Patented June 27, 1950 2,512,719

UNITED STATES PATENT OFFICE

2,512,719

ELECTRODEPOSITION OF TIN

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No Drawing. Application September 18, 1945, Serial No. 617,167

4 Claims. (Cl. 204—54)

1

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 and a salt containing the radical $Fe(CN)_6$.

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 sodium, potassium, or ammonium ferricyanide or ferrocyanide.

It is not entirely clear by virtue of what action these agents exercise their beneficial effects upon stannous plating baths. The soluble ferricyanide or ferrocyanide appears to combine with, sequester, and nullify the effects of iron and copper compounds which probably act as oxidation catalysts for stannous tin. It is to be observed, however, that even in the absence of iron and copper 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 ferricyanide or ferrocyanide exercises a remarkable stabilizing influence upon a stannous electrodepositing bath or composition. It is particularly surprising that even when a

2

small excess over that needed to react with iron and copper is used, the ferricyanide or ferrocyanide is not inactivated by the relatively large amount of tin present.

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, when operated at pH 2 to 5 (preferably 2.5–4). There may preferably 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 baths must have a pH of 2 to 5. Dry, solid electrodepositing compositions should similarly be of such composition that upon being dissolved in water they will have a pH of 2 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 ferricyanide or ferrocyanide, by which I mean sodium, potassium, or ammonium ferricyanide or ferrocyanide. The ferricyanides are generally preferable.

The amount of a bath-soluble ferricyanide or ferrocyanide to use in a particular stannous bath is related to the content of iron and copper. The ferricyanide or ferrocyanide should ordinarily be used in at least an amount sufficient to take out any iron and copper which is present and to take out iron and copper which is carried into the bath by the article being plated. It is desirable to maintain an additional small excess to take care of the iron and copper brought into the bath, as by steel strip being plated.

From about 0.005 to 2 grams per liter of a bath-soluble ferricyanide or ferrocyanide may be used under average conditions. 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.

The amounts of ferricyanide and ferrocyanide above indicated are particularly applicable to stannous tin baths which contain from about 15 to 45 grams per liter of tin computed as the metal in the form, of course, of a soluble compound. With more particular reference to the preferred baths of the invention, the indicated amounts of a ferricyanide or ferrocyanide are employed with from about 30 to 90 grams per liter of stannous chloride, or more specifically from about 45 to 75 grams per liter of stannous chloride.

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

pH 2.5

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

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

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

pH 2.0

Example III

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

	Per cent
Stannous chloride	45.5
Sodium fluoride	18.0
Sodium bifluoride	36.0
Potassium ferricyanide	0.5

This composition is employed simply by dissolving in the required amount of water to give a bath like that of Example I. The pH will be substantially correct, but may, if needed, be adjusted. Addition agents, etc., may be added as desired. Instead of using the bifluoride, a correspondingly larger amount of fluoride may be used and the pH adjusted later to about pH 2.5 by the use of an acid such as hydrochloric. Instead of using sodium fluoride compositions such as that shown, there may be used another alkali fluoride. When reference is made herein to an alkali fluoride it will be understood that sodium, potassium, or ammonium fluoride or bifluoride may be used, or mixtures of any two or more may be employed.

A composition for maintenance will have a somewhat different composition from that shown above for initial preparation of a bath. Such a composition is as follows:

	Per cent
Sodium fluoride	30
Sodium bifluoride	60
Potassium ferricyanide	10

While such a composition is ideal where high anode efficiencies maintain the tin content of the bath, the following composition is better where operating conditions lead to lower anode efficiencies and sludge loss:

	Per cent
Stannous chloride	49
Sodium bifluoride	49
Potassium ferricyanide	2

Under still different conditions, first one and then the other of the above may be used as desired.

As has been illustrated above, dry prepared stannous electrodepositing compositions of the present invention may be made up by including a 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. The composition may also be sold as concentrated solutions. For the purposes of the present invention it is important only that a ferricyanide or ferrocyanide be included with the stannous compound.

A preferred composition for the preparation of a bath of the invention may be made up using about 37.5 to 60.19% of stannous chloride from about 39.8 to 62.0% of an alkali fluoride, and from about 0.01 to 0.5% of an alkali ferricyanide or ferrocyanide.

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 ferricyanide or ferrocyanide without departing from the spirit of this invention.

This application is a continuation-in-part of my co-pending application, Ser. No. 494,506, filed July 13, 1943. The latter application was abandoned on September 27, 1945.

I claim:

1. In a process for treating an aqueous, stannous plating bath of a pH from about 2 to 5, the step comprising treating the bath with a slight excess over that required to precipitate copper and iron of a compound selected from the group consisting of alkali ferricyanides and ferrocyanides.

2. In a process for the electrodeposition of tin, the steps comprising effecting deposition from a solution of a stannous compound at a pH from about 2 to 5 and which contains a slight excess over that required to precipitate iron and copper of a compound selected from the group consisting of alkali ferricyanides and ferrocyanides, and thereafter during bath operation maintaining dissolved in the bath a small amount of one of said alkali compounds.

3. In the operation of an aqueous tin-plating bath which contains about 15 to 45 grams per

liter of tin in the form of a stannous compound, and which is at a pH from about 2 to 5, the step comprising operating the bath while there is dissolved therein from about 0.01 to 0.5 grams per liter of a compound selected from the group consisting of alkali ferricyanides and ferrocyanides.

4. In the operation of an aqueous tin-plating bath which contains about 15 to 45 grams per liter of tin in the form of a stannous compound and which is at a pH from about 2 to 5, the step comprising operating the bath while there is dissolved therein from about .005 to 2 grams per liter of a compound selected from the group consisting of alkali ferricyanides and ferrocyanides.

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