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ADDITIVES FOR TIN ELECTROPLATING BATH

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ABSTRACT OF THE DISCLOSURE

The tinplating bath additive contains a mixture of thiourea, a glycol alkyl ether, a polyethylene oxide or mixtures of polyalkylene oxides having a molecular weight in the range from about 600 to 20,000 and water.

Summary of the invention

Solutions of stannous chloride containing relatively large amounts of alkali metal fluoride have been utilized to produce excellent deposits of electroplated tin. These solutions are referred to in the trade as halogen tin electroplating baths and are described in detail in U.S. Patent 2,407,579. In using tinplating baths of this type, considerable difficulty has been experienced by the formation of insoluble material, chiefly, fluo-stannate, which settles to the bottom of the plating bath forming a sludge which must be periodically removed. Various means have been proposed for inhibiting the sludge formation. The most satisfactory method heretofore known has been the addition of a small amount of an alkali metal ferrocyanide or ferricyanide. The addition of thiourea has been found to be helpful in inhibiting the sludge formation. Also, addition of a polyalkylene oxide has been found to improve the quality of the electrodeposit.

Although thiourea is only slighly soluble in an aqueous medium, the start-up of a halogen tin electroplating bath can be effected by separately adding thiourea and the polyalkylene oxide to a new plating bath. It is necessary, however, to replenish these materials from time to time after the bath is in operation. The thiourea and polyalkylene oxide are depleted at approximately the same rate. Therefore, for control purpose, it would be desirable to be able to make a single addition of these materials to the plating bath. It is essential, however, that the thiourea be solubilized in order to perform its sludge inhibition function in the bath.

A problem has been encountered in attempting to combine the aforementioned materials due to the relative insolubility of thiourea in an aqueous thiourea-polyalkylene oxide system. Due to its solubility characteristic, the thiourea tends to crystallize from the system as the temperature drops. In fact, with certain materials, the combination of ingredients congeals upon freezing and after thawing either remains in a solid gel or turbid state.

It has been found that by combining thiourea, a glycol alkyl ether, a polyalkylene oxide and water in proportions specified in detail later herein, the solubility of thiourea in the system is markedly improved and a freeze-thaw stable additive is provided.

Detailed description of the invention

The halogen tin electroplating bath additives of this invention consist of the following essential ingredients: (A) from about 5 to 20% by weight of thiourea; (B) from about 5 to 45% by weight of a polyalkylene oxide or mixture of polyalkylene oxides having molecular weights in the range from about 600 to 20,000; and (C) from about 50 to 90% of a mixture consisting of 10 to 75 parts by weight of a glycol alkyl ether and from about 15

to 80 parts by weight of water. Various combinations of the ingredients can be made within the limits just specified to provide clear, freeze-thaw stable additives for halogen tin plating baths. In a preferred embodiment of this invention, the ingredients are combined to provide an additive consisting of: (A) from about 15 to 20% by weight of thiourea; (B) from about 15 to 40% by weight of polyalkylene oxide; and (C) from about 20 to 40% by weight of the glycol alkyl ether and from about 20 to 30% by weight of water.

Sufficient additive should be included in the electroplating bath to maintain a concentration of polyalkylene oxide of from 0.001 to 25, preferably 1 to 5 grams per liter and a concentration of thiourea of about 0.1 to 5, preferably 2 to 3 grams per liter. When added to a halogen tin electroplating bath of the type described in U.S. Patent 2,407,579 there is a significant reduction in the amount of sludge formed without affecting the quality of the tin plate.

The additives of this invention may be prepared by adding the ingredients in the proportions previously specified to a container and heating the mixture of ingredients to a slightly elevated temperature, e.g., 40 to 80° C. By gentle stirring, a clear solution is obtained. The solution is storage stable and retains its clarity at elevated temperatures. If subjected to freezing temperatures, the solution will solidify; however, the clear appearance is restored upon thawing with no deleterious effects.

The ingredients for the additives of this invention may be obtained from commercial sources. The glycol alkyl ether may be selected from a variety of available materials such as ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether and glycol monomethyl ether. The polyalkylene oxides are of the type described in U.S. Patent 2,457,152 and the U.S. patents identified therein. In general, these polyalkylene oxides having a molecular weight, calculated as specified in U.S. Patent 2,457,152, in the range from about 600 to 20,000 are used, with the polyalkylene oxides having a molecular weight from about 4,000 to 20,000 being preferred. Polyethylene oxide or a mixture of polyethylene oxides having molecular weights within the just-mentioned range are preferred.

The following examples in which parts and percentages are by weight unless otherwise specified further illustrate the present invention.

EXAMPLE I

Three separate preparations of halogen tin plating bath additives were made by combining the following ingredients in a glass container equipped with a magnetic stirrer.

Table 1

	Grams
Thiourea	18.0
Glycol ethyl ether [1]	34.5
Water	25.0
Polyethylene oxide (M.W. 6,000)	7.5
Polyethylene oxide (M.W. 4,000)	7.5
Polyethylene oxide (M.W. 20,000)	7.5

[1] In the three preparations diethylene glycol monoethyl ether, diethylene glycol monomethyl ether and glycol monoethyl ether, respectively, were used.

The mixtures were each gently stirred at a temperature between 50 and 60° C. to provide a clear solution. Each solution was then cooled overnight in a deep freeze compartment at a temperature below 0° C. When the containers were removed from the deep freeze, the solutions were found to have solidified. The separate preparations were allowed to thaw at room temperature after which they are examined and found to be clear.

A standard halogen-tin electroplating bath having a pH of 3.3 was prepared by combining the following ingredients:

Table 2

	Grams
Stannous chloride	42.8
Sodium fluoride	38.3
Sodium difluoride	21.7
Sodium chloride	36.9
Sodium ferrocyanide	1.2
Water, to make 1 liter.	

In separate experiments Hull cells were filled with the plating bath solution just described and 0.4 ml. of each of the preparations of plating bath additive was added, thereby providing a concentration of 0.25 gram per liter of thiourea and 0.33 gram per liter of polyethylene oxides. Steel Hull cell panels were pickled in an aqueous hydrochloric acid solution (1:1), rinsed in water and plated in the Hull cell using a current of 3 amperes for 30 seconds with the bath temperature being maintained in the range from 130 to 140° F. A normal appearing, semibright tin electrodeposit was obtained throughout the current density range of 2.5 to 150 amperes per square foot.

In a control experiment in which no additive was included in the plating bath the plate was dull throughout most of the range and no plate was obtained at very low current densities.

EXAMPLE II

The experiment of Example I was repeated except that the three preparations consisted of the following ingredients:

Table 3

	Percent by weight
Preparation No. 1:	
Thiourea	18.0
Ethylene glycol monoethyl ether	34.5
Water	25.0
Polyethylene oxide (M.W. 6,000)	22.5
Preparation No. 2:	
Thiourea	18.0
Ethylene glycol monoethyl ether	34.5
Water	25.0
Polyethylene oxide (M.W. 20,000)	5.62
Polyethylene oxide (M.W. 6,000)	11.25
Polyethylene oxide (M.W. 4,000)	5.63
Preparation No. 3:	
Thiourea	18.0
Ethylene glycol monoethyl ether	34.5
Water	25.0
Polyethylene oxide (M.W. 20,000)	11.25
Polyethylene oxide (M.W. 6,000)	5.62
Polyethylene oxide (M.W. 4,000)	5.63

All three solutions were clear after exposure to the freeze-thaw cycle. When added to a standard tin plating solution as described in Example I, a semibright tin electrodeposit is obtained.

EXAMPLE III

Example I is repeated except the tin plating bath and additive are comprised of the following ingredients:

Table 4

	Grams
Stannous chloride	16.2
Sodium fluoride	14.5
Sodium difluoride	58.0
Sodium chloride	14.0
Sodium ferrocyanide	4.55
Water, to make 1 gal.	
Additive:	
Thiourea	18.0
Diethylene glycol monomethyl ether	24.5
Water	35.0
Polyethylene oxide (M.W. 6,000)	22.5

A portion of the tin plating bath solution was added to a Hull cell and sufficient additive was added to provide a concentration of 1.7 gm./l. of thiourea and 2.2 gm./l. of polyethylene oxides. The plating was carried out in the conventional manner using a current of 3 amperes for 30 seconds while maintaining the bath at 140° F. The tin electrodeposit had a normal semibright appearance over substantially all of the plated area. In a control experiment in which the additive was omitted the plate was dull over substantially all of the surface and a small portion of the steel sample was found to be unplated.

EXAMPLE IV

Example I is repeated except that the additive consists of the following ingredients:

Table 5

	Percent by weight
Thiourea	5
Ethylene glycol monomethyl ether	75
Water	15
Polyethylene oxide (M.W. 6,000)	5

A clear solution is provided. The solution remains clear after exposure to the freeze-thaw cycle. In a Hull cell plating experiment the tin electrodeposit has a normal appearance when the additive is included in the Hull cell as described in Example I.

EXAMPLE V

Example I is repeated with similar results except that the additive consists of the following ingredients:

Table 6

	Percent by weight
Thiourea	20
Ethylene glycol monomethyl ether	10
Water	25
Polyethylene oxide (M.W. 6,000)	45

EXAMPLE VI

Example I is repeated except that the additive consists of the following ingredients:

Table 7

	Percent by weight
Thiourea	5
Ethylene glycol monomethyl ether	10
Water	80
Polyethylene oxide (M.W. 6,000)	5

The solution obtained is clear and freeze-thaw stable. When added to the halogen tin plating bath of Example III, a semibright electrodeposit is obtained.

As shown in the foregoing examples the additives of this invention provide semibright tin electrodeposits when added to standard halogen tin electroplating baths. The additives are stable and remain clear after they are subjected to a freeze-thaw cycle.

We claim:

1. An additive for a halogen tin electroplating bath consisting of the following essential ingredients: (A) from about 5 to 20% by weight of thiourea; (B) from about 5 to 45% by weight of a polyalkylene oxide having a molecular weight in the range from about 600 to 20,000; and (C) from about 50 to 90% by weight of a mixture consisting of 10 to 75 parts by weight of a glycol alkyl ether and from about 15 to 80 parts by weight of water.

2. The additive of claim 1 wherein said glycol alkyl ether is ethylene glycol monomethyl ether.

3. The additive of claim 2 wherein said polyalkylene oxide is a polyethylene oxide or mixture of polyethylene oxides having molecular weights in the range from about 4,000 to 20,000.

4. The additive of claim 1 wherein said ingredients are present in the following amounts: (A) from about 15 to 20% by weight of thiourea; (B) from about 15 to 40% by weight of said polyalkylene oxide; and (C) from about 20 to 40% by weight of said glycol alkyl ether and from about 20 to 30% by weight of water.

5. The additive of claim 4 wherein said glycol alkyl ether is ethylene glycol monomethyl ether.

6. The additive of claim 5 wherein said polyalkylene oxide is a polyethylene oxide or mixture of polyethylene oxides having molecular weights from about 4,000 to 20,000.

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