United States Patent Office 3,314,868 Patented Apr. 18, 1967

3,314,868

ACID NICKEL ELECTROPLATING BATHS AND PROCESSES

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No Drawing. Filed Jan. 28, 1964, Ser. No. 340,787
Claims priority, application Germany, May 15, 1963, D 41,559
20 Claims. (Cl. 204—49)

This invention relates to a process for nickel electroplating and to a nickel electroplating bath containing additive compounds. It more specifically relates to the use of aromatic nitrogen compounds as leveling additives for nickel electroplating baths.

It is already known to use reaction products of heterocyclic nitrogen bases of the aromatic type with sultones as leveling agents in nickel electroplating baths. According to their chemical structure, these products are inner salts of amino-alkane-sulfonic acids, so-called sulfobetaines. The leveling effect of these products is entirely satisfactory. However, under certain conditions they are subject to decomposition by virtue of which the leveling effect may be adversely affected.

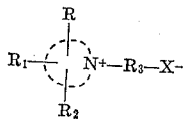
It is, therefore, an object of this invention to provide a process and bath for obtaining level nickel electrodeposits.

Another object of this invention is to provide a leveling additive for nickel electroplating which is not decomposed during operation of the electroplating process.

Another object is to provide a leveling additive for nickel electroplating which produces an improved leveling effect and leveling depth distribution.

These and other objects of our invention will become apparent as the description thereof proceeds.

It has now been found that the objects of the invention may be attained and the disadvantages of the prior art overcome by use of organic betaine additives of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom.

R, R_1 and R_2 represent the substituents CH_3, C_2H_5 or another alkyl substituent, which may also be omitted.

R_3 is an alkylene radical with 1 to 12 carbon atoms which may be interrupted by oxygen and/or substituted.

X is a sulfuric acid or phosphoric acid ester radical wherein at least one $—R_3—X^-$ radical is present in the molecule attached to a nitrogen atom.

The betaine compounds according to the present invention may be derived from heterocyclic nitrogen bases which comprise a single nitrogen atom such as pyridine, picoline, lutidine, kollidine, ethylpyridine, quinoline, isoquinoline, quinaldine, lepidine, acridine, phenanthridine, and the like.

The betaine compounds may also be derived from heterocyclic nitrogen bases which comprise two or more nitrogen atoms in the ring system, which may be, for example, pyridazine, pyrimidine, pyrazine, phthalazine, quinazoline, quinoxaline, phenazine, and the like, where

the acid alkanic acid ester radical ($—R_3—X^-$) may also be present on several ring nitrogen atoms.

The additives may be used in nickel electroplating baths, for example, a Watts type nickel plating bath. The baths modified with the products according to the present invention may be subjected to extremely high bath loads without the occurrence of interfering decomposition products. Moreover, the agents according to the present invention are clearly superior to previously known products with respect to the leveling effect and leveling depth distribution.

Products of the above indicated general formula which are characterized by very good stability and leveling action in acid nickel electroplating baths, include for example pyridinium-(methylsulfate) betaine, pyridinium-(ethylsulfate-2) betaine, pyridinium(hexylsulfate-6) betaine, pyridinium-(decylsulfate-10) betaine, pyridinium-(dodecylsulfate-12) betaine, pyridinium-(3,6-dioxaoctylsulfate-8) betaine, pyridinium-(2-hydroxypropylsulfate-3) betaine, pyridinium-(3-hydroxypropylsulfate-2) betaine, γ-picolinium-(ethylsulfate-2) betaine and quinolinium-(ethylsulfate-2) betaine. The phosphoric acid ester betaines corresponding to the above-mentioned sulfate betaines have a similar effect in the acid nickel electroplating bath.

The concentrations for the leveling agents according to the present invention lie between 0.05 to 3 gm./l., preferably between 0.1 to 0.5 gm./l. of bath fluid. The operative current densities lie within the range of 0.1 to 9 amp/dm.^{2} at a bath operating temperature of about 50 to 60° C.

In addition to the leveling agents according to the present invention, the nickel electroplating baths may be modified with customary brightening agents well known in the art, such as benzene-m-disulfonic acid, diaryldisulfimides, sulfonamides and the like, and also with other known agents, such as wetting agents.

The following specific examples are presented to illustrate the invention and to enable persons skilled in the art to better understand and practice the invention and are not intended to be limitative.

Example I

The leveling agent according to the present invention may be prepared by the following method. 85.7 gm. of pyridine were added dropwise at 75 to 80° C. over the course of 20 minutes to 268 gm. of ethylenechlorohydrin. Thereafter the mixture was refluxed, whereby the temperature rose in the course of 20 additional minutes to a maximum of 150° C. At this temperature the reaction mixture was stirred for 30 minutes; thereafter cooled to 40° C., and the excess ethylenechlorohydrin was distilled off in vacuo. The solid brownish residue was suspended in 150 ml. of acetone and was then separated by vacuum filtration, whereby 159.5 gm. of hydroxyethylpyridinium-chloride were obtained. This compound was suspended in 600 ml. of chloroform, and while vigorously stirring 128 gm. of chlorosulfonic acid dissolved in 100 ml. of chloroform were added dropwise at 0 to 5° C. to the suspension over the course of 75 minutes. Subsequently, the mixture was heated to 40° C. in the course of 60 minutes, then stirred for one hour. Nitrogen was then passed therethrough for two hours to drive off the hydrogen chloride formed by heating, and then the mixture was stirred for two additional hours at 35 to 40° C. The solid substance obtained from the suspension was first washed with chloroform and then with methanol and finally with acetone, and after drying yielded 193 gm. (95% of theory) of pyridinium-(ethylsulfate-2) betaine.

Example II

A nickel bath of the Watts-type was modified with 2 gm./l. of o-toluene-disulfonimide as a brightening agent,

0.5 gm./l. of sodium dodecylsulfate as a wetting agent and 0.25 gm./l. of pyridinium-(ethylsulfate-2) betaine as a leveling agent. Full bright and high-leveled nickel deposits of good ductility were obtained at a bath temperature of 50 to 60° C. in a current density range of 0.5 to 9 amp/dm.^{2}. After a bath load of up to 1000 amp.-hour/l., no interfering decomposition products were determinable in the baths.

Example III

In the nickel bath described in Example I the leveling agent was replaced by an equal amount of pyridinium-(decylsulfate-10) betaine. An equally good leveling effect of the nickel electrodeposits was achieved even down to a current density range of 0.1 amp/dm.^{2}.

Example IV

In a nickel bath of the Watts-type, 3 gm./l. of N-(benzene-sulfonyl)-benzoylamide were dissolved as a brightening agent, 0.5 gm./l. of sodium dodecylsulfate as a wetting agent and 0.2 gm./l. of pyridinium-(ethylphosphate-2) betaine as a leveling agent. This bath furnished full bright, ductile and well-leveled nickel electrodeposits at an operating temperature of 50 to 60° C. in a current density range of 0.25 to 7 amp/dm.^{2}.

Example V

In the nickel bath of Example IV the pyridinium-(ethylphosphate-2) betaine was replaced by the same amount of γ-picolinium-ethylsulfate-2) betaine as a leveling agent. Nickel electrodeposits of equally good quality were obtained.

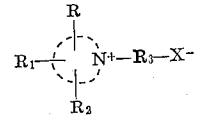
Example VI

A nickel bath of the Watts-type was modified with 1.5 gm./l. of N-(benzene-sulfonyl)-acetamide as a brightening agent, 0.5 gm./l. of sodium dodecylsulfate as a wetting agent and 0.3 gm./l. of pyridinium-(3,6-dioxaoctylsulfate-8) betaine as a leveling agent. Full bright, ductile and high-level nickel electrodeposits were obtained at a bath temperature of 50 to 60° C. in a current density range of 0.5 to 8 amp/dm.^{2}.

While certain specific examples and preferred modes of practice of the invention has been set forth it will be understood that this is solely for the purpose of illustration and that various changes and modifications may be made without departing from the spirit of the disclosure and the scope of the appended claims.

We claim:

1. An aqueous acid nickel electroplating bath for obtaining level nickel electrodeposits, which comprises an organic betaine additive compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom,

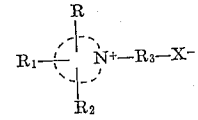
R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said additive being added in sufficient amount to obtain said level nickel deposits.

2. An aqueous acid nickel electroplating bath, which comprises an organic betaine additive compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom,

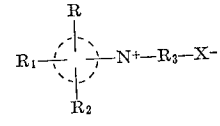
R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said additive being added in an amount from about 0.05 to 3 gm./l.

3. An aqueous acid nickel electroplating bath, which comprises an organic betaine additive compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom,

R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said additive being added in an amount from about 0.01 to 0.05 gm./l.

4. The bath of claim **1** wherein said additive is a pyridiniumalkane sulfate betaine.

5. The bath of claim **1** wherein said additive is a pyridiniumalkane phosphate betaine.

6. An aqueous acid nickel electroplating bath comprising as an additive compound from about 0.05 to 3 gm./l. of pyridinium-(ethylsulfate-2) betaine.

7. An aqueous acid nickel electroplating bath comprising as an additive compound from about 0.05 to 3 gm./l. of pyridinium-(decylsulfate-10) betaine.

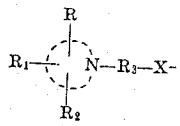
8. An aqueous acid nickel electroplating bath comprises as an additive compound from about 0.05 to 3 gm./l. of pyridinium-(ethylphosphate-2) betaine.

9. An aqueous acid nickel electroplating bath comprising as an additive compound from about 0.05 to 3 gm./l. of pyridinium-(ethylphosphate-2) betaine.

10. An aqueous acid nickel electroplating bath comprising as an additive compound from about 0.05 to 3 gm./l. of pyridinium-(3,6-dioxaoctylsulfate-8) betaine.

11. A method for producing level nickel electrodeposits

which comprises forming said electrodeposits in an aqueous acid nickel electroplating bath to which has been added a betaine compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom,

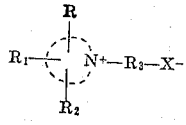
R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said compound being added in sufficient amount to obtain said level nickel electrodeposits.

12. A method for producing level nickel electrodeposits which comprises forming said electrodeposits in an aqueous acid nickel electroplating bath to which has been added a betaine compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear heterocyclic nitrogen base groups having at least one nitrogen atom,

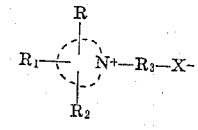
R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said additive being added in an amount from 0.05 to 3 gm./l.

13. A method for producing level nickel electrodeposits which comprises forming said electrodeposits in an aqueous acid nickel electroplating bath to which has been added a betaine compound of the general formula



wherein



represents a member selected from the group consisting of mono- and polynuclear aromatic heterocyclic nitrogen base groups having at least one nitrogen atom,

R, R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups,

R_3 is an aliphatic radical with 1 to 12 carbon atoms, and

X is selected from the group consisting of an acid sulfuric acid ester radical and an acid phosphoric acid ester radical,

wherein a radical $—R_3—X^-$ is attached to at least one nitrogen atom of said aromatic heterocyclic base group, said additive being added in an amount from about 0.01 to 0.05 gm./l.

14. The process of claim **11** wherein said additive is a pyridinium-alkane sulfate betaine.

15. The process of claim **11** wherein said additive is a pyridinium-alkane phosphate betaine.

16. The process of claim **11** comprising as said additive compound from about 0.05 to 3 gm./l. of pyridinium-(ethylsulfate-2) betaine.

17. The process of claim **11** comprising as said additive compound from about 0.05 to 3 gm./l. of pyridinium-(decylsulfate-10) betaine.

18. The process of claim **11** comprising as said additive compound from about 0.05 to 3 gm./l. of pyridnium-(ethylphosphate-2) betaine.

19. The process of claim **11** comprising as said additive compound from about 0.05 to 3 gm./l. of γ-picolinium-(ethylsulfate-2) betaine.

20. The process of claim **11** comprising as said additive compound from about 0.05 to 3 gm./l. of pyridinium-(3,6-dioxaoctylsulfate-8) betaine.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,314,868 April 18, 1967

Wolf-Dieter Willmund et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 67, for "compris-" read -- comprising --; line 71, for "pyridinium" read -- γ picolinium --.

Signed and sealed this 14th day of November 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents