United States Patent Office 3,483,100 Patented Dec. 9, 1969

3,483,100

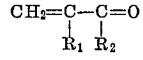
TIN PLATING BATHS

Jan Johannes Engelsman, Gerrit Krijl, and Petrus Baeyens, Emmasingel, Eindhoven, Netherlands, assignors, by mesne assignments, to U.S. Philips Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Sept. 11, 1967, Ser. No. 666,983
Claims priority, application Netherlands, Sept. 14, 1966, 6612936
Int. Cl. C23b 5/46, 5/14
U.S. Cl. 204—54 4 Claims

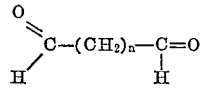
ABSTRACT OF THE DISCLOSURE

Acid electrolyte bath for obtaining bright tin deposit containing sulfate, sulfonates or fluoroborate ions; an unsaturated aldehyde or ketone brightener, for example, furfural; and as a secondary brightener a polymerizable compound of the formula



wherein R_1 is hydrogen, alkyl or phenyl and R_2 is OH,

R_3 and R_4 being hydrogen, alkyl or phenyl or OR_5 wherein R_5 is alkyl where at least one hydrogen has been replaced by amino, alkylamino or hydroxyl groups or a secondary brightener of the formula



n being 0–5 and possibly one or more hydrogen atoms in the CH_2 group being replaced by hydroxyl groups. Examples of these secondary brighteners are glyoxal, vinylacetate and N-vinyl carbazole.

The invention relates to an acid tin-plating bath containing sulphate, sulphonate or fluoborate anions and brighteners by means of which bright tin deposits can be obtained.

Acid tin-plating baths are known which contain as brightener a condensation product of an aliphatic aldehyde and an organic compound having a basic nitrogen-containing group, for example a reaction product of acetaldehyde and o-toluidine. These brighteners become resinous very soon, however, so that the bath has only a short stability.

Furthermore, acid tin-plating baths are known which contain as brightener an aromatic or heterocyclic aldehyde. These baths have the disadvantage, however, that they produce bright deposits only in a very limited current density range, only between about 5 and 20 A/sq. dm. This means that strongly profiled workpieces having sharp edges and small perforations, the electrolytic coating of which involves current density variations of a factor of even as low as 100, cannot be coated with a thin layer of uniform thickness and brightness. The current density variations are considerably larger if the electrolytic coating process is carried out in a drum.

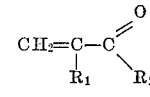
Further, electrolyte tin-plating baths have become known recently which contain a brightener consisting of a compound of the general formula X—CH=CH—Y in which X represents an isocyclic or heterocyclic ring that may be substituted and Y is one of the groups —H,

—CHO, —COOH, —CH_2OH, —R or —OR is a corresponding nonsaturated ketone. These baths moreover contain formalin, imidazolin or derivatives and mixtures thereof.

According to the invention, a number of organic compounds have been found which, when added instead of formalin together with a brightener to an electrolyte tin-plating bath, have the advantage that they have a larger brightening effect on the tin obtained and that they do not have disagreeable odors. The usable compounds can be found in a few chemical classes which are chemically not at all related to each other. However, the applicant has found a common electrochemical criterion which the said compounds must satisfy. By the addition of a non-ionic surface-active substance to a solution of sulfuric acid, an aryl sulphonate or a fluoborate, the overvoltage for the separation of hydrogen at a cathode of tin is raised. Those compounds have proved usable which, when added to these solutions, are capable of reducing this overvoltage. This criterion can be easily applied. By means of a simple test it can be determined for each individual case whether a given compound is usable. For this purpose, an electrolytic cell is utilized the electrolyte of which only consists of dilute sulfuric acid and a non-ionic surface-active substance, while this cell is operated at a constant current density, for example, of 2 A./sq. dm., the cell containing a platinum anode and a tin cathode; the EMF is measured between the tin cathode and the platinum anode or an auxiliary calomel electrode provided in the cell, a small quantity of the substance to be tested being added to the electrolyte liquid. If the EMF decreases after addition of X the substance, the latter suits the purpose of the invention. If η reprsents the said EMF in millivolts and c the concentration of the substance to be added in millimol/litre, this requirement can be briefly represented by

$$-\left(\frac{\Delta\eta}{\Delta c}\right)_{\Delta c \to 0} \geq 1$$

A class of chemical compounds which are capable of considerably reducing the said EMF and hence provide a considerable increase in brightness and exhibit a larger current density range than formalin-containing tin-plating baths, may be represented by the general formula:

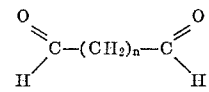


where R_1 reprsents a hydrogen atom, an alkyl group or a phenyl group and R_2—OH,

R_3 and R_4 each representing a hydrogen atom, an alkyl or a phenyl group, or —OR_5, R_5 representing an alkyl group in which either a hydrogen atom has been replaced by an alkylated or non-alkylated nitrogen atom or one or more hydrogen atoms have been replaced by OH groups.

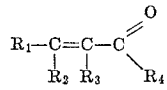
The solubility of the latter compound should be at least 0.1% by weight in 2 N H_2SO_4. A second class of chemical compounds producing a considerable reduction of the said EMF and hence providing a considerable increase in brightness and a larger current density range

than formalin-containing tin-plating baths may be represented by the general formula:

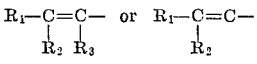


where n a value 0, 1, 2, 3, 4 or 5, while in the CH_2 groups one or more hydrogen atoms are allowed to be replaced by OH groups.

In applicants' copending application, Ser. No. 521,803, filed Jan. 20, 1966, an acid tin-plating bath has been described which contains bivalent tin ions, an anions sulphate-, sulphonate- or fluoborate ions a surface-active compound of non-ionic nature and as brightener a sufficiently soluble compound corresponding with the general formula:



where each of the symbols R_1, R_2 and R_4 represents a hydrogen atom, an aromatic, heterocyclic or aliphatic group or a similar group which may be entirely or partly hydrated and which may have substituents which cannot be ionized or cannot be reduced in this medium, R_3 represents hydrogen, an alkyl group or an esterified carboxyl group, or where the combination



represents a ring system, on the understanding that the group —C=C— has a purely non-saturated character. With the aid of these baths which contain beside the aforementioned constituents also formalin, bright tin deposits can be obtained without difficulty, even on workpieces which are strongly profiled, have sharp edges or small perforations, and even if the electrolytic coating process is carried out in a drum. During operation of this bath, current density variations of a factor 1000 are unobjectionable. Moreover, these tin-plating baths have an extremely high stability.

In a preferred embodiment of the method according to the invention, a further improvement is obtained by the use of the last-mentioned baths, i.e. a larger brightness and an even larger current density range if instead of formalin such a compound which is capable of reducing the overvoltage for the evolution of hydrogen at a tin cathode, is added to the tin-plating bath.

A number of baths will now be described by way of example, in which workpieces, having sharp edges which had been punched out of conventional sheet iron, were tin-plated at a bath temperature of approximately 20° C. and at average current densities lying between 0.5 and 5 A./sq. dm. The articles thus tin-plated all had a uniform brightness of excellent quality throughout their surface.

For this purpose, there was added to one of the three following known tin-plating baths containing per litre of liquid the following dissolved constitutents:

	G.
(a):	
Stannous sulphate	40
Sulfuric acid (d=1.84)	120
"Lissapol N"	5
(b):	
Tin fluoborate $Sn(BF_4)_2$	30
Fluobroic acid	200
"Lissapol N"	5
(c):	
Tin sulphate	40
m-Benzene disulphonic acid	170
"Lissapol N"	3

one of the following brighteners in the indicated quantities:

	G./l.
Dihydrotolylaldehyde	0.12
Benzalacetone	0.16
Furfural	1.20

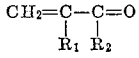
Moreover, one of the following constituents was added to these baths in the indicated quantities.

	G./l.
Acrylic acid	0.3
Methacrylic acid	2.0
Acrylicamide	0.2
Methacrylicamide	0.2
Glycidylacrylate	0.2
Propylene glycolacrylate	0.15
Dimethylaminoethylmethacrylate	3.0
Glyoxal	4.0
Glutaric dialdehyde	0.2
α-Hydroxyadipicaldehyde	0.2
N-vinylpyroolidone	1.0
p-Diethylaminobenzaldehyde	0.1
N-vinylcarbazole	1.0
2-vinylpyridine	0.5
Tetrahydrofuran	2.3
Vinylacetate	1.0
Alkylglycidyl ether	1.5

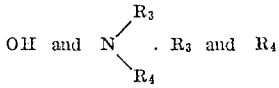
These baths had an extremely high stability. "Lissapol N" is a non-ionic wetting agent which consists of a condensation product of polyoxyethylene and alkylphenol.

What we claim is:

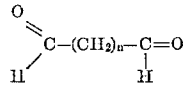
1. In an aqueous acid electrolyte bath for the electrolytic deposition of bright tin said bath containing bivalent tin ion anions selected from the group consisting of sulfate, organic sulfonate and fluoborate ions, a non-ionic surface active agent and an olefinically unsaturated organic carbonyl primary brightener and as a secondary brightener a polymerizable organic compound capable of reducing the overvoltage for the evolution of hydrogen at a tin cathode, the improvement wherein said polymerizable organic compound is selected from the group consisting of a compound of the formula



wherein R_1 is a member of the group consisting of hydrogen, alkyl and phenyl, R_2 is a member selected from the group consisting of



being selected from the group consisting of phenyl, hydrogen, alkyl and OR_5 wherein R_5 is alkyl wherein at least one hydrogen atom has been replaced by a member selected from the group consisting of amino, alkylamino and hydroxyl and a compound of the formula



n being an integer ranging from 0 to 5 and the hydroxy substituted derivatives thereof, said primary and secondary brighteners being present in an amount sufficient to provide a bright tin electrodeposit.

2. The electrolyte bath for depositing tin of claim **1** wherein it contains as the primary brightener a carbonyl compound selected from the group consisting of aromatic and heterocyclic ring containing aldehydes wherein the carbonyl group is directly attached to one of said rings and α, β olefinically unsaturated carbonyl compounds; said carbonyl compounds being free of ionizable and reducible substituents, nitrogen containing substituents and com-

pounds hydrolyzable in said bath to said carbonyl compound.

3. The electrolyte bath of claim 2 wherein the primary brightener is present in a quantity lying between 25 and 300 mg. and the secondary brightener is present in a quantity lying between 0.01 and 10 g. per litre of bath liquid.

4. The electrolyte bath of claim 1 wherein said primary brightener is benzalacetone and said secondary brightener is acrylic acid.

References Cited

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6501841 8/1966 Netherlands.

JOHN H. MACK, Primary Examiner

G. L. KAPLAN, Assistant Examiner

PO-1050
(5/69)

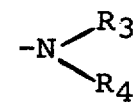
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,483,100 Dated December 9, 1969

Inventor(s) JAN JOHANNES ENGELSMAN ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 34, "reprsents" should read -- represents --

Column 2, lines 56-60, "  " should read -- 

Column 4, line 20, "N-vinylpyroolidone" should read

-- N-vinylpyrrolidone --.

Signed and sealed this 25 day of August 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents