herewith, the amounts and/or concentrations of the secondary brightener and wetting agent will vary considerably depending on the results desired.

As purely illustrative of acid tin-plating baths which may be used, in accordance herewith, one may note the following bath formulation:

Stannous sulfate (SnSO <sub>4</sub> )	30 g./l.
Concentrated sulfuric acid (S.G. 1.84)	105 ml./l.
Primary brightener	0.25 g./l.
Carrier	4 g./l.
Secondary brightener	10 ml./l.

The secondary brightener is preferably formaldehyde in a 37 percent solution. The carrier may be any well-known nonionic-alkoxylated wetting agent, such as, for example, Tergitol NonIonic NP-35, a product of Union Carbide and being a polyethoxylated nonyl phenol having an average of 15 oxethylene groups. The wetting agent is generally added as an aqueous stock solution in the amount of 400 g./l., and added to the bath at a concentration of 40 ml./l., or 4 percent by volume. The primary brightener generally is added in the form of a stock solution in an organic solvent such as, for example, Cellosolve, ethylene glycol monoethyl ether, in the amount of preferably 25 g./l. The stock solution is added to the bath at a concentration of 10 ml./l., or 1 percent by volume.

As a further feature of this invention, it has been found that by using a periodic current interruption cycle during plating, that further enhanced results are achieved, in accordance herewith, of deposits of brightness improved even over those deposits obtained by utilizing the primary brightener in accordance herewith in otherwise conventional acid tin-plating baths and procedures without the periodic current interruption cycle taught herein. For example, in utilizing the representative bath noted above, with an ambient operating temperature, anodes of pure tin and a cathode current density of between about 10–30 a.s.f., and cathode rod agitation, that if periodic current interruption is applied in a cycle of 10-seconds plating current followed by 2-seconds current interruption, deposits of surprisingly increased brightness are achieved. Whereas the sequence of periodic current interruption noted above is preferred, it has been found, in accordance herewith that a sequence within the range of between about 10–20 seconds plating time followed by between about 1–5 seconds of current interruption may be utilized in accordance herewith.

Although the periodic current interruption cycle may be used both for rack-and-barrel plating, it is of particular advantage for rack plating because in rack plating generally only moving cathode rod-type agitation can be used, which does not always provide sufficient agitation to maintain proper concentration of brightening additives, especially adjacent the cathode surface.

With utilization of the periodic current interruption cycle, in accordance with this invention however, these difficulties are overcome because it has been found, in accordance herewith, that during the current interruption period, fresh brightener diffuses into the cathode film, thereby replenishing

the brightener, and providing enhanced luster which advantage has not been found before in bright acid tin plating.

In considering generally the conditions for preparing the primary brightener, in accordance herewith, it may be well to note that satisfactory results have been achieved and under satisfactorily and economically attractive conditions on commercial scale operations by reacting furfural and crotonaldehyde in the range of between about equimolar quantities and 15-percent mole excess of furfural, and preferably about 10-percent mole excess of furfural in the presence of a catalytic amount of an alkali, preferably sodium hydroxide and preferably in an aqueous solution, although an organic solvent may be employed, if desired, such as, for example, Cellosolve, ethylene glycol monoethyl ether produced by Union Carbide, or dioxane.

For example, 1.1 mole of furfural and 1 mole of crotonaldehyde may be reacted. An excess of crotonaldehyde should be avoided because it has been found that excessive concentrations of crotonaldehyde may result in a self-polymerization product which is to be avoided as it has been found to produce striations in the final deposits. The reaction temperature is generally maintained within the range of between about –5° and 50° C., and preferably between about 0° and 25° C. Although effective results have been achieved in the higher operating ranges, and even up to the maximum of 50° C., it appears from subsequent use that the brightening constituents of the primary brightener herein are obtained in higher concentrations when the lower operating temperatures are utilized.

As purely illustrative of a procedure for obtaining the primary brightener in accordance herewith, one may note example 1 below, in which equimolar quantities of furfural and crotonaldehyde were reacted.

#### EXAMPLE 1

41.4 ml. of furfural (0.5 mole) and 45 ml. of 90 percent crotonaldehyde (0.5 mole) were added to 200 ml. of water. The suspension obtained was cooled with an ice-salt bath to a temperature within the range of between about –1° and +4° C. 4 grams of sodium hydroxide (0.1 mole) were dissolved in 50 ml. 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 15° C. was reached, the stirring was continued for another 2 hours. Thereafter, the solution was acidified to litmus with glacial acetic acid. The bottom layer of product was extracted with three 150 ml. 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. 83 grams of reaction product were obtained. The product was a yellow brown liquid, appearing slightly viscous.

The reactants for carrying out the procedure noted in example 1 are readily available as commercial products. For example, crotonaldehyde is available from Union Carbide as crotonaldehyde 89 percent in drum quantity, and furfural is available in almost 100 percent purity from Quaker Oats Company.

As further illustrative of methods, in accordance herewith for obtaining the primary brightener of this invention, one may note examples 2 and 3 below.

#### EXAMPLE 2

205 ml. of furfural (2.5 moles), 225 ml. of 90 percent crotonaldehyde (2.5 moles) and 500 ml. of water were mixed and cooled in an ice-salt bath. When the temperature went down below 0° C., a solution of 20 grams of sodium hydroxide (0.5 mole) dissolved in 150 ml. of water was added drop by drop with stirring and cooling. A maximum reaction temperature below 20° C. was maintained.

After the addition of the sodium hydroxide solution, the resulting solution was stirred for another 3 hours. 35 ml. of glacial acetic acid (a slight excess of 0.5 mole) was added with stirring. The reaction mixture was transferred to a 2-liter separatory funnel. 200 ml. of saturated sodium chloride solution were added to facilitate the separation of the two layers. The bottom layer containing the active component was separated (394 grams).

The aqueous layer was extracted with chloroform and 28 grams more of a thick yellow brown liquid were obtained, to give a total combined yield of 422 grams of primary brightener.

### EXAMPLE 3

#### Reaction vessel:

25-gallon stainless steel container immersed in 100-gallon plastic tank filled with crushed ice.

#### Materials:

Furfural (Quaker Oats)	6 gallons
Crotonaldehyde (Union Carbide anhydrous)	5 gallons
Water	10 gallons
Sodium Hydroxide	840 g. C.P. pellets in 1 gal. water
Glacial Acetic Acid	1,700 ml.

#### Procedure:

The furfural, crotonaldehyde and water were stirred together and cooled to 1° C. The NaOH solution was added slowly to the mixture and when a total of 800 ml. had been added the temperature began to rise. At about 45° C. an internal tantalum coil with 4° C. water running through it was installed and the maximum temperature rise was to 50° C. within a time of about 1 hour. When the temperature had been reduced to about 15° C. after about 1 hour, the remainder of the NaOH solution was added and no further rise in temperature occurred.

The mixture was then stirred for 4 hours and 1,700 ml. of glacial acetic acid were added in small increments to pH of about 6.0. The reaction mixture was allowed to stand overnight and the aqueous top layer was siphoned off. The thick remaining material was transferred into 13 polyethylene 1-gallon containers. These were allowed to stand to effect further separation of water which was then decanted off. Total weight of product was about 120 pounds.

Although aqueous solutions were used in the three examples noted above, it is within the purview of this invention that syntheses may be carried out in which the reactants are dissolved in organic solvents such as, for example, Cellosolve and dioxane, as separate solvents. With such an arrangement, only a trace of sodium hydroxide is sufficient to initiate the reaction and the products obtained are essentially the same as those utilizing the aqueous medium. The products obtained either in the aqueous or solvent media have been found useful as the novel primary brightener, in accordance herewith.

Although the exact identity and/or content of the reaction product obtained for use as the primary brightener, in accordance herewith, is not known it can be theorized that the product is comprised of a plurality of components each of which may cooperate with the other components in order to provide the enhanced results achieved in accordance herewith. Although the exact identity and concentration of each component is not known, it can be theorized further that perhaps some of the components may be inert, or at least brightener-inactive and that some interact in a manner not known in order to provide the enhanced results obtained.

Although these components are not known, it can be theorized that they may be comprised of such possible components as 2-furylacrolein; 2-furylpentadienal; 2-(1-hydroxy ethyl) 3-(2-furyl)-acrolein and acetaldehyde, and perhaps even some unreacted starting materials. However, in certain tests carried out, it was found that the proposed possible individual components such as, for example, 2-furylacrolein, furfural and crotonaldehyde do not provide any brightening

action at all in the conventional acid tin baths noted above. These proposed individual components have not proved effective in combination in any known testing procedures of the various individual combinations which can be made from these proposed components. Thus, it can be theorized that the entire reaction product obtained from syntheses such as those noted above in examples 1-3, are necessary to achieve the results noted in accordance herewith and that there is some cooperation, not understood, which is necessary between some or possibly all the components, to achieve the results, in accordance herewith.

As noted above, enhanced results are achieved in utilizing the reaction products substantially the same as those obtained in the three examples noted above as the primary brightener in otherwise conventional bright acid tin-plating baths. This primary brightener and/or additive cooperates with other additives to give a lustrous deposit throughout a very wide current density range. The degree of luster will depend on the degree of agitation, concentration of brightener and how the current is manipulated. The periodic current interruption noted above will markedly increase the rate of brightening. The deposits obtained are very lustrous, and may have a very slight haze providing an esthetically pleasing sheen to the deposit. In addition, good low current density luster is obtained in addition to good adhesion of the deposits on the metallic substrate being coated. A large plurality of metallic substrates may be plated in accordance herewith including iron, copper, nickel, cobalt, and a variety of alloys containing these metals, etc.

The range of concentration of the primary brightener, in accordance herewith, contained in the bath will vary widely depending upon the results attempting to be achieved, and the various other additives and components of the bath. However, too low a content will result in a grey to dull, nonuniform, somewhat grainy deposit. On the other hand, too high a concentration level does not seem to do any particular harm although the rate of consumption of the additive may be increased, thus increasing the cost of the operation. Generally, it can be said that the range of primary brightener in the bath will be between about 0.1 g./l. and 1 g./l., with a preferred range being between about 0.2 g./l. and 0.4 g./l.

As further illustrative of the results achieved in accordance herewith, one may note the following examples in which a plurality of Hull Cell tests were carried out utilizing the reaction products of the examples 1-3, inclusive noted above.

### EXAMPLE 4

Into a standard Hull Cell equipped with a magnetic stirrer to provide mild agitation there were introduced 250 ml. of an acid tin stock solution containing 30 g./l.  $\text{SnSO}_4$  and 105 ml./l. of C.P. concentrated sulfuric acid (Sp. Gr. 1.84). To the solution there were added 4 g./l. Tergitol NonIonic NP-35. A polished brass panel was cleaned, given a 1-minute cyanide copper strike and after water rinsing, dilute acid dipping and water rinsing was immersed in the Hull Cell at a cell current of 1 ampere for 5 minutes at room temperature.

The deposit obtained was dull white, uniform and smooth and gave good low current density coverage.

### EXAMPLE 5

Example 4 was repeated after adding as an additional bath component 10 ml./l. of 37 percent formaldehyde solution.

The high current density one-third of the panel area had a nonuniform, dark, smutty deposit while the remainder of the plated area was dull white as in example 4.

### EXAMPLE 6

Example 5 was repeated after adding as an additional bath component 0.25 g./l. of the primary brightener of example 1 as a 25 g./l. stock solution in Cellosolve.

The deposit obtained was uniformly lustrous throughout the entire current density range of 0 to about 6 amperes per square decimeter (ASD) and had a pronounced gloss.

## EXAMPLE 7

In this example, example 6 was repeated but as the primary brightener the product obtained from example 2 above was used as a 25 g./l. stock solution in Cellosolve. Again, the deposit obtained was uniformly lustrous throughout the entire current density range, and had a pronounced glossy appearance.

## EXAMPLE 8

In this example, example 6 was repeated but using as the primary brightener the product obtained from example 3 noted above as a 25 g./l. stock solution in Cellosolve with essentially the same results obtained.

## EXAMPLE 9

A 4-liter volume of acid tin stock solution having a concentration of 30 g./l.  $\text{SnSO}_4$  and 105 ml./l. of C.P. concentrated sulfuric acid (SP. Gr. 1.84) was set for electrolysis at ambient temperature (about 20° C.) in a rectangular glass battery jar. In the solution there was immersed, by suspending from a titanium wire, a slab of 99.99 percent pure tin as anode. The cathode was a polished brass strip having dimensions of 20.3×2.54×0.1 cm. After cleaning, it was immersed in the plating bath to a depth of 18 cm. at a distance of 10 cm. from the anode with the front of the cathode parallel to the anode. The cathode was moved in a plane parallel to the anode using a 5 cm. reciprocating stroke with a total distance travel of about 160 cm. per minute.

To the 4-liter bath there were added 0.25 gram of the primary brightener of example 2, 4 g./l. of Tergitol Nonlonic NP-35 and 10 ml./l. of 37 percent formaldehyde solution. A current of 2.5 amperes was applied for 10 minutes. The deposit was uniformly glossy but had a definite milky appearance.

## EXAMPLE 10

Example 9 was repeated using a periodic current interruption cycle of 10 seconds plate—2-seconds no-plate and using a current of 2.5 amperes for a total time of 12 minutes to give the same total plating time as for example 9. The resulting deposit was remarkably brighter than the one of example 9, with only a very slight milky haze.

## EXAMPLE 11

Using the 4-liter solution of example 9, additives included, a barrel-plating test was run using a small laboratory Lucite barrel of the horizontally rotating type having the following description:

Cross section	hexagonal
Length	25 cm.
Diameter (ave.)	10 cm.
Speed of rotation	5 r.p.m.
Anodes	External, slab
99.99% pure tin	

A load of steel nails weighing 310 grams, length of each 3.8 cm., total area 930 sq. cm., was suitable cleaned and transferred into the plating barrel. The load was plated for 1 hour using a cell current of 5 amperes (to give an average cathode current density of 0.5 ASD). After plating the load was thoroughly rinsed and dried. The deposit on the nails had a uniform, brilliant appearance and the deposit thickness obtained was an average of 0.00064 cm.

## EXAMPLE 12

Example 11 was repeated using a current of 10 amperes for 30 minutes. The resulting deposit was uniform and brilliant and also had an average thickness of 0.00064 cm.

As further illustrative of the results achieved in accordance herewith, a life test was run with the bath of example 9 for a period of 3 weeks, with 8 hours of daily electrolysis, and with

periodic additive replenishment. At the end of the 3-week period, the bath was still in excellent operating condition. Furthermore, no accumulation of harmful decomposition products of additives were evidenced in this life test.

Accordingly, and as will be apparent from the foregoing, there are provided in accordance herewith, methods and compositions for imparting bright lustrous tin deposits on a variety of metallic substrates with baths containing the primary brightener in accordance herewith of the reaction product obtained from reacting furfural and crotonaldehyde, and in a manner in which the baths are easily maintained and controlled. Furthermore, baths incorporating the primary brightener in accordance herewith may be maintained over extended periods of time with only replenishment of the bath components and the primary brightener in accordance herewith in the absence of the problem of the baths becoming inoperable, thus making the methods and compositions in accordance herewith highly advantageous commercially. In addition, methods are provided here for a program of current manipulation in which even further enhanced results are achieved, as desired.

While the methods and compositions herein disclosed form preferred embodiments of this invention, this invention is not limited to the specific methods and compositions, and changes can be made therein without departing from the scope of this invention which is defined in the appended claims.

1. An aqueous acid bright tin-electroplating solution including a tin salt, free acid, and, as the primary brightener therefor, an amount sufficient to produce a bright tin electrodeposit, of a yellow brown liquid reaction product characterized as being produced by the steps which comprise placing furfural and crotonaldehyde as reactants in a reaction zone, said reactants being placed in said reaction zone in the ratio in the range between equimolar quantities and 15-percent mole excess of furfural; maintaining the temperature of the said reaction zone between about -5° and 50° C.; reacting the said reactants in the presence of a catalytic amount of an alkali to obtain a reaction product; adding an acid to said reaction product for the acidification thereof; and separating the reaction product from the acid reaction zone.

2. A solution as recited in claim 1 in which about 10-percent mole excess of furfural to crotonaldehyde is added to said reaction zone.

3. A solution as recited in claim 2 and including as the secondary brightener formaldehyde.

4. A solution as recited in claim 3 and including a wetting agent.

5. A solution as recited in claim 4 in which said wetting agent is nonionic.

6. A solution as recited in claim 4 in which said wetting agent is a polyethoxylated nonyl phenol having an average of 15 oxyethylene groups.

7. A solution as recited in claim 1 which comprises the steps of dissolving sodium hydroxide in water, carrying out the reaction step by adding the aqueous solution of sodium hydroxide dropwise to said reaction zone, and in which the contents of said reaction zone are stirred during the reaction step.

8. A solution as recited in claim 7 and including as the secondary brightener formaldehyde.

9. A solution as recited in claim 26 and including a wetting agent.

10. A solution as recited in claim 8 in which said wetting agent is nonionic.

11. A solution as recited in claim 8 in which said wetting agent is a polyethoxylated nonyl phenol having an average of 15 oxyethylene groups.

12. A solution as recited in claim 1 wherein the said separating step is carried out by extracting the reaction product by the addition of a plurality of separate portions of chloroform, and withdrawing the chloroform from the product in said extracting step to obtain the reaction product of the said reacting step.

13. A solution as recited in claim 12 and including as the secondary brightener formaldehyde.

14. A solution as recited in claim 13 and including a wetting agent.

15. A solution as recited in claim 14 in which said wetting agent is nonionic.

16. A solution as recited in claim 14 in which said wetting agent is a polyethoxylated nonyl phenol having an average of 15 oxyethylene groups.

17. A solution as recited in claim 1 and including as the secondary brightener formaldehyde.

18. A solution as recited in claim 17 and including a wetting agent.

19. A solution as recited in claim 18 in which said wetting agent is nonionic.

20. A solution as recited in claim 18 in which said wetting agent is a polyethoxylated nonyl phenol having an average of 15 oxyethylene groups.

21. In a method for electrodepositing bright tin on an article and having tin as the anode, a source of plating current and means providing current flow communication from said source to said anode; the steps which comprise making said article the cathode in an aqueous solution as recited in claim 19, directing a plating current from said source to said anode through flow communication means, and plating tin from said anode onto said article.

22. A method as recited in claim 21 which includes the additional step of sequentially applying and interrupting plating current through said flow communication means.

23. A method as recited in claim 23 in which said sequence provides for the application of current for a period of time between about 10 and 20 seconds, and the interruption of current for a period of time of between about 1 and 5 seconds.

24. A method as recited in claim 23 in which said current application portion of the sequence is for 10 seconds and said current interruption portion of the sequence is 2 seconds.

25. A method as recited in claim 21 in which said reacting step is carried out in the presence of an aqueous solution of sodium hydroxide.

26. A method as recited in claim 25 which includes the additional step of dissolving sodium hydroxide in water, and in which said reacting step is carried out by adding the aqueous solution of sodium hydroxide dropwise to said reaction zone, and in which the contents of said reaction zone are stirred during the said reacting step.

27. A method as recited in claim 21 in which about 10-percent mole excess of furfural to crotonaldehyde is added to said reaction zone.

28. A method as recited in claim 21 in which the said separating step is carried out by extracting the product by the addition of a plurality of separate portions of chloroform, and withdrawing the chloroform from the product in said extracting step to obtain the reaction product of the said reacting step.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,634,212 Dated January 11, 1972

Inventor(s) Sylvester Paul Valayil and Frank Passal

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 23, Line 1.

The number of the claim dependent from should be 22.

Signed and sealed this 11th day of July 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents