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# ELECTRODEPOSITION OF TIN

George F. Eckert, Niagara Falls, N. Y., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the electro-desposition of tin from acidic stannous plating baths and is more particularly directed to electro-depositing processes and compositions wherein such baths are improved by the inclusion of maganous and nitrate ions, or either of them.

Acidic stannous plating baths are being used at higher and higher temperatures as production lines are speeded up and as the thickness of deposits is increased. The use of maganous and nitrate ions, or either of them, stabilizes such stannous baths against oxidation and sludge formation. Manganous and nitrate ions can advantageously be used over a wide range of bath operating conditions and temperatures and they are especially effective at elevated temperatures at which stabilizing agents ordinarily fail or offer disadvantages.

In a preferred embodiment of the invention manganese nitrate is added in small amount to fluoride-stannous chloride baths such as those described in Schweikher 2,407,579.

The specific fluoride-stannous chloride baths which are preferred for use according to the invention are those which comprise from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and which satisfy the equation:

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true; the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 pH–0.265 to 0.055 pH–0.370.

The baths may be made with sodium, potassium, or ammonium fluoride or bifluoride or mixtures of two or more of them. When the solutions contain as much as, say, about half of the alkali metal as potassium, ranging upwardly to all of the alkali as potassium, there is an increased tendency to form sludge and the use of manganous and nitrate ions is especially helpful.

Further detailed description of the baths of Schweikher of 2,407,579 appears unnecessary since they are fully described in the patent and they are, moreover, well known in commercial use.

Instead of the specific fluoride-stannous chloride baths of the Schweikher patent the invention can be applied to still other acidic, stannous plating baths. Stated somewhat more broadly the preferred baths contain a soluble stannous compound and an alkali metal fluoride. The ratio of alkali metal fluoride per mole of stannous compound is from 2:1 to 12:1. The pH is between 2 and 5. In preferred baths the aqueous solution contains from 37.5 to 150 grams per liter of stannous chloride and 37.5 to 150 grams per liter of an alkali fluoride.



Still more broadly, any acidic tin electro-depositing bath which contains part or all, and preferably at least a major amount, of its tin as a stannous compound can be improved according to the present invention. It is preferred that it be operated at a pH from 2 to 5.

There may be used, for example, stannous baths in which the tin is present as stannous sulfate, stannous chloride, phenol sulfonate or other stannous salts of sulfonic acids. It is also to be noted that baths of these types, like those previously more specifically described, frequently include acids such as hydrofluoric acid, hydrochloric acid, sulfuric acid or aromatic sulfonic acids.

The stannous plating baths may, of course, include sodium chloride and other such materials commonly used to increase bath conductivity and they may include various of the organic "addition agents."

There may be used, for example, "Schaeffer's" salt or related materials. Similarly there may be used various of the polyethylene oxides. These and other suitable organic addition agents are described in the previously mentioned Schweikher patent. The amounts of addition agent to use are of course in accord with prior practices and constitute no part of the present invention.

In describing stannous baths no reference has been made to the fact that most commercial baths contain small amounts of iron and sometimes copper, chromium and nickel as well. These are present as impurities and are brought into the bath in commercial operation. These apparently act as oxidation catalysts and accelerate the formation of sludge. The use of manganese nitrate or of manganous or nitrate ions according to the invention offsets the effect of these catalytic metals though it should be noted that these ions are effective in stabilizing the bath even in the absence of any observable quantity of a catalytic metal.

In the operation of tin electroplating processes of the invention there is added to a plating bath such as above described, a soluble compound which supplies manganous manganese ions in the solution. As the operation of the bath proceeds it is desirable to maintain therein manganous maganese.

The manganous compound is preferably added as manganous nitrate because, as will be explained hereafter, it is desirable also to include the nitrate ion in the bath. As will be noted, it is often desirable to include even more nitrate than can be added as the manganese compound.

The manganous compound can be added to the bath as other compounds of manganese. There may be used for example manganous sulfate, manganous fluoride, manganous chloride, or manganous carbonate.

It is ordinarily preferable to use inorganic compounds as suggested above, but organic manganous salts can be used such as manganous acetate and manganous benzoate.

Instead of using a manganous compound, manganese compounds with a valence higher than +2 can be used. There is some small disadvantage in using a manganese compound of higher valence because it will first be reduced by the tin. It thus acts to some extent as an oxidizing agent and to this rather minor degree is objectionable. Of course the amount of oxidation is not great and such manganese compounds can be used. For example, manganese trichloride or manganese dioxide can be employed. Sodium permanganate, and other alkali metal permanganates can be used.

The amount of a manganous compound to use will vary somewhat from bath to bath and will depend in part upon the quantities of iron, copper and other such impurities. In general at least about 0.01 gram per liter of manganous manganese should be provided in a bath to obtain effects of any consequence.

Manganous compounds are not very soluble in the

plating baths and they can be used up to the limit of their solubility in the bath. The solubility in a halogen-tin bath is as follows:

| Temperature, ° C.: | Solubility of $Mn^{++}$, grams per liter |
|---|---|
| 30 | 0.65 |
| 60 | 0.15 |
| 90 | 0.06 |

There is no point in using large excesses of manganous compounds over those soluble in the bath, though some excess can be present to replenish the supply of manganese. Generally one would not use more than about, say, 1 gram per liter of manganous manganese in a halogen-tin bath though more can be added.

More specifically, the lower limit will ordinarily be about 0.05 gram per liter, especially if the manganous compound is one other than manganous nitrate, for it will be understood that the nitrate ion has itself an effect according to the invention. In preferred practices of the invention there will ordinarily be used more narrowly from about 0.05 gram per liter up to the limit of solubility of manganous manganese. It is preferred that these amounts be maintained in the bath. It will be understood that manganous nitrate can be used as indicated in somewhat smaller amounts than the other manganous compounds though the ranges given are crudely practical for all of the compounds listed since in no event is the range more than indicative of the practical operating limits.

The amount of nitrate to add can similarly be varied, depending upon the particular bath and the amounts of iron, copper, and other metals present as impurities. If the nitrate is added with the manganese no separate consideration need be given to the quantity to use. The nitrate, however, is readily soluble and can be added as the anion of other compounds. For example, if the pH of the bath permits it can be added as nitric acid. Again, it can be added as sodium, potassium, ammonium or stannous nitrates. These compounds, and particularly the sodium, tin and possibly the potassium, will not usually add cations additional to those already present in the bath. In other words, it is most desirable to use cations which will have no disadvantageous effects in the bath.

Other inorganic nitrates which can be used include those of calcium, magnesium, barium, lead, zirconium, and cerium. It will be noted that some of these, like lead and cerium, form insoluble fluorides and leave the nitrate in the bath without introducing any undesired cation. It will of course be understood that metals such as iron, copper, chromium and nickel which adversely affect the bath should preferably not be introduced as their nitrates. Of course, one can use the nitrates of these metals and obtain some positive benefits but there is no need to incur the disadvantages of introducing these materials which are known to be deleterious.

The amount of nitrate to add can be varied, depending upon the bath and conditions of operation. There should be used at least about 0.01, or better 0.1, gram per liter of $NO_3$. Broadly then, one may use from about say 0.01 to 8 grams per liter of $NO_3$ in the form of a nitrate. More narrowly, it is preferred that there be added to a bath and preferably that there be maintained therein from about 1 to 4 grams per liter of $NO_3$.

It will be understood that when reference is made herein to a bath containing manganese nitrate or other such compounds, the compound in each instance will be present in an equilibrium state. As is well understood, the ionization of such a compound will result in there being some cations and anions present and combinations of the cations and anions with various of the other anions and cations present in the bath. It is further to be understood that when reference is made herein to a bath containing manganous ions or nitrate ions, that these are present either in the ionized state or combined with various cations or anions. This nomenclature is in accord with that customarily used in which it is said that a compound is present if the ions which constitute it are present, regardless of how they are combined. Similarly, it may be said that the ions are present if chemical analysis shows their existence, without regard to their state of ionization or manner of combination.



In order that the invention may be better understood reference should be had to the following illustrative examples:

*Example 1*

An electrolyte of the Schweikher Patent 2,407,579 was prepared from C. P. salts to make the following composition:

| | Grams per liter |
|---|---|
| Stannous chloride $SnCl_2.2H_2O$ | 60 |
| Sodium fluoride NaF | 60 |
| Hydrogen fluoride HF (48% solution) | 20 |
| Sodium chloride | 15 |
| Polyethylene oxide (mol. wt. 6000 five per cent solution) | 2 |

To this electrolyte there was added 0.05 gram per liter of Fe as $FeSO_4$. This was added to simulate the presence of iron as in commercial operations.

To the bath there was then added an aqueous solution containing five per cent by weight of $Mn(NO_3)_2$ the amount being that required to supply 1 gram per liter of manganous manganese. This amounted to about 3 grams per liter of $Mn(NO_3)_2$.

The solution was then operated under conditions which effect a considerable amount of aeration and oxidation. The oxidation of the solution as measured by the change in stannous tin content from time to time was reduced 90 per cent as compared with a bath which did not contain the manganous nitrate.

It is further to be observed that even when no iron was added to the bath, oxidation was markedly reduced by the addition of the manganous nitrate to the solution.

*Example 2*

A bath was made up as in Example 1 and containing 0.05 gram per liter of iron. To this there was added manganous sulfate in an amount to provide 1 gram per liter of manganous manganese. Oxidation in the plating solution was reduced 75 per cent as compared with a bath which did not contain the manganous sulfate.

*Example 3*

An electroplating solution was made up as in Example 1 and 0.005 gram per liter of copper was added. To the bath thus prepared there was added sodium nitrate in an amount to provide one gram per liter of $NO_3$; that is 1.5 grams per liter of sodium nitrate.

Oxidation in this bath was reduced thirty-five per cent by the addition of the nitrate. An eighty per cent reduction in oxidation was obtained with the nitrate when 0.05 gram per liter of ferrous iron was present as a catalyst.

I claim:

1. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous, acidic solution of a stannous compound at a pH between 2 and 5 and containing 2 to 12 mols of alkali metal fluoride per mol of stannous compound, said bath also containing about 0.01 to 1 gram per liter of manganous manganese as manganous nitrate.

2. In a tin electroplating process the step comprising electrodepositing tin from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true;

the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 ph–0.265 to 0.055 pH–0.370 said bath also containing about 0.01 to 1 gram per liter of manganous manganese as manganous nitrate.

3. In a tin electroplating process the step comprising electrodepositing tin from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation.

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true; the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 ph–0.265 to 0.055 pH–0.370 said bath also containing manganous ions equal to about 0.01 to 1 gram per liter of manganous manganese.

4. In a tin electroplating process the step comprising electrodepositing tin from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true; the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 ph–0.265 to 0.055 pH–0.370 said bath also containing nitrate ions equal to about 0.01 to 8 grams per liter of $NO_3$.

5. A bath for the electrodeposition of tin comprising an aqueous, acidic solution of a stannous compound at a pH between 2 and 5 and containing 2 to 12 moles of alkali metal fluoride per mole of stannous compound, said bath also containing manganous nitrate in an amount to supply 0.01 to 1 gram per liter of manganous manganese.

6. A bath for the electrodeposition of tin comprising an aqueous solution containing 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true;



the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 ph–0.265 to 0.055 pH–0.370 said bath also containing manganous nitrate equal to about 0.01 to 1 gram per liter of manganous manganese.

7. A bath for the electrodeposition of tin comprising an aqueous solution containing 37.5 to 150 grams per liter of stannous chloride and 37.5 to 150 grams per liter of alkali fluoride in the proportion of 2 to 12 moles of said fluoride to one mole of stannous chloride and having a pH between 2 and 5 said bath also containing manganous ions equal to about 0.01 gram per liter to saturation of manganous manganese.

8. In a tin electroplating process the step comprising electrodepositing tin from an aqueous bath comprising from about 37.5 to 150 grams per liter of an alkali fluoride, and from about 37.5 to 150 grams per liter of stannous chloride and satisfying the equation:

$$pH=\frac{k\ (\text{moles MF})}{\text{moles } SnCl_2}$$

wherein the following conditions are simultaneously true; the pH is between 2 and 5, $k$ has a value from 0.1 to 1.0, MF is alkali fluoride, and the mole ratio

$$\frac{MF}{SnCl_2}$$

is about from 2 to 12, the static solution potential of tin in the bath being equal in volts to from 0.055 ph–0.265 to 0.055 pH–0.370 said bath also containing nitrate ions equal to about 0.01 to 8 grams per liter of $NO_3$.

9. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous, acidic solution of a stannous compound at a pH between 2 and 5 and containing 2 to 12 mols of alkali metal fluoride per mol of stannous compound, said bath also containing nitrate ions equal to about 0.01 to 8 grams per liter of $NO_3$.

10. In a process for the electrodeposition of tin the step comprising effecting deposition from an aqueous, acidic solution of a stannous compound at a pH between 2 and 5 and containing 2 to 12 mols of alkali metal fluoride per mol of stannous compound, said bath also containing manganous ions equal to about 0.01 to 1 gram per liter of manganous manganese.

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