Addition Agents for Electrodeposition of Tin from Stannous Sulfate—Hydrofluoric Acid Solutions

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General Statement

Numerous studies have been made of addition agents for the electroposition of tin from sulfuric acid solutions, but only a few publications (1, 2, 3, 4, 8) of research with hydrofluoric acid or fluorides in the baths have appeared. The object of having fluorides in the bath is that hydrolysis with consequent precipitation of basic stannic salts is avoided.

It is necessary to add small quantities of organic material to tin plating baths in order to obtain smooth, solid cathode deposits rather than loose masses of crystals that are always formed if no suitable restraining or "addition agent" is present.

Electroplating of tin has become very important in coating iron for the making of "tin" cans. By the electro-method any thickness of tin can be applied, whereas, by the old process of dipping the iron in molten tin, only much thicker coatings can be obtained. Thus a great saving of tin is possible.

Experimental

Wax beakers of about 150 ml. capacity were used. Wax coated glass stirrers, run at about 90 r.p.m., provided the necessary agitation.

The cast tin anodes had an area of 16 sq. cm. The iron cathodes had an area of six sq. cm. and were prepared from used cans which were detinned in a solution of hot sodium hydroxide and sodium nitrate.

Since stannous fluoride was not available, a mixture of stannous sulfate, 100 g./l., and hydrofluoric acid, 35 g./l., was used. Each experimental bath had a volume of 100 ml., and one cathode and one anode were used in each.

The procedure for testing addition agents was as follows: One-tenth gram (1 g./l.) of the addition agent being tested was added to the bath. If the deposit was unsatisfactory, further multiples of this weight were added until one gram (10 g./l.) had been added. If the results were still negative an additional gram of the addition agent was added whereby the total concentration of addition agent would be 20 g./l. If the deposit deteriorated upon increasing the amount of addition agent, a new bath was prepared with less than one tenth gram of the addition agent (less than 1 g./l.). New cathodes were used with each change in concentration of the compound being tested. Obviously, the quantity of any addition agent that could be used was limited by the solubility for those that were not very soluble. In some cases parallel baths containing 100 g./l. of sulfuric acid instead of the hydrofluoric acid were tested to obtain a comparison of the two types of baths. All baths were operated at room temperature. The cathode current density was held at 3 amp./sq.dm. or about 28 amp./sq. ft.

Since glue is widely used as an addition agent in many plating baths and since glue (5, 6) with cresol or naphthol gives excellent results in the sulfate tin bath, a series of baths was tested containing 1 g./l. of animal glue (freshly prepared). Glue, by itself, was of little value. However, glue together with o-cresol, β -naphthol, or NWO¹ gave smooth deposits without badly projecting crystalline growths but of a visibly crystalline nature. Glue plus resorcinol, tannic acid (an insoluble precipitate formed), eugenol, m-cresol, sorghum molasses, β -hydroxyethyl-p-toluidine, cymenetergitol-4 suspension, phloroglucinol, sulfanilic acid, tartaric acid, salicylic acid, thiourea, gum tragacanth, quinoline, glycine, tergitol-4, or β -hydroxyethyl-m-toluidine gave coarsely crystalline deposits.

Parallel experiments with all sulfate baths, always gave better deposits than did the baths containing hydrofluoric acid. However, anode corrosion was good and less sludge and precipitated material formed in the hydrofluoric acid baths.

Gum tragacanth, by itself, was ineffective and in combination with all the various other things listed above with glue, it gave loose, crystalline deposits. The combination with eugenol was a little less crystalline than the others.

Potato starch² with eugenol, quinoline, tartaric acid, salicylaldehyde, thymolsulfonthalein, *m*-cresol, β -naphthol, glycine, guaiacol, sulfanilic acid, sorgham molasses, catechol, tergitol-4, resorcinol, *p*-hydroxyacetophenone, or β -hydroxyethyl-*p*-toluidine gave very crystalline deposits. The potato starch with β -hydroxyethyl-*m*-toluidine, thymolsulfonthalein, or eugenol gave deposits that were less crystalline, but analogous baths without the starch gave equivalent deposits.

Dextrin with the other materials was ineffective except that there was some improvement with eugenol.

Gum arabic, tested with a few other materials, gave loose, crystalline deposits in all cases.

Caramel, a patented (7) addition agent, was ineffective either alone or in combination with eugenol, gum tragacanth, quinoline, β -hydroxyethyl-*m*-toluidine, or peptone.

Sorghum molasses, by itself, in a concentration of 10 g./l. (dry weight) definitely restrained the formation of loose crystals; greater concentrations did not increase the effect. Sorghum with glue, *m*-cresol, gum tragacanth, quinoline, dextrin, tannic acid, vinylphenol, 8-hydroxyquino-

¹NWO is a mixture of aromatic phenolic compounds recovered in refining of mineral oils.

² The addition agent was prepared by boiling starch in distilled water and adding aliquots of this solution.

line, sulfanilamide, phoridizin, guinea green B (NaOH solution), *p*-tertamyl-o-cresol, tergitol-4, thymolsulfonthalein, β -naphthol, catechol, or quinoline was ineffective; β -hydroxyethyl-*m*-toluidine, eugenol, NWO, or guaiacol proved somewhat effective; with quinoline, β -hydroxyethyl-*m*toluidine, or tergitol, the deposits were without projecting trees but were visibly crystalline.

Sunset yellow³, a water soluble dye, in quantities less than 10 g./l. seemed entirely ineffective. With concentrations greater than this, compact but coarsely crystalline deposits were obtained. Ponceau 3R⁴ and carmine were ineffective.

Thymolsulfonthalein (1 g./l.) gave firm but crystalline deposits. Greater concentrations did not improve the deposits. Eugenol and eugenol with starch, or β -naphthol with thymolsulfonthalein gave similar deposits. Thymolsulfonphthalein with *m*-cresol, glue, β -hydroxyethyl-*m*-toluidine, or sorghum gave loosely crystalline deposits.

Guinea green⁵, 0.1 g./l., gave heavy firm crystals. This dye with *p*-tert-amyl-*o*-cresol, sorghum, gum arabic, quinoline, 8-hydroxyquinoline, tergitol-4, *a*,*a*'-dimethylbenzylphenol, or β -hydroxyethyl-*m*-toluidine gave less satisfactory deposits than with the dye alone. Guinea green, together with quinoline, tergitol-4, and sorghum gave very dense white deposits. A similar bath substituting 8-hydroxyquinoline for quinoline gave somewhat coarser but brighter deposits. Guinea green B together with both β -hydroxyethyl-*m*-toluidine and *n*-octyl alcohol gave visibly crystalline deposits without projecting crystals.

Quinoline was ineffective, but with eugenol, tergitol-4, or guaiacol, the crystalline growth was restrained. With vinylphenol or glycine only loose crystals were obtained. 8-Hydroxyquinoline was ineffective as were its combinations with tergitol-4 or guaiacol. With β -hydroxyethyl-*m*-toluidine, the excessively crystalline growth at the edges was decreased.

Sulfanilic acid, cyclohexylamine, glycine, *o*-aminophenol, hydroquinone, 2-amino-2-methyl-1-propinol, pyridine, *o*-toluidine, *p*-toluidine, and *o*-anisidine were all ineffective.

 β -Hydroxyethyl-*m*-toluidine, but not β -hydroxyethyl-*p*-toluidine, prevented the growth of projecting crystals and with starch, *m*-cresol, or cymenesulfonic acid, there was no further improvement. With glue, peptone, or carbowax 1500, loose crystals resulted.

M-cresol, *o*-cresol, eugenol, β -naphthol, or catechol, was of no value as an addition agent. Eugenol with cymene sulfonic acid and quinoline gave compact but visibly crystalline deposits. Guaiacol prevented excessively loose crystal formation and treeing. However, the surface of the deposit was coarsely crystalline.

³ A search through the dye catalogs available failed to establish its identity. It is a legal food color dye.

⁴ Sodium salt of β-cumene-azo-β-naphthol-3,6-disulfonic acid.

⁵Sodium salt of diphenyl diethyl diamino triphenyl carbinol sulfonic acid anhydride.

Tergitol-4⁶ alone or with n-octyl alcohol, cymene sulfonic acid, m-cresol, glue, or eugenol was of no value.

The following were ineffective: Naphthalene-1,5-disulfonic acid alone or in combination with o-anisidine, carmine or o-toluidine; toluene sulfonic acid alone or with m-cresol, eugenol, or o-cresol; Turkey red oil or sulfonated tall oil alone or with m-cresol; egg albumin, cellusolve, saponin, carbowax 1500, carbowax 4500, Victor wetting agent 54B, 4-tertbutyl-m-cresol, peptone, dioxane, potassium ethyl xanthate, triethylcarbinol, tannic acid, n-octyl alcohol, trisodium phosphate, phloroglucinol, or phloridizin.

Conclusions

A wide variety of materials was tested for their effect as addition agents for the stannous sulfate-hydrofluoric acid electrolytic bath. Of the phenols, *m*-cresol, *o*-cresol, β -naphthol, NWO, and guaiacol were found effective if used together with another addition agent of the type glue, sorghum, or tergitol-4. Eugenol was found effective with a variety of compounds.

Guinea green B used with various materials in the concentration 0.1 g./l. was effective as an addition agent. β -Hydroxyethyl-*m*-toluidine was a good addition agent.

Tergitol-4 was shown to be a fair addition agent in a few combinations but its effect was variable.

The use of hydrofluoric acid was a distinct advantage in that the baths remained clear and free from any precipitate. However, hydrofluoric acid was distinctly objectional in that it always caused the deposits to be more crystalline and less firm than with the same addition agents in a sulfuric acid bath.

Corrosion of the anodes was generally good. Intercrystalline corrosion was at a minimum. Usually a very loose, finely divided, black, but easily removed, film formed upon the anodes during operation.

There was no gasing at the electrodes.

Tests were made on a sufficient number of baths to indicate a cathode efficiency approaching one hundred per cent. No tests were made on anode efficiency.

Although very many substances were tried as addition agents for the first time, no new ones were found that could be recommended for use in electroplating.

References

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⁶ 2-methyl-7-ethyl-4-undecanol sulfate.