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TIN OXIDE SOL, PROCESS FOR PREPARING SAME, AND PROCESS FOR ELECTRODEPOSITING TIN UTILIZING SAID SOL

Frank Passal, Detroit, and Arthur James Tomson, Novi, Mich., assignors to M & T Chemicals Inc., New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, the process of this invention for electrodeposition of tin from a tin plating bath, whereby the tin content of the plating bath may be depleted, may comprise electrodepositing tin from an aqueous tin plating bath onto a cathode thereby depleting tin from said bath, and replenishing tin in said aqueous tin plating bath by addition thereto of a tin oxide sol characterized by substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C., said tin oxide sol being prepared by the process comprising contacting aqueous solution containing alkali metal stannate with a cation exchange resin selected from the group consisting of hydrogen form cation exchange resin and ammonium form cation exchange resin; and recovering said tin oxide sol as effluent from said cation exchange resin.

This invention relates to a novel process for electroplating of tin. More specifically it relates to a novel technique for replenishing the tin content of a tin-plating bath.

As is well known to those skilled-in-the-art, tin may be electroplated onto various basis metal cathode from electrolytic baths containing alkali metal stannate, preferably potassium stannate, and alkali metal hydroxide, preferably potassium hydroxide. As plating continues, tin is removed from the bath. The tin content of the bath may be restored continuously by the use of a soluble tin anode. Use of a soluble anode system is disadvantageous in that it requires operation within a rather limited range of anode current density. Operation outside of this limited range may yield either a rough dark plate or alternatively inactivation of the anode with resulting failure of the anode to replenish the tin depleted from the bath, this being accomplished by an undesirable increase in concentration of alkali metal hydroxide, as shown by the following equation:

$$K_2Sn(OH)_6 \rightarrow Sn + 2KOH + O_2 + 2H_2O$$

Many practical plating operations may require operation outside the narrow limits of anode current density required by the use of soluble anodes, and in such systems, it may not be advantageous to use a soluble tin anode.

Accordingly, it has been common to use inert anodes, typically stainless steel anodes, and to replenish the depleted tin by the addition to the bath of tin compounds. Typically alkali metal stannate, e.g. potassium stannate, may be added; but this is highly disadvantageous in that it adds alkali metal ion to the bath and this ultimately may build up the concentration thereof to a point at which no more alkali metal stannate will dissolve, at which point the bath must be discarded. Another disadvantage may be that the concentration of alkali metal hydroxide increases and this must be corrected by neutralization with acid, preferably acetic acid, with the very real danger of over-neutralization and sludging.

It is an object of this invention to provide a process for the electrodeposition of tin whereby the tin content of the plating bath may be replenished without the formation of undissolvable matter due to precipitation in the bath by the common ion effect. It is a further object of this invention to prepare a composition which may be employed to replenish the tin content of plating baths, and a novel process for preparing this composition. Other objects will be apparent to those skilled-in-the-art from inspection of the following description.

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In accordance with certain of its aspects, the process of this invention for electrodeposition of tin from a tin plating bath, whereby the tin content of the plating bath may be depleted, may comprise electrodepositing tin from an aqueous tin plating bath onto a cathode thereby depleting tin from said bath, and replenishing tin in said aqueous tin plating bath by addition thereto of a tin oxide sol characterized by substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C., said tin oxide sol being prepared by the process comprising contacting aqueous solution containing alkali metal stannate with a cation exchange resin selected from the group consisting of hydrogen form cation exchange resin and ammonium form cation exchange resin; and recovering said tin oxide sol as effluent from said cation exchange resin.

In accordance with certain of its other aspects, this invention may comprise a process for preparing tin oxide sol, characterized by its substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C. which comprises contacting aqueous solution containing alkali metal stannate with a cation exchange resin selected from the group consisting of hydrogen form cation exchange resin and ammonium form cation exchange resin thereby forming a tin oxide sol; and recovering said tin oxide sol as effluent from said cation exchange resin.

The aqueous solution containing alkali metal stannate which may be converted to the tin oxide sol in the practice of certain aspects of this invention may be an aqueous solution which contains alkali metal stannate, in amount up to saturation, and typically 15 g./l. to saturation, say 70 g./l. of potassium stannate. Preferably this aqueous solution may be a tin plating solution containing 15 g./l. to saturation, say 70 g./l. of alkali metal stannate and 5–100 g./l., typically 20 g./l., of alkali metal hydroxide. The alkali metal of each alkali metal compound may be different (i.e. mixed alkali metals), but preferably the alkali metal of each is the same. Such tin plating solutions may be employed in e.g., immersion tinning of aluminum pistons or in electroplating of tin.

The alkali metal which may be employed in this invention may be any of the alkali metals, e.g. lithium, sodium, potassium, etc., but preferably sodium or potassium. The most highly preferred alkali metal may be potassium since potassium stannate possesses high solubility in water. Thus, it is the most commonly used alkali metal stannate in tin plating baths, as the potassium ion concentration of the bath may be higher than in the case of other alkali metals.

It is a particular feature of this invention that aqueous solutions wherein the specific alkali metal stannate possesses lower solubility than potassium stannate, e.g. sodium stannate, may be used since the formation of precipitate due to the common ion effect may be prevented by replenishing the bath with tin from the tin oxide sol prepared according to the novel process of this invention.

In practice of this invention, the desired tin oxide sol may be prepared by contacting the aqueous solution containing alkali metal stannate with a cation exchange resin thereby forming a tin oxide sol.

The cation exchange resins which may be employed may be those resins, generally available in granular form, which permit exchange of the alkali metal cation of the stannate solution preferably with a hydrogen or more preferably with an ammonium exchange cation. Typically, such resins may be available in the form HA wherein A represents the resin moiety and H represents the mobile exchange hydrogen. When the resin is present in its ammonium form, the ammonium cation NH_4+ may replace the hydrogen cation in the resin. While the cation exchange resin is often available in its hydrogen form and may be used as such, it may more preferably be treated to substitute for the hydrogen a less acidic cation such as ammonium. This may typically be done by washing the hydrogen form of the resin successively, for example, with a 5% aqueous solution of ammonium hydroxide followed by washing with distilled water until the effluent is free of ammonium hydroxide.

If the cation exchange resin is not initially in its hydrogen form, e.g., if it is initially in its sodium form, it may first be converted to the hydrogen form, for example by washing with 5% aqueous solution of hydrochloric acid and then distilled water. If desired, the ammonium cation may then be introduced. The same tin oxide sol may be obtained from a cation exchange resin in its hydrogen form as in its ammonium form.

Typical of the cation exchange resins which may be employed may be water insoluble carboxylic type cation exchange resins or water insoluble sulfonated cation exchange resins.

Typical illustrative resins which may be employed include:

(a) Carboxylic type resins such as acrylic type resins typified by water insoluble resins prepared from acrylic acids such as acrylic acid se, methacrylic acid, ethacrylic acid, etc.

A typical preferred acrylic may be those sold under the trademark Amberlite. A preferred resin may be a carboxylic type cation exchange resin prepared by polymerizing methacrylic acid with about 10% by weight of divinyl benzene using a peroxide catalyst. Typical of such a resin may be that sold under the trademark Amberlite IRC–50. Other carboxylic type resins which may be employed include those sold under the trademark Ionac, such as Ionac C–270.

(b) Sulfonic type resins typified by water insoluble sulfonated carbonaceous exchangers including sulfonate modified aromatic hydrocarbon polymers, sulfonated humic organic materials such as sulfonated coal, lignin, peat, etc., sulfonate modified phenolic resins including sulfonated resins of phenol se, diphenylol sulfone, catechol or naturally occurring phenols such as quebracho, and sulfonate modified (or sulfite modified) insoluble phenol-formaldehyde resins wherein sulfonate (or sulfite) groups are introduced either on the ring or on methylene groups. A typical preferred sulfonate type resin may be sulfonate modified aromatic hydrocarbon polymers such as those sold under the trademark Dowex. A preferred resin of this type may be a sulfonic type cation exchange resin prepared by polymerizing styrene with divinyl benzene which is present to the extent of about 10% by weight of styrene in the presence of chlorosulfonic acid. Typical of such a resin may be that sold under the trademark Dowex 50Wx8. Other sulfonic type cation exchangers which may be employed include those sold under the trademarks Nalcite HCR and Zeo-Karb.

The aqueous solution containing alkali metal stannate may be treated with the cation exchange resin. Contact with the resin may be effected continuously or non-continuously. Most preferably the solution may be continuously passed through a bed or column of resin.

The aqueous solution containing alkali metal stannate may be contacted with the cation exchange resin, which

may preferably be in the form of a column which may typically contain as little as 35 cubic centimeters of resin such as the ammonium form of Amberlite IRC 50, per liter of solution contacted therewith, preferably continuously at a rate of about 1 ml./cm.^{2}/min., and a temperature of 15° C.–30° C., typically 20° C. It will be obvious that the rate of contact of the alkali metal stannate with the cation exchange resin may vary considerably from the suggested rate so long as the rate permits establishment of cation exchange conditions to permit removal of maximum alkali metal cation within the resin column. The cation exchange resin may preferably be present in excess amount to permit maximum exchange of alkali metal cation without prematurely exhausting the resin.

In practice of this invention, the tin oxide sol may be recovered as effluent from the cation exchange resin.

The sol effluent may be characterized as containing all of the tin originally present. If alkali metal hydroxide were originally present, it may be found to be present only in radically reduced amounts in the sol effluent, say from 5 to 50% of the original content, typically about 15%.

In accordance with certain aspects of this invention, as the effluent separates from the ion exchange resin, it may be collected as a tin sol. The tin oxide sols thus formed during reaction with cation exchange resin may be substantially pure and may, for example, be introduced into tin plating baths containing alkali metal hydroxide to replenish tin. The tin oxide sol effluent or eluate may be characterized by its substantially complete conversion to stannate when in contact with solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide.

It is a particular feature of this invention that the aqueous solution containing alkali metal stannate which may be utilized in preparing the tin oxide sol may be a tin plating bath, e.g. a tin electroplating or immersion tinning bath, from which the tin content has been depleted during tin plating, and the alkali metal hydroxide content increased. Typically, a portion of such tin plating baths may be contacted with the cation exchange resin in order to form the tin oxide sol. When tin oxide sol effluent prepared in this manner, or from other aqueous solutions of alkali metal stannate, is added to aqueous tin plating solution to replenish tin, substantially complete conversion to stannate may occur without any substantial increase in the concentration of alkali metal ion in the bath.

The cation exchange resin which may be exhausted through use, may be regenerated to the acid form by washing with a solution of an acid such as hydrochloric, sulfuric, sulfamic, formic, acetic, etc. followed by washing with distilled water. The ammonium form may be regenerated by first converting to the acid-form and then treating with solutions of bases such as ammonium hydroxide. Other nitrogen containing bases may include hydroxides of low volatility, e.g. methylammonium, ethylammonium, etc., typically methylammonium hydroxide. Following this treatment the resin may be washed with distilled water.

The tin oxide sol prepared according to the novel process of this invention when added to a tin plating bath, such as that previously described, to replenish tin in accordance with certain aspects of this invention may be used in connection with the electrodeposition of tin. Such tin plating baths may have immersed therein an insoluble anode, e.g. stainless steel, and a cathode upon which tin may be plated. Typical cathodes may include steel, brass, copper, etc. Electroplating may be conducted at a temperature of 50° C.–100° C., preferably 80° C., at a cathodic current density of up to 10 amperes per square decimeter (a.s.d.), typically 6 a.s.d., over a period of time sufficient to plate tin on the cathode and deplete tin from the bath. The anodic current density may be several times greater than the cathodic current density, typically as high as 50 a.s.d. After such plating conditions have been effected, the tin content of the bath may be replenished by introduction of the tin oxide sol. The bath may preferably be replenished with tin frequently enough by this operation in order to maintain maximum cathode efficiency and bath plating conditions.

It may be noted that should the tin oxide sol employed as additive to a tin plating bath have been prepared utilizing a cation exchange resin in its ammonium form, any ammonium cation which may be in the sol medium is removed as ammonia at the temperature of electroplating.

Practice of this invention may be observed from the following examples:

EXAMPLE 1

1 liter of an aqueous tin electroplating bath containing 20.0 grams of potassium hydroxide (contributing potassium ion in amount of 14.0 grams) and 278.3 grams of potassium stannate may be contacted with an insoluble stainless steel anode and a steel cathode having an area of 0.09 sq. dec. A current of 0.53 amperes (cathodic current density of 6 a.s.d.) may be passed through the bath for 10 hours at 80° C. to plate 5.5 grams of tin on the cathode. At this point, the bath may contain 25.3 grams of potassium hydroxide (contributing potassium ion in amount of 17.6 grams, an increase of 3.6 grams) and 250 grams of potassium stannate.

In order to restore the original concentration of potassium ion (from potassium hydroxide) to 14.0 grams while replenishing the bath with tin, 170 milliliters of the bath present after plating as above which contains a total potassium ion concentration (from both potassium stannate and potassium hydroxide) of 82.7 grams, may be passed through a column containing 6.4 cc. of Amberlite IRC–50 resin in its ammonium form at a rate of 1 ml./cm.^{2}/min. and a temperature of 20° C. The tin oxide sol effluent may be returned to the tin electroplating bath as it leaves the ion exchange resin column thereby replenishing tin in the bath, without causing precipitation. The replenished bath so obtained may then be found to contain the original composition present prior to plating in substantially the original amounts.

EXAMPLE 2

The above process may be repeated, substituting sodium stannate and sodium hydroxide in the tin plating bath for potassium stannate and potassium hydroxide.

EXAMPLE 3

A tin oxide sol may be prepared by passing 1 liter of an aqueous solution containing 900 grams of potassium stannate (a total potassium ion concentration of 238 grams) through a column containing 3050 cc. of Amberlite IRC–50 in its hydrogen form at a rate of 1 ml./cm.^{2}/min. and a temperature of 20° C. Tin in the effluent may be found to be recovered in its original concentration.

EXAMPLE 4

A tin oxide sol may be prepared by adding 200 milliliters of an aqueous solution containing 62.5 grams of potassium stannate (a total potassium ion concentration of 16.3 grams) to a column of 25 cc. of Dowex 50Wx8 in its ammonium form at a rate of 1 ml./cm.^{2}/min. and a temperature of 20° C. Tin oxide sol effluent may be recovered from the column.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

We claim:

1. A process for electrodeposition of tin from a tin plating bath whereby the tin content of the plating bath may be depleted which comprises electrodepositing tin from an aqueous tin plating bath onto a cathode with an insoluble anode thereby depleting tin from said bath, and replenishing tin in said aqueous tin plating bath by addition thereto of a tin oxide sol characterized by substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C., said tin oxide sol being prepared by the process comprising contacting aqueous solution containing alkali metal stannate with a cation exchange resin selected from the group consisting of hydrogen form cation exchange resin and ammonium form cation exchange resin thereby forming a tin oxide sol; and recovering said tin oxide sol as effluent from said cation exchange resin.

2. A process for electrodeposition of tin from a tin plating bath as claimed in claim **1** wherein said alkali metal stannate is potassium stannate.

3. A process for electrodeposition of tin from a tin plating bath as claimed in claim **1** wherein said alkali metal stannate is sodium stannate.

4. A process for replenishing tin in tin plating baths which comprises preparing a tin oxide sol by contacting aqueous solution containing alkali metal stannate with a cation exchange resin selected from the group consisting of hydrogen form cation exchange resin and ammonium form cation exchange resin thereby forming a tin oxide sol, recovering said tin oxide sol as effluent from said cation exchange resin, and introducing said tin oxide sol effluent into a tin plating bath containing alkali metal stannate in amount up to saturation and 5 g./l.–100 g./l. parts by weight of alkali metal hydroxide.

5. A process for replenishing tin in tin plating baths as claimed in claim **4** wherein the alkali metal of each alkali metal compound is potassium.

6. A process for replenishing tin in tin plating baths as claimed in claim **4** wherein the alkali metal of each alkali metal compound is sodium.

7. A process for preparing tin oxide sol characterized by substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C., which comprises passing aqueous solution containing alkali metal stannate in amount up to saturation and 5–100 g./l. of alkali metal hydroxide, the alkali metal of each compound being the same, through a column of carboxylic type cation exchange resin in its ammonium form, thereby forming a tin oxide sol in said solution; and recovering said solution containing said tin oxide sol as effluent from said cation exchange resin.

8. A tin oxide sol characterized by substantially complete convertibility to stannate when in contact with aqueous solutions containing 5 g./l.–100 g./l. of alkali metal hydroxide at temperature of 50° C.–100° C. prepared by the process comprising passing aqueous solution containing alkali metal stannate in amount up to saturation and 5–100 g./l. of alkali metal hydroxide, the alkali metal of each compound being the same, through a column of carboxylic type cation exchange resin in its ammonium form, thereby forming a tin oxide sol in said solution; and recovering said solution containing said tin oxide sol as effluent from said cation exchange resin.

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RICHARD D. LOVERING, Primary Examiner

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