

UNITED STATES PATENT OFFICE

2,552,920

ELECTROLYTIC TIN PLATING BATH

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No Drawing. Application August 27, 1947,
Serial No. 770,956

8 Claims. (Cl. 204—54)

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This invention relates to electrolytic tin plating baths and to addition agents therefor.

In electrolytic processes for plating tin on steel, steel is immersed in a plating bath from which tin is electrically deposited on the surface. Subsequently the plated metal may be subjected to further treatment, such as heating, to melt the tin deposit and enhance its luster. The baths are ordinarily aqueous solutions of a tin salt, various acids or alkalis and various addition agents.

Baths with which the present invention is concerned consist of an aqueous solution of a stannous salt and acid, such as phenolsulfonic acid, phenolsulfonic acid and a phenol, sulfuric acid, or fluoboric acid, besides the addition agent. Many materials have been used as addition agents in such baths, perhaps the most common being glue, beta-naphthol or sulfones, such as dihydroxy diphenyl sulfone. The action of addition agents is not fully understood, but satisfactory tin deposits cannot be produced in their absence.

There are several variables that must be controlled in plating processes, these including current density, bath temperature, agitation, and the tin and acid contents of the bath. It is desirable that the operable range of each variable be as broad as possible, and such ranges may be broadened by proper selection of the addition agent. The interrelation of these variables is such that broadening the operable range of one ordinarily has a broadening effect on the others. For example, an addition agent that broadens the operable current density range over that obtained with the usual sulfone addition agent likewise broadens the operable temperature range at fixed current density. It is apparent that broadening the operable ranges of the variables facilitates plating operations, since less precise control is needed.

Accordingly, the principal object of the present invention is to provide improved addition agents for electrolytic tin plating baths for broadening the range of current densities capable of producing satisfactory tin deposits.

A further object of the invention is to provide improved addition agents for electrolytic tin plating baths that in the concentrations employed are soluble throughout the range of temperatures encountered and are stable compounds, not subject to decomposition by hydrolysis.

A further object of the invention is to provide improved baths for electrolytic tin plating by use of which control of the operation may

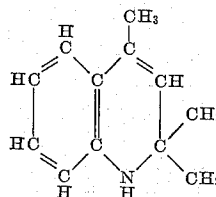
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be less precise than with previous baths with which I am familiar.

A further object of the invention is to provide improved electrolytic tin plating baths capable of forming heavier tin deposits of good quality, that is, melting to a high luster, than other baths with which I am familiar.

The addition agents of the present invention consist essentially of the polymerized reaction product of an aromatic primary amine and an aliphatic ketone. Specifically the monomers of these agents may be formed by combining one mol of an amine of the group consisting of aniline and ortho, meta and para toluidine with two mols of a ketone of the group consisting of acetone and methyl ethyl ketone. Each reaction yields a monomer which is a dihydroquinoline derivative.

In the case of aniline and acetone, the monomer is 2,2,4 trimethyl-1,2 dihydroquinoline, which has the structural formula:



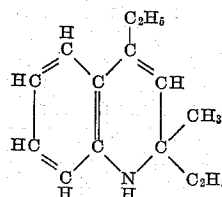
Similarly, ortho, meta and para toluidine with acetone yield, respectively:

2,2,4,8 tetramethyl-1,2 dihydroquinoline

2,2,4,7 tetramethyl-1,2 dihydroquinoline

2,2,4,6 tetramethyl-1,2 dihydroquinoline

In the case of aniline and methyl ethyl ketone, the reaction product is 2 methyl-2,4 diethyl-1,2 dihydroquinoline, which has the structural formula:



Similarly ortho, meta and para toluidine with methyl ethyl ketone yield, respectively:

2,8 dimethyl-2,4 diethyl-1,2 dihydroquinoline

2,7 dimethyl-2,4 diethyl-1,2 dihydroquinoline

2,6 dimethyl-2,4 diethyl-1,2 dihydroquinoline

It is to be noted in each of the foregoing compounds that the term "dihydro" is used to signify the saturation of the double bond normally present in quinoline between the N and the adjacent C, despite the substitution of an aliphatic group for one of these hydrogens.

Each of the foregoing compounds is capable of polymerization in the presence of an acid. Polymers suitable as additional agents in accordance with the present invention conveniently may be prepared by mixing about four parts by weight of one of the aforementioned dihydroquinoline derivative monomers with about three parts by weight of 50% H_2SO_4 and heating the mixture to 90° to 100° C. for twenty-four hours. The proportions of monomer and acid stated are not critical, and may be varied considerably and still produce satisfactory polymers. The polymer thus formed is a relatively viscous liquid which can be neutralized by a suitable base (e. g. NaOH) to form granules of the basic polymer.

Since the foregoing monomers and polymers per se are known and available commercially, it is deemed unnecessary to describe in detail processes for their preparation.

Either the unneutralized acid solution of the polymer or the basic polymer is suitable as the addition agent. In some instances the basic polymer may be dissolved directly in the bath, although I usually prefer to dissolve the basic polymer first in H_2SO_4 and add the resulting solution to the bath.

The addition agent is added to acid baths in amounts in the range of 0.20 to 7.00 grams of agent per liter of bath. The baths contain tin in the form of a stannous salt usually within the limits of 10 to 80 grams of metal per liter of solution with baths for strip plating usually having a tin concentration in the lower portions of the range on account of agitation of the bath on strip travel. The acid content varies with different acids but is always sufficient to produce a solution having a pH value of not more than 2. Phenol sulfonic acid baths contain from 35 to 220 grams of the acid per liter, or on the basis of H_2SO_4 equivalent 6 to 40 grams per liter. To this may be added up to 10 grams per liter of a phenol. Either ordinary carboric acid may be used or other phenolic compounds, such as o, m or p cresol, resorcinol, naphthol, etc. Sulfuric acid baths contain from 6 to 40 grams of the acid per liter. Fluoborate baths contain from 5 to 30 grams of hydrofluoboric acid per liter, usually with a slight excess of free boric acid. The operating temperature is usually in the neighborhood of 100° to 110° F. and in the case of strip plating, a considerable degree of agitation is produced by movement of the strip through the bath.

For any particular polymer and any particular bath composition and operating conditions, the optimum concentration of the agent within the range stated may be determined empirically. In general for sulfonic acid and sulfate baths optimum concentrations are in the lower end of the range (0.2 to 4.0 grams of agent per liter) and for fluoborate baths in a slightly higher range (0.3 to 7.0 grams of agent per liter). The optimum concentration of agents formed with methyl ethyl ketone as the ketone constituent is in general lower than those formed with acetone.

Baths containing the improved addition agents produce satisfactory tin deposits over a wide range of current densities. The rate of depletion of the materials is slower than with baths containing as addition agents sulfoxides or sulfones, the most satisfactory previously used agents of which I

have knowledge. The agents are completely soluble in acid solution and therefore do not crystallize and separate on cooling of the solution. They are stable compounds and do not hydrolyze. Tin deposits made using these agents produce unusually lustrous coatings on subsequent melting.

To demonstrate the efficacy of addition agents of the present invention, the following examples of baths containing these agents and the resulting current density ranges are cited:

Example I

A phenol sulfonic acid bath was prepared consisting of an aqueous solution of:

109 grams/liter 65% phenol sulphonic acid
65 grams/liter stannous sulfate
2.0 grams/liter polymerized 2,2,4 trimethyl-1,2 dihydroquinoline

The bath analysis was:

	Grams/liter
Free acid (H_2SO_4 equivalent)	20
Tin (stannous)	35
Agent	2.0

The operating conditions were:

Temperature ° F. 100
Agitated

The operable current density range was found to be 30 to 1150 amperes/sq. ft.

Example II

Polymerized 2,2,4,8 tetramethyl-1,2 dihydroquinoline was substituted as the addition agent in a bath otherwise identical to that of Example I, the concentration of agent remaining 2.0 grams/liter, and operating conditions remaining the same. The operable current density range was found to be 75 to 150 amperes/sq. ft.

Example III

Polymerized 2,2,4,7 tetramethyl-1,2 dihydroquinoline was substituted as the addition agent in a bath otherwise identical to that of Example I, the concentration of agent being 0.75 gram/liter and operating conditions remaining the same. The operable current density range was found to be 35 to at least 600 amperes/sq. ft.

Example IV

A phenol sulfonic acid bath was prepared consisting of an aqueous solution of:

109 grams/liter 65% phenol sulfonic acid
65 grams/liter stannous sulfate
5 grams/liter phenol
0.25 gram/liter polymerized 2,2,4 trimethyl-1,2 dihydroquinoline

The bath analysis was:

	Grams/liter
Free acid (H_2SO_4 equivalent)	20
Tin (stannous)	35
Phenol	5
Agent	0.25

The operating conditions remained as in Example I. The operable current density range was found to be 30 to 740 amperes/sq. ft.

Example V

A phenol sulfonic acid bath was prepared consisting of an aqueous solution of:

109 grams/liter 65% phenol sulfonic acid
36 grams/liter stannous sulfate
5 grams/liter phenol
0.25 gram/liter polymerized 2,2,4 trimethyl-1,2 dihydroquinoline

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The bath analysis was:

	Grams/liter
Free acid (H ₂ SO ₄ equivalent)-----	20
Tin (stannous)-----	20
Phenol-----	5
Agent-----	0.25

The operating conditions were:

Temperature-----	° F-- 110
Agitated	

The operable current density range was found to be 30 to 1220 amperes/sq. ft.

Example VI

A sulfate bath was prepared consisting of an aqueous solution of:

42 grams/liter sulfuric acid
81 grams/liter stannous sulfate
3.0 grams/liter polymerized 2,2,4 trimethyl-1,2 dihydroquinoline

The bath analysis was:

	Grams/liter
Free acid-----	42
Tin (stannous)-----	45
Agent-----	3.0

The operating conditions were:

Temperature-----	° F-- 100
Agitated	

The operable current density range was found to be 75 to at least 600 amperes/sq. ft.

Example VII

Sulfate baths were prepared consisting of aqueous solutions of:

20 grams/liter sulfuric acid
65 grams/liter stannous sulfate
3 to 4 grams/liter polymerized 2,2,4,6 tetramethyl-1,2 dihydroquinoline

The bath analyses were:

	Grams/liter
Free acid-----	20
Tin (stannous)-----	35
Agent-----	3 to 4

The operating conditions were:

Temperature-----	° F-- 100
Agitated	

The operable current density ranges were found to be 50 to at least 600 amperes/sq. ft.

Example VIII

Fluoborate baths were prepared consisting of aqueous solutions of:

20 grams/liter hydrofluoboric acid
6 grams/liter boric acid
86 grams/liter stannous fluoborate
3.0 to 7.0 grams/liter polymerized 2,2,4 trimethyl-1,2 dihydroquinoline

The bath analyses were:

	Grams/liter
Hydrofluoboric acid-----	20
Boric acid-----	6
Tin (stannous)-----	35
Agent-----	3.0 to 7.0

The operating conditions were:

Temperature-----	° F-- 100 to 140
Agitated	

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The operable current density ranges were found to be 25 to at least 600 amperes/sq. ft.

Example IX

A phenol sulfonic acid bath was prepared consisting of an aqueous solution of:

109 grams/liter 65% phenol sulfonic acid
65 grams/liter stannous sulfate
0.5 gram/liter polymerized 2 methyl-2,4 diethyl-1,2 dihydroquinoline

The bath analysis was:

	Grams/liter
Free acid (H ₂ SO ₄ equivalent)-----	20
Tin (stannous)-----	35
Agent-----	0.5

The operating conditions were:

Temperature-----	° F-- 100
Agitated	

The operable current density range was found to be 50 to at least 600 amperes/sq. ft.

In each of the foregoing examples, light reflectivity tests were employed to determine whether the deposit was satisfactory. When the coating after melting possesses a high degree of light reflectivity, the deposit is considered satisfactory.

It is seen from the examples that sulfonic acid baths, sulfate baths or fluoboric baths containing addition agents of the present invention produce satisfactory coatings over wide ranges of current density. In each instance the current density range is considerably broader than that obtained with sulfoxides or sulfones as the addition agents. Operable ranges of other variables likewise are increased as hereinbefore pointed out.

While I have disclosed but certain specific compounds and ranges and cited but a limited number of examples of bath compositions, it is apparent that further modifications may arise. For example, the agents disclosed may be used in combination with each other. Therefore, I do not wish to be limited by the disclosure set forth, but only by the scope of the appended claims.

I claim:

1. An electrolytic tin plating bath consisting essentially of an aqueous acid solution having a maximum pH value of 2, of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of sulfuric acid, phenolsulfonic acid and hydrofluoboric acid and 0.2 to 7.0 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

2. An electrolytic tin plating bath consisting of an aqueous acid solution having a maximum pH value of 2, of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of sulfuric acid, phenolsulfonic acid and hydrofluoboric acid and 0.2 to 7.0 grams per liter of a polymer of 2,2,4 trimethyl-1,2 dihydroquinoline.

3. An electrolytic tin plating bath consisting essentially of an aqueous acid solution having a

maximum pH value of 2, of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of sulfuric acid, phenolsulfonic acid and hydrofluoboric acid and 0.2 to 7.0 grams per liter of an addition agent, the acidity being produced by the presence of an acid of the group consisting of phenolsulfonic acid, phenolsulfonic acid and a phenol, sulfuric acid, and hydrofluoboric and boric acids, the addition agent being a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

4. An electrolytic tin plating bath consisting essentially of an aqueous solution of 10 to 80 grams per liter of tin initially in the form of stannous sulfate, 35 to 220 grams per liter of phenol sulfonic acid, and 0.2 to 7.0 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

5. An electrolytic tin plating bath consisting essentially of an aqueous solution of 10 to 80 grams per liter of tin initially in the form of stannous sulfate, 35 to 220 grams per liter of phenol sulfonic acid, a phenol in an amount up to 10 grams per liter, and 0.2 to 7 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

6. An electrolytic tin plating bath consisting essentially of an aqueous solution of 10 to 80 grams per liter of tin initially in the form of stannous sulfate, 35 to 220 grams per liter of phenol sulfonic acid, and 0.2 to 4 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 tri-

methyl-1,2 dihydroquinoline; 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

7. An electrolytic tin plating bath consisting essentially of an aqueous solution of 10 to 80 grams per liter of tin initially in the form of stannous sulfate, 6 to 40 grams per liter of sulfuric acid, and 0.2 to 7 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

8. An electrolytic tin plating bath consisting essentially of an aqueous solution of 10 to 80 grams per liter of tin initially in the form of stannous fluoborate, 5 to 30 grams per liter of hydrofluoboric acid, and 0.2 to 7 grams per liter of an addition agent which is a polymer of a monomer of the group consisting of: 2,2,4 trimethyl-1,2 dihydroquinoline, 2,2,4,8 tetramethyl-1,2 dihydroquinoline, 2,2,4,7 tetramethyl-1,2 dihydroquinoline, 2,2,4,6 tetramethyl-1,2 dihydroquinoline, 2 methyl 2,4 diethyl-1,2 dihydroquinoline, 2,8 dimethyl 2,4 diethyl-1,2 dihydroquinoline, 2,7 dimethyl 2,4 diethyl-1,2 dihydroquinoline, and 2,6 dimethyl 2,4 diethyl-1,2 dihydroquinoline.

WILLIAM S. ALLEN.

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