United States Patent

Engelsman et al.

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[54] ACID ELECTROPLATING BATH FOR DEPOSITING TIN

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[21] Appl. No.: **54,596**

[30] **Foreign Application Priority Data**

July 16, 1969 Netherlands.....6910903

[52] **U.S. Cl.** .....**204/54 R**

[51] **Int. Cl.** **C23b 5/14**

[58] **Field of Search** .....204/54 R

[56] **References Cited**

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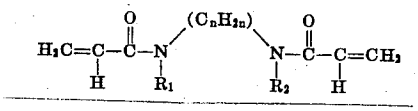
Primary Examiner—F. C. Edmundson

Attorney—Frank R. Trifari

[57] **ABSTRACT**

An electroplating bath for depositing lustrous tin which bath contains bivalent tin ions, sulphate, sulphonate, sulphamate or fluoborate anions, a surface-active substance, a lustering agent of an unsaturated character having aldehyde or ketone groups and a compound of the type



in which $n = 1$, 2 or 3 and R_1 and R_2 represent hydrogen, alkyl, or combined represent a ring system.

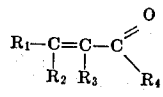
4 Claims, No Drawings

ACID ELECTROPLATING BATH FOR DEPOSITING TIN

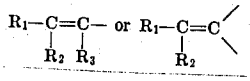
The invention relates to an acid tin-plating bath on the basis of sulphate, sulphonate, sulphamate or fluoroborate with the aid of which it is possible to obtain bright tin depositions.

The U.S. Pat. specification No. 3,483,100 describes such baths which contain bivalent tin ions, sulphate, sulphonate, sulphamate or fluoborate as anions, a surface-active substances, an unsaturated compound having an aldehyde or ketone group as a brightening agent and in addition one organic compound which is capable of reducing the overvoltage on a cathode consisting of tin for the evolution of hydrogen. The last-mentioned organic compound is preferably polymerizable.

As a brightening agent a compound is preferably used which is described in the British specification 1,141,283 which is defined by the general formula:



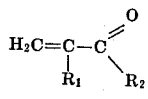
wherein each of the symbols R_1, R_2 and R_4 represent a hydrogen atom, an aliphatic, heterocyclic or aromatic group or such a completely or partially hydrated group which optionally contains nonionizable substituents or substituents which are nonreducible in this milieu, R_3 hydrogen, an alkyl group or an esterified carboxyl group, or wherein the combination



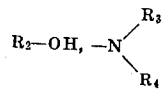
represents a ring system by means of connection of the substituents R_2R_3 and R_1R_2, provided that the group

has a purely unsaturated character therein.

An effective class of polymerizable organic compounds which can reduce the overvoltage for the evolution of hydrogen is the class which may be defined by the general formula



wherein R_1 represents a hydrogen atom, an alkyl group or a phenyl group and



wherein R_3 and R_4 each represent a hydrogen atom, an alkyl group or a phenyl group, or $-OR_5$, wherein R_5 represents an alkyl group in which a hydrogen atom is either replaced by an alkylated or nonalkylated nitrogen atom, or in which one or more hydrogen atoms are replaced by OH groups.

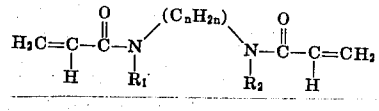
A drawback of baths having these additions is that the polymerization occurring during use of the bath gives rise to pollution because the polymeric products have such a colloidal nature that they cannot be removed by filtering.

As compared with previously described lustrous tin baths, the above-mentioned known electroplating baths provide a tin deposit which has a fine brightness over a wide range of current densities. This is notably important for tin-plating articles having a complicated shape, for example, highly profiled workpieces having sharp edges and small holes. In this case variations in the current density by a factor of not less than 100 occur. However, at low values of the current density the brightness leaves something to be desired.

The present invention provides an acid tin-plating bath which produces deposits having a hard uniform bright appearance throughout the current density range during tin-plating of the above-mentioned workpieces having a complicated shape, thus also at the lowest values of the current density occurring in practice.

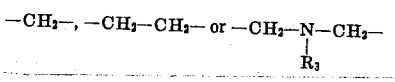
In addition the baths do not give rise to the above-mentioned pollution. It is true that polymers are produced during use of the baths, but these are produced in such a shape that they can be removed by filtering without difficulty.

The bath according to the invention which contains bivalent tin ions, sulphate ions, sulphonate ions, sulphamate ions or fluoborate ions as anions, a surface-active compound, an unsaturated compound having an aldehyde or ketone group as a brightening agent and at least one organic compound which contains an acryloyl group, is characterized in that the acryloyl-containing compound is defined by the following formula:



wherein n is 1, 2 or 3, and

R_1 and R_2 each represent hydrogen or an alkyl group or R_1 and R_2 combined, while being formed to a ring of five- or six-membered rings consist of the group



in which R_3 is hydrogen, an acyl group or an alkyl group while each of the groups R_1 to R_3 may comprise substituents with the exception of NO_2.

According to a preferred composition the bath according to the invention includes sulphate ions and in a further preferred composition the surface-active compound consists of a polyoxyethylene compound.

The invention will now be described with reference to a few Examples of tin-plating baths in which highly profiled workpieces blanked from standards sheet iron were tin-plated at a bath temperature of approximately 20° C. at average current densities of between 0.5 and 5 A./sq.dm. The articles tin-plated in these baths had a uniform, very hard brightness throughout their surface.

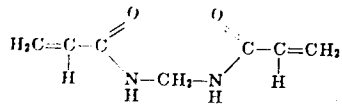
The brightening agent benzalacetone was added in a quantity of 0.16 g./l. to one of the following four known tin-plating baths which contained the following dissolved components per litre of liquid.

a. stannous sulphate	40 g.
sulphuric acid (d=1.84)	120 g.
"Lissapol N"	10 g.
b. tin fluoborate $Sn(BF_4)_2$	30 g.
fluoboric acid	200 g.
"Lissapol N"	5 g.
c. tin sulphate	49 g.
m-benzene disulphonic acid	170 g.
"Lissapol N"	3 g. and
d. tin sulphamate	60 g.

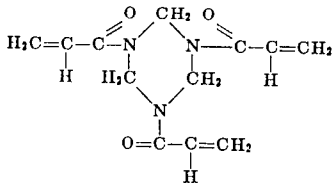
sulphamine acid	100 g.
"Ethomene S 20"	10 g.

In addition one of the following compounds in the quantities indicated was added to these baths:

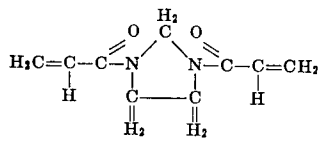
NN' methylene-bis-acrylamide 0.050 g./l.



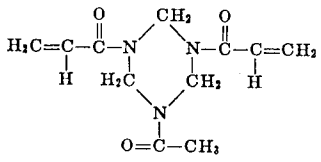
1,3,5-triacryloyl-hexahydro-s-trazine 0.100 g./l.



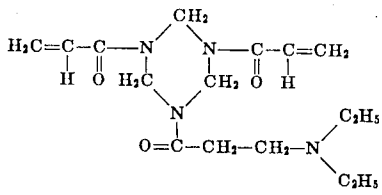
N, N' bisacryloyl-imidazoline 0.200 g./l.



5 acetyl, 1,3-bisacryloyl-hexahydro-s-triazine 0.100 g./l.



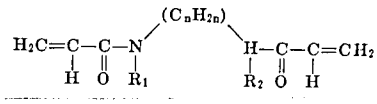
β-diethylaminopropionyl, 1,3-bisacryloyl-hexahydro-s-triazine 0,2 g./l.



("Lissapol N" is a nonionic surface-active substance which comprises a condensation product of polyoxyethylene and alkyl phenol; "Ethomene S 20" is a cation-active wetting agent comprising polyoxyethylene (10) soyamine).

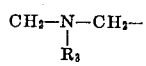
What is claimed is:

1. An acid electroplating bath for depositing tin, which bath contains bivalent tin ions, sulphate ions, sulphonate ions, sulphamate ions, or fluoborate ions as anions, a surface-active compound, an unsaturated compound having an aldehyde or ketone group as a brightening agent and at least one organic compound which contains an acryloyl group, characterized in that the acryloyl-containing compound is defined by the following formula:



wherein n is 1, 2 or 3 and

R_1 and R_2 each represent hydrogen or an alkyl group or R_1 and R_2 combined, while forming a five- or six-membered ring consist of the group $-CH_2-$, $-CH_2-CH_2-$ or



, in which R_3 represents hydrogen, an acyl group or an alkyl group while each of the groups R_1 to R_3 may contain substituents with the exception of NO_2.

2. An acid electroplating bath for depositing tin as claimed in claim 1, characterized in that it contains sulphate ions as anions.

3. An acid electroplating bath for depositing tin as claimed in claim 1, characterized in that the surface-active compound is on the basis of polyoxyethylene.

4. An acid electroplating bath for depositing tin as claimed in claim 1, characterized in that the acryloyl-containing compound is chosen from N,N'-methylene bisacrylamide, 1,3,5-triacryloyl, hexahydro-s-triazine, 5-acetyl, 1,3 bisacryloyl hexahydro-s-triazine and NN'bisacryloyl imidazoline.

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