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TIN COATING OF COPPER SURFACES BY REPLACEMENT PLATING

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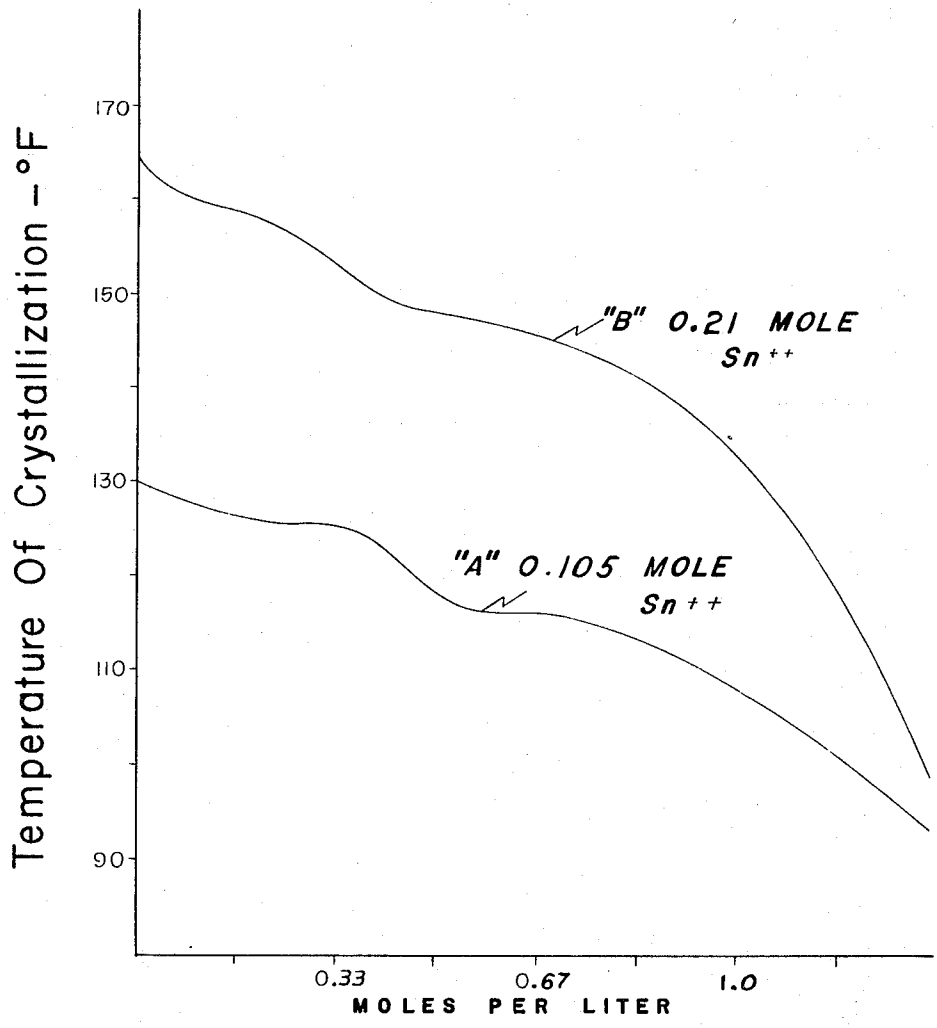

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TIN COATING OF COPPER SURFACES BY REPLACEMENT PLATING

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This invention relates to improvements in the plating of tin on copper, copper alloys, and other metals by chemical replacement, and is a continuation-in-part of application Ser. No. 116,673, now abandoned.

Immersion plating solutions for providing a coating of tin over copper and the like comprising a tin salt, thiourea and an acid have been heretofore known, and are disclosed, for example, in U.S. Patents 2,282,511, 2,369,620, and 2,891,871. While these solutions and methods are operative, the resulting tin coatings are not as pure, bright, dense, nor as resistant to etchants as is sometimes desirable. Furthermore the thickness of the coating of tin which can be applied therewith is limited by the fact that extended deposition produces a coating of poor quality.

It is the principal object of the present invention to provide improved tin deposition methods and solutions which are more stable, which produces a better quality coating, and which permit deposition to be continued for a longer period of time than heretofore possible. Further objects include the provision of brighter, denser, and more uniform coatings of tin which are more resistant to etchants than coating heretofore obtainable.

In accordance with the present invetnion it has been discovered that tin deposition solutions of the above type, namely those of the type containing acid, thiourea or equivalent, and a soluble tin salt, are much improved by the inclusion therein of hypophosphite ion. This ion can be obtained by dissolving in the solution hypophosphorous acid or the alkali metal salts thereof, preferably sodium hypophosphite. The amount of this ingredient is not critical, even small amounts providing some improvement, and large amounts being tolerable. Preferred amounts are those equivalent to sodium hypophosphite between about 3 to 400 grams per liter, and most preferably 10 to 100 grams per liter. In these solutions, it is known that the tin salt is the source of tin, thiourea is a complexing agent, and the acid provides the desired pH.

The hypophosphite ion does not reduce stannous ions to metal to form the deposit, the deposit continues to be formed by replacement of copper or the like in the surface undergoing plating. However it performs a number of other useful functions including maintenance of the stability of the plating bath during storage and use, increasing the solubility of the stannous complex in the bath, and/or providing a more uniform coating over the surface area during plating. It is believed that the ion functions to stabilize the bath as an anti-oxidant to prevent or limit the formation of stannic ion which has been found to be harmful.

It is also preferred that an organic acid, for example, acetic acid, citric acid, malic acid, maleic acid, glucoheptonic acid, hydroxyacetic acid, or glucono-delta-lactone, be included in the composition. This acid is not essential nor is its amount critical. While either a mineral acid or an organic can be used alone, a mixture of the two is preferred. The pH is preferred not greater than about 2.0 and most preferably not greater than about 1.0. All acids, whether organic or mineral, should be non-oxidizing in the bath. A small amount of a suitable wetting agent is also preferred in the composition, for example, octylphenoxyethanol, but is not essential.

Compositions according to the invention are illustrated by the following examples, Example 1 being currently most preferred.

EXAMPLE 1

$SnCl_2$ (anhydrous) g.	20
Thiourea, g.	75
HCl (conc.), ml.	50
$NaH_2PO_2.H_2O$, g.	16
Wetting agent, g.	1
Water to make 1 liter.	

The present solutions can be operated at any temperature at which the tin complex remains soluble, which may be from about room temperature up to approximately the boiling point of the solution. For the above Example 1, the preferred temperature range is from about 150° F. to about 180° F. For low temperature operation, it is preferred to substitute sulphuric acid for the hydrochloric and to dilute the solution somewhat, for example by about half, to improve the solubility of the tin. If desired, the concentration can also be substantially increased, for example three fold, although at the higher concentrations it may be necessary to elevate the temperature to keep the tin in solution.

While the above materials and concentrations are preferred, the concentrations are not critical and equivalent materials can be employed. The tin salt, thiourea or its equivalents, hypophosphite ion, and sufficient non-oxidizing acid to provide a suitable pH are required.

While stannous chloride is the preferred source of stannous ions, other known acid soluble stannous salts can be employed, for example stannous sulphate and stannous fluoroborate. The thiourea forms a tin complex, two mols of thiourea per mol of stannous ion, and it is preferred to use excess thiourea as illustrated in the above example and cited patents. Derivatives of thiourea can be substituted therefor as disclosed in U.S. Patent No. 2,891,871. Other known equivalents for the above materials are disclosed in the art, for example, in the above three cited prior art patents.

While the amount of stannous ion present in the solutions is not critical, small amounts providing some deposition, substantial amounts are preferable to increase the speed of deposition, about 20 to 60 grams stannous chloride per liter being the most preferred. If desired, the concentration can be 2.0 mols per liter or even saturation at the use temperature. The use of hypophosphite ion as disclosed herein substantially increases the amount of stannous ion that can be usefully incorporated in the solution.

To effect a tin coating, it is merely necessary to treat a clean copper surface with the above bath, preferably by immersion. The surface can be treated for sufficient time to build up the desired thickness. This time of treatment can substantially exceed the 15 to 30 minutes maximum possible with prior art solutions. Typical thicknesses provided over copper surfaces with the solution of the above Example 1 are illustrated below in Table I, the thicknesses being in millionths of an inch:

Table I

5 minutes	53
10 minutes	95
30 minutes	132
60 minutes	189

Further examples are given below in Table II of solutions best operating at different temperatures and wherein the hypophosphite ion serves to substantially increase the amount of stannous ion present.

Table II

	2	3	4	5
Ingredient:				
$SnCl_2$ (anhydrous), g	20	40	40	150
Thiourea, g	75	150	150	250
HCl (conc.), ml	80	90		
H_2SO_4 (96%), ml			40	45
$NaH_2PO_2.H_2O$, g	90	120	120	200
Wetting Agent, g	1	1	1	1
Water, to make, liters	1	1	1	1
Operating Temperature, ° F	(1)	(2)	(1)	(3)

[1] 100° F. or above.
[2] 140° F. or above.
[3] 175° F. or above.

The drawing illustrates the increase of stannous complex solubility obtained by use of hypophosphite ion. In the drawing, the crystallization temperature, observed without agitation, is plotted as ordinate against the concentration of hypophosphite ion in plating baths having constant stannous chloride, thiourea, and acid concentrations. These ingredients were present as follows:

	Curve "A"	Curve "B"
$SnCl_2$ (anhydrous), g	24	12
HCl (conc.), ml	50	50
Thiourea, g	90	45
Hypophosphite, mols	0 to .77	0 to .77
Water, to make, ml	600	600

The hypophosphite ion was added as a solution obtained by adding to a 50% by volume aqueous solution of hypophosphorous acid, $NaH_2PO_2.H_2O$ in an amount equal in grams to the volume in ml. of the 50% acid solution. The solutions were prepared hot, at about 180° F. and allowed to cool slowly and the temperature at which crystallization first appeared was recorded.

While the above solution may be prepared and stored as set forth in the above example, it is more practical for storage and shipment, to mix the dry ingredients, for example, the stannous chloride, thiourea, sodium hypophosphite, and the wetting agent of Example 1, and then to dissolve them in the water and acid just prior to use. Since hypophosphorous acid is a liquid, its alkali metal salts are preferably used in the dry composition.

In addition to providing tin coatings on copper, and its alloys such as bronze and brass, the invention has also successfully provided a tin coating on gold and lead or their alloys, and should provide a useful tin coating over any metal displaceable with tin from a thiourea type complex.

It should be understood that the foregoing description is for the purpose of illustration only and that the invention includes all equivalents and modifications falling within the scope of the appended claims.

I claim:

1. In the method in which a cupreous surface is coated by replacement with tin comprising treatment with an aqueous acid solution containing thiourea and an acid soluble stannous salt and having a pH not substantially greater than 2.0, the improvement comprising adding thereto a material selected from the group consisting of hypophosphorous acid and the alkali metal salts thereof.

2. The method according to claim **1** wherein said solution also contains a non-oxidizing organic acid.

3. The method according to claim **1** wherein said solution contains hypophosphite ion in an amount equivalent to about 3 to 400 grams sodium hypophosphite per liter.

4. The method of forming an adherent tin coating on a cupreous surface, said method comprising as steps treating said surface with an aqueous tin solution for a time sufficient to deposit the desired coating thereon, and thereafter removing said surface from the solution, said solution containing a non-oxidizing acid sufficient to provide a pH not greater than about 2.0, a dissolved stannous tin salt in an amount sufficient to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter, at least 2 mols of thiourea per mol of stannous ion, and a material selected from the group consisting of hypophosphorous acid and the alkali metal salts thereof.

5. The method according to claim **4** wherein said solution contains hypophosphite ion equivalent to from about 3 to 400 grams sodium hypophosphite per liter.

6. A solid composition adapted for mixing with acidified water to effect replacement plating of tin over copper and copper-base alloys, said composition consisting essentially of an acid-soluble stannous salt in an amount adapted on dissolution to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter of solution having a pH not exceeding about 2.0, at least 2 mols of thiourea per mol of stannous ion and an alkali metal salt of hypophosphorous acid in an amount equivalent to about 3 to 400 grams sodium hypophosphite per liter.

7. A composition according to claim **6** wherein said composition also contains a non-oxidizing organic acid.

8. An aqueous solution for immersion coating of tin by replacement, said solution consisting essentially of a non-oxidizing acid sufficient to provide a pH not exceeding about 2.0, an acid-soluble stannous salt in an amount sufficient to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter, at least 2 mols thiourea per mol of stannous ion, and a material selected from the group consisting of hypophosphorous acid and its alkali metal salts.

9. The solution according to claim **8** wherein said solution contains a non-oxidizing mineral acid and a non-oxidizing organic acid.

10. The solution according to claim **9** wherein said stannous salt is stannous chloride, and said material is sodium hypophosphite.

11. The solution according to claim **8** wherein said material is present in an amount equivalent to from about 3 to about 400 grams sodium hypophosphite per liter.

12. In the method in which a cupreous surface is coated with tin by treatment with an aqueous acid solution containing thiourea and an acid soluble stannous salt and having a pH not substantially greater than 2.0, the improvement comprising stabilizing the solution by adding thereto a material selected from the group consisting of hypophosphorous acid and the alkali metal salts thereof.

13. The method of forming an adherent tin coating on a cupreous surface, said method comprising as steps treating said surface with an aqueous tin solution for a time sufficient to deposit the desired coating thereon, and thereafter removing said surface from the solution, said solution containing a non-oxidizing acid sufficient to provide a pH not greater than about 2.0, a dissolved stannous tin salt in an amount sufficient to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter, at least 2 mols of thiourea per mol of stannous ion, and, as stabilizer, a material selected from the group consisting of hypophosphorous acid and the alkali metal salts thereof.

14. A solid composition adapted for mixing with acidified water to effect replacement plating of tin over copper and copper-base alloys, said composition consisting essentially of an acid soluble stannous salt in an amount adapted on dissolution to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter of solution having a pH not exceeding about 2.0, at least 2 mols of thiourea per mol of stannous ion and, as stabilizer, an alkali metal salt of hypophosphorous acid.

15. An aqueous solution for immersion coating of tin by displacement, said solution consisting essentially of a non-oxidizing acid sufficient to provide a pH not exceeding about 2.0, an acid-soluble stannous salt in an amount sufficient to provide a useful tin deposit but not substantially exceeding about 2.0 mols per liter, at least 2 mols thiourea per mol of stannous ion, and, as stabilizer, a material selected from the group consisting of hypophosphorous acid and its alkali metal salts.

16. The solution according to claim 15 wherein said stabilizer is present in an amount equivalent to from about 3 to about 400 grams sodium hypophosphite per liter.

References Cited by the Examiner

UNITED STATES PATENTS

2,282,511	5/1942	Bradley	106—1
2,762,723	9/1956	Talmey et al.	106—1

2,827,398	3/1958	Eisenberg	106—1
2,829,059	4/1958	Eisenberg	106—1
2,883,288	4/1959	Dobbs	106—1
2,976,180	3/1961	Brookshire	106—1
2,994,369	8/1961	Carlin	106—1
3,046,159	7/1962	Brookshire	106—1

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,303,029 February 7, 1967

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawing, for "A" read -- B --, in the lower curve and "B" read -- A --, in the upper curve.

Signed and sealed this 28th day of November 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents