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2,876,177

ADDITIVES FOR NICKEL ELECTROPLATING BATHS

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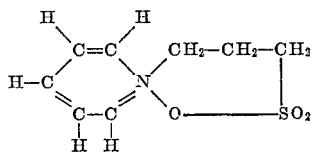
10 Claims. (Cl. 204-49)

This invention relates to additives for electroplating baths, and more particularly to nickel electroplating baths modified with internal salts of quaternary ammonium-N-alkyl-sulfonic acids.

We have found that high-grade nickel electrodeposits are produced if the customary nickel electroplating bath is modified with internal salts of quaternary ammonium-N-alkyl-sulfonic acids either before or during the electroplating procedure.

The internal salts used as additives for nickel electroplating baths in accordance with the present invention are formed by a reaction of tertiary monocyclic or bicyclic heterocyclic nitrogen compounds of the aromatic type, especially pyridine and its homologues, with lower 1,3- or 1,4-alkylsultones, especially propanesultone and 1,3- or 1,4-butanedisultone. The reaction products formed thereby are internal salts of quaternary ammonium-N-propane- ω -sulfonic acids or the corresponding butane- ω -sulfonic acids, depending upon the alkylsultone used, wherein the nitrogen atoms are members of an aromatic ring system. Such compounds may be produced in a very simple manner in accordance with the method described by Helberger in Liebigs Annalen, vol. 565, page 24, by reacting equimolar amounts of the above reactants in the presence of organic solvents or even in an aqueous medium. As a rule, this method produces excellent yields of the reaction product. The internal heterocyclic sulfonates can be readily isolated from the reaction mixture; they crystallize very readily and are very stable under virtually all conditions. When added to nickel electroplating baths, these internal salts effect marked improvement in the brightness and, above all, in the smoothness of the nickel electrodeposits produced from such modified baths.

The simplest and most readily accessible of these compounds is the internal salt of pyridinium-N-propane- ω -sulfonic acid having the following structural formula:



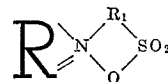
which may be obtained, for example, by a reaction of pyridine with 1,3-propanedisultone under the conditions set forth by Helberger, supra. However, other analogous internal sulfonic acid salts may also be used in place of the above pyridinium salt, for example those in which the heterocyclic ring system is a C-substituted pyridine radical, such as a picoline, lutidine, ethylpyridine radical, and the like. Similarly, those analogous compounds which contain a polycyclic heterocyclic radical in place of the pyridine or substituted pyridine radical, such as a quinoline, isoquinoline, quinaldine, lepidine, acridine, phenanthridine radical, and the like, may also be used

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as modifiers of nickel electroplating baths in accordance with the present invention. Finally, also those internal sulfonic acid salts of the above general class, wherein the pyridine ring is replaced by a heterocyclic radical comprising more than one nitrogen atom in the ring, have been found to be effective additives for nickel electroplating baths, such as the internal sulfonic acid salts of pyridazine, pyrimidine, pyrazine, phthalazine, quinoxaline, phenazine, and the like. In this last group of compounds the other nitrogen atoms in the heterocyclic ring system may also be linked to additional internal alkylsulfonic acid radicals of the type shown in the structural formula above. Moreover, any of the heterocyclic radicals recited herein may carry substituent such as halogen, nitro-groups, and the like.

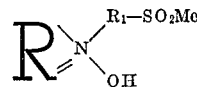
In addition to 1,3-propanedisultone or 1,3- and 1,4-butanedisultone, other sultones may be used to produce the above-described class of additives for nickel electroplating baths. For example, substituted sultones such as 1,1-dimethyl-1,3-propanedisultone (isopentanesultone) may be reacted with the various types of heterocyclic compounds above described to produce internal salts of quaternary ammonium-N-dimethyl-propane- ω -sulfonic acid. Such compounds are also effective additives for nickel electroplating baths and produce the above-mentioned advantageous effects upon nickel electrodeposits. Finally, internal sulfonic acid salts of heterocyclic compounds which have been analogously formed from cycloaliphatic sultones such as tolylsultone, 1,8-naphthalenedisultone, and the like, may also be used for the purpose herein set forth.

In other words, we have broadly discovered that compounds having the general structural formula



wherein R is a cyclic radical which includes the nitrogen atom and has carbon atoms or carbon and additional nitrogen atoms in the ring, and R₁ is a lower aliphatic cycloaliphatic or aromatic radical, are effective additive for nickel electroplating baths which will produce a marked improvement in the brightness and smoothness of the nickel electrodeposits.

In practice, the compounds herein described are added to the nickel electroplating bath either as such, that is in the form of the internal salt, or also in the form of the corresponding metal sulfonates produced by reacting the internal salt with a suitable inorganic metal base, where by the cyclic sulfonic radical is cleaved to produce the compound



where Me represents the metal atom. The quantity of these compounds which is added to the nickel electroplating bath to achieve the desired results may range between 0.1 and 10 gm. per liter of bath, but amounts between 0.4 and 1 gm. per liter of bath are preferred. In general, the best results are obtained if the nickel is electrodeposited from baths modified in accordance with the present invention at a temperature of about 60° C. and at current densities up to about 8 amp./dm.².

While nickel electroplating baths modified solely with the above compounds will produce the desired improvement in the nickel electrodeposits, such baths may additionally comprise known brighteners, porosity-preventing agents, wetting agents and/or salts which increase the conductivity of the bath.

The nickel electroplating baths modified in accordance with our invention may be employed to deposit nickel or

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11 types of metals and alloys, for example on iron, aluminum, copper, brass and many more; moreover, the compounds may be added to nickel-plating baths employed in 11 types of industrial nickel-plating processes, including the drum-plating method.

We have found it particularly advantageous to employ the internal salts described herein in combination with known brighteners, especially with diarylsulfimides or their salts, such as ditolylsulfimide; when used in this manner, the smoothness of the nickel electrodeposits is improved to a remarkable degree, while their ductility remains unimpaired.

The following examples will further illustrate the present invention and enable others skilled in the art to understand the invention more completely. It must be emphasized, however, that our invention is not limited to the particular compounds mentioned in the examples.

Example I

0.8 gm. of the inner salt of pyridinium-N-propane- ω -sulfonic acid and from 4 to 8 gm. of the sodium salt of ditolyl-disulfimide were added to each liter of a Watts-type nickel electroplating bath and dissolved therein. Iron and copper sheet metal were electroplated in this modified bath at a temperature of about 60° C. and an average current density of 6 amp./dm.². The sheet metal was provided with full-bright, ductile nickel deposits, marked by a high degree of smoothness.

Example II

0.2 gm./l. of the inner salt of the isoquinolinium-N-propane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example III

0.2 gm./l. of the inner salt of the quinolinium-N-propane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example IV

0.5 gm./l. of the inner salt of the 2-methyl-pyridinium-1-butane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example V

0.4 gm./l. of the inner salt of the 2,4-dimethyl-pyridinium-N-propane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example VI

0.1 gm./l. of the inner salt of the 3-bromo-pyridinium-1-butane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example VII

0.05 gm./l. of the inner salt of the acridinium-N-propane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example VIII

0.15 gm./l. of the inner salt of the pyrazinium-N-butane- ω -sulfonic acid were used instead of the inner salt of pyridinium-N-propane- ω -sulfonic acid of Example I. A full-bright nickel deposit was obtained.

Example IX

6 gm./l. of the sodium salt of di-p-tolyl di-sulfimide were substituted for the sodium salt of ditolyl disulfimide. A full-bright nickel deposit was obtained.

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Example X

8 gm./l. of the sodium salt of di-o-tolyl disulfimide were substituted for the sodium salt of ditolyl disulfimide. A full-bright nickel deposit was obtained.

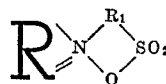
Example XI

6 gm./l. of the sodium salt of dibenzene disulfimide were substituted for the sodium salt of ditolyl disulfimide. A full-bright nickel deposit was obtained.

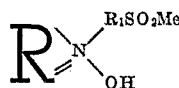
While we have illustrated the general principle of our invention by a specific embodiment, it will be apparent to persons skilled in the art that the invention is not limited thereto, and that various changes and modifications may be made without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An acid Watts-type nickel electroplating bath having dissolved therein a heterocyclic compound having the general structural formula selected from the group consisting of



and

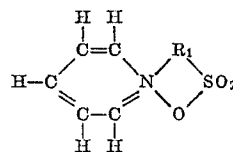


wherein



is a heterocyclic radical, R being a cyclic radical with 0 to 1 ring nitrogen atoms, the remainder being carbon atoms, and R₁ is selected from the group consisting of lower aliphatic, cycloaliphatic and aromatic radicals, and Me is an alkali metal atom, said compound being present in an amount sufficient to produce smooth and ductile nickel electrodeposits.

2. An acid Watts-type nickel electroplating bath having dissolved therein about 0.1–10 grams per liter of an internal salt of pyridinium-N-alkylsulfonic acid having the structural formula



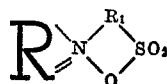
wherein R₁ is a lower alkyl radical having from 3 to 4 carbon atoms.

3. An acid Watts-type nickel electroplating bath having dissolved therein about 0.1–10 grams per liter of the internal salt of pyridinium-N-propane- ω -sulfonic acid.

4. An acid Watts-type nickel electroplating bath as in claim 3, comprising in addition from about 4 to 8 grams per liter of a compound selected from the group consisting of diarylsulfimides and their water-soluble salts.

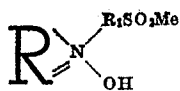
5. An acid Watts-type nickel electroplating bath as in claim 3, comprising in addition from about 4 to 8 grams per liter of the sodium salt of ditolyl-disulfimide.

6. The method of producing bright and smooth nickel electrodeposits on metal objects, which comprises electroplating said objects in an acid Watts-type nickel bath having dissolved therein a heterocyclic compound having the general structural formula selected from the group consisting of



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and

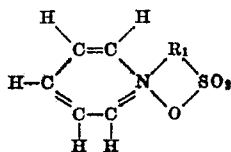


wherein



is a heterocyclic radical, R being a cyclic radical with 0 to 1 ring nitrogen atoms, the remainder being carbon atoms, and R₁ is selected from the group consisting of lower aliphatic, cycloaliphatic and aromatic radicals, and Me is an alkali metal atom, said compound being present in an amount sufficient to produce smooth and ductile nickel electrodeposits.

7. The method of producing bright and smooth nickel electrodeposits on metal objects, which comprises electroplating said objects in an acid Watts-type nickel bath having dissolved therein about 0.1–10 grams per liter of an internal salt of pyridinium-N-alkylsulfonic acid having the structural formula



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wherein R₁ is a lower alkyl radical having from 3 to 4 carbon atoms.

8. The method of producing bright and smooth nickel electrodeposits on metal objects, which comprises electroplating said objects in an acid Watts-type nickel bath having dissolved therein about 0.1–10 grams per liter of the internal salt of pyridinium-N-propane- ω -sulfonic acid.

9. The method of producing bright and smooth nickel electrodeposits on metal objects, which comprises electroplating said objects in an acid Watts-type nickel bath having dissolved therein about 0.1–10 grams per liter of the internal salt of pyridinium-N-propane- ω -sulfonic acid and from about 4 to 8 grams per liter of a compound selected from the group consisting of diarylsulfimides and their water-soluble salts.

10. The method of producing bright and smooth nickel electrodeposits on metal objects, which comprises electroplating said objects in an acid Watts-type nickel bath having dissolved therein about 0.1–10 grams per liter of the internal salt of pyridinium-N-propane- ω -sulfonic acid and from about 4 to 8 grams per liter of the sodium salt of ditolyl-sulfimide.

References Cited in the file of this patent

UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,876,177

March 3, 1959

Wolfgang Gundel et al.

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

Column 2, line 52, for " R_1-SO_2Me " read -- R_1-SO_3Me --; column 4, line 27, for " R_1SO_2Me " read -- R_1-SO_3Me --; column 5, line 2, for " R_1SO_2Me " read -- R_1SO_3Me --.

Signed and sealed this 13th day of October 1959.

(SEAL)

Attest:

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Attesting Officer

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