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TIN ELECTRODEPOSITING COMPOSITION
AND PROCESS

Ernest W. Schweikher, Shaker Heights, Ohio, as-
signor to E. I. du Pont de Nemours & Company,
Wilmington, Del., a corporation of Delaware

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This invention relates to the electrodeposition of tin and is more particularly directed to compositions and processes for the electrodeposition of tin employing a stannous compound, a thiocyanate and, if desired, a salt containing the radical $\text{Fe}(\text{CN})_6$.

Among the best tin-plating compositions are those in which the tin is present as a stannous compound but unfortunately these plating compositions are none too stable. Dry compositions containing a stannous compound become partly insoluble after extended storage, and electroplating baths containing stannous compounds form sludge. Sludge formation is a particularly great problem under the severe conditions of commercial employment of large volumes of solution with considerable agitation of the solution.

It is an object of the present invention to provide tin electrodepositing compositions and baths which contain stannous tin but which are of increased stability during storage and in commercial use. It is a further object to provide electrodepositing baths which contain stannous tin and which may be subjected to considerable agitation without excessive sludging. It is a still further object to provide stabilizing agents which are effective in small concentrations and which produce no undesirable effects upon the tin deposits. It is a still further object to provide tin electrodepositing compositions which contain stannous tin and which can be used by a plater by simply adding the required amount of water. Still further objects will become apparent hereinafter.

The foregoing and other objects of the invention are attained by the addition to an electrodepositing composition or bath containing stannous tin of a soluble thiocyanate and also, preferably, of a soluble ferricyanide or ferrocyanide.

It is not entirely clear by virtue of what action these agents exercise their beneficial effects upon stannous plating baths. It is thought that the thiocyanate combines with, sequesters, and in some manner nullifies the effect of copper compounds which would otherwise act as oxidation catalysts for stannous tin. The soluble ferricyanide or ferrocyanide similarly appears to combine with, sequester, and nullify the effects of iron compounds which probably act as oxidation catalysts for stannous tin. It is to be observed, however, that even in the absence of iron the ferricyanide or ferrocyanide exercises a stabilizing influence on a stannous electrodepositing bath. Whatever the cause of their efficacy and without being committed to any theory or explanation for their action it can simply be observed that a bath-soluble thiocyanate, preferably when used with a bath-soluble ferricyanide or ferrocyanide, exercises a remarkable stabilizing

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influence upon a stannous electrodepositing bath or composition.

Any acid-tin electrodepositing bath which contains part or all, and preferably at least a major amount, of its tin as a stannous compound may be improved according to the present invention.

There may be used, for instance, newly developed baths employing stannous chloride and sodium fluoride. Numerous other prior art baths may similarly be used in which tin is present as stannous chloride, stannous sulfate, stannous fluoride, phenol sulfonate or other stannous salts of sulfonic acids. Baths of these types frequently include acids such as hydrofluoric acid, hydrochloric acid, sulfuric acid, or aromatic sulfonic acids. These baths may also include organic addition agents and metal brighteners in the customary way, the important consideration for the purposes of the present invention being that the bath contain tin in the form of a soluble stannous compound and any such bath may be improved according to the teachings of this invention.

While any acid stannous electrodepositing bath or composition may be improved according to the present invention it will be found that the best results are obtained with baths having a pH of 1.5 to 5.0. Dry, solid electrodepositing compositions should similarly be of such composition that upon being dissolved in water they will have a pH of 1.5 to 5.0, though sometimes it will be found desirable to let the pH of the resulting bath be adjusted by the addition of a suitable acid. According to the invention, there may be used an alkali thiocyanate, by which I mean sodium, potassium, or ammonium thiocyanate.

Ordinarily from about 0.005 to 5 grams per liter of a soluble thiocyanate should be used in electrodepositing baths or compositions of the present invention. More specifically it has been found that a stannous electrodepositing bath or composition should contain from about 0.01 to 0.5 gram per liter while still more specifically a bath in operation should contain from about 0.01 to 0.10 gram per liter of a bath-soluble thiocyanate. While the amounts above indicated are satisfactory for most baths and compositions it will be understood that if a particular bath or composition contains unusually large amounts of copper then the quantities above indicated should be used in addition to the amount of thiocyanate required to combine with the copper.

An alkali ferricyanide or ferrocyanide is similarly introduced into stannous electrodepositing compositions or baths according to the present invention. By "alkali" I mean sodium, potassium, or ammonium ferricyanide or ferrocyanide. The ferricyanides are generally preferable.

From about 0.005 to 5 grams per liter of a bath-soluble ferricyanide or ferrocyanide may be used.

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More specifically from about 0.01 to 0.5 gram per liter is preferred. A bath in operation can most satisfactorily be maintained with from about 0.01 to 0.20 gram per liter of a bath-soluble ferricyanide or ferrocyanide.

While a ferricyanide or ferrocyanide will generally be used in the amounts above indicated it will be understood that if a particular plating composition or bath contains excessively large amounts of iron, then, an amount of ferricyanide or ferrocyanide equivalent to the iron should be employed in addition to the amounts above indicated.

Example I

A tin electrodepositing bath was made up as follows:

Stannous chloride.....	grams per liter...	75
Sodium fluoride.....	do.....	37.5
Sodium bifluoride (NaHF ₂).....	do.....	37.5
Sodium chloride.....	do.....	22.5
Hydrochloric acid (20° Bé.).....	cc. per liter...	12.5
"Carbowax" 1500.....	grams per liter...	0.1
"Schaeffer's" salt.....	do.....	1.0
Potassium ferricyanide.....	do.....	0.25
Sodium thiocyanate.....	do.....	0.25

pH 2.5.

The "Carbowax" 1500 is a polyethylene oxide of molecular weight about 1500.

The above bath containing a thiocyanate and a ferricyanide according to the present invention was much more stable and formed far less sludge than a bath otherwise similar but omitting the thiocyanate and ferricyanide. Similar results were obtained using ferrocyanide.

Example II

A stannous electrodepositing bath of the present invention was prepared with the following:

	Grams per liter
Stannous sulfate.....	68
Sodium fluoride.....	26
Sodium bifluoride.....	41
Sodium sulfate.....	75
Beta naphthol ethylene oxide.....	0.1
Potassium ferrocyanide.....	1.0
Sodium thiocyanate.....	0.25

pH 2.0.

Example III

A dry prepared composition formulated according to the present invention was made up as follows:

	Per cent
Stannous chloride.....	66
Sodium fluoride.....	33
Potassium ferricyanide.....	0.5
Sodium thiocyanate.....	0.5

The above composition can be employed simply by dissolving in the required amount of water to

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give a bath like that of Example I and by adjusting the acidity to about pH 2.5 with a suitable acid such as hydrochloric.

As has been illustrated above, dry prepared stannous electrodepositing compositions of the present invention may be made up by including a soluble thiocyanate and if desired a soluble ferricyanide or ferrocyanide together with the stannous compound and any other desired electrodepositing ingredient. Thus part or all of the materials to make up an electrodepositing bath may be included in such a composition and may be used by the plater simply by adding water. For the purposes of the present invention it is important only that a thiocyanate and a ferricyanide or ferrocyanide be included with the stannous compounds.

While I have shown numerous illustrative processes and compositions it will be understood that the invention is not to be limited thereby but that numerous stannous electrodepositing baths and compositions may be prepared employing a thiocyanate and a ferricyanide or ferrocyanide without departing from the spirit of this invention.

I claim:

1. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous solution of a stannous compound at a pH of about 1.5 to 5.0, the solution containing from about 0.01 to 0.5 gram per liter of an alkali thiocyanate and from about 0.01 to 0.5 gram per liter of a compound selected from the group consisting of alkali ferricyanides and alkali ferrocyanides.

2. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous solution of a stannous compound at a pH of about 1.5 to 5.0, the solution having added thereto from about 0.005 to 5.0 grams per liter of an alkali thiocyanate and from about 0.005 to 5.0 grams per liter of a compound selected from the group consisting of alkali ferricyanides and alkali ferrocyanides.

3. A bath for the electrodeposition of tin comprising an aqueous solution of a stannous compound at a pH of about 1.5 to 5.0, the solution having added thereto from about 0.005 to 5.0 grams per liter of an alkali thiocyanate and from about 0.005 to 5.0 grams per liter of a soluble compound selected from the group consisting of alkali ferricyanides and alkali ferrocyanides.

4. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous acid solution of a stannous compound which contains from about 0.005 to 5.0 grams per liter of an alkali thiocyanate and from about 0.005 to 5.0 grams per liter of a soluble compound selected from the group consisting of alkali ferricyanides and alkali ferrocyanides.

ERNEST W. SCHWEIKHER.