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COMPOSITION FOR THE ELECTROLYTIC DEPOSITION OF WELL LEVELLED AND DUCTILE NICKEL COATINGS OF MIRROR-LIKE LUSTER

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The present invention relates to a composition and more particularly to an electrolyte composition suitable for the electrolytic deposition of well levelled and ductile nickel coatings of mirror-like luster.

It is known that electrolyte baths containing certain organic sulfoxy compounds in combination with certain heterocyclic compounds substituted at their heterocyclic nitrogen atom by an allyl halogenide group or, respectively, by a vinyl halogenide group, such as, for instance, N-allyl quinolinium bromide produce a well levelled nickel deposit of high luster. Although such deposits meet the ordinary requirements for nickel coatings, their levelling effect as well as their ductility are rather unsatisfactory.

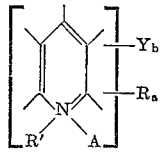
It is one object of the present invention to provide an electrolyte composition useful in nickel plating which composition has an excellent levelling effect in relation to the thickness of the deposited nickel coating, the luster and brilliancy of the nickel coating produced therein being far superior to the luster and brilliancy of heretofore produced coatings, the speed with which such luster and brilliancy is produced therein being much greater than the speed with heretofore used electrolyte baths, and the ductility of the nickel coating obtained therein being considerably increased.

Another object of the present invention is to provide a simple and effective electroplating process which permits the production of well levelled and ductile nickel coatings of mirror-like luster.

Other objects of the present invention and advantageous features thereof will become apparent as the description proceeds.

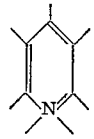
In principle, the electrolyte composition according to the present invention is characterized by the simultaneous presence, in acid aqueous nickel electrolyte baths, of brightening agents of the type of organic sulfoxy compounds and of quaternary heterocyclic compounds containing a heterocyclic nitrogen atom in their heterocyclic nucleus which is free of sulfonic acid substituents. The quaternary compounds are substituted in their heterocyclic ring by halogen and/or hydrocarbon radicals and at their quaternary nitrogen atom by an anion and a triple bond unsaturated hydrocarbon radical and preferably by an alkynyl radical having 2 to 6 carbon atoms.

Such electrolyte additives of derivatives of the acetylene series correspond to the following Formula I:



(I)

Such heterocyclic compounds contain a pyridinium ring of Formula II:



(II)

Characteristic representatives of such compounds are,

for instance, pyridinium, quinolinium, isoquinolinium, acridinium compounds and their lower alkyl homologues, and especially their methyl and ethyl homologues, in which the lower alkyl radicals are attached to carbon atoms of the heterocyclic ring system.

A in said Formula I represents the anion of a water soluble acid, and especially the anion of hydrochloric, hydrobromic, hydroiodic acid or the sulfonic acid group $—SO_3H$.

R' indicates a triple bond unsaturated radical having 2 to 6 carbon atoms, and especially an alkynyl radical such as the ethynyl, propynyl, butynyl, pentynyl, or hexynyl radicals.

R indicates a lower alkyl radical attached to a carbon atom of the heterocyclic ring system;

Y indicates a halogen atom, such as chlorine or bromine, attached to a carbon atom of the heterocyclic ring system;

a is a numeral between 0 and 2;

b is a numeral between 0 and 1, the sum of $a+b$ is one when the heterocyclic compound is a pyridinium compound; the sum of $a+b$ is not greater than 2 when the heterocyclic compound is a quinolinium or isoquinolinium compound; and the sum of $a+b$ is zero when the heterocyclic compound is an acridinium compound.

Such quaternary heterocyclic compounds are added to the electrolyte bath in amounts between about 0.001 g./l. and about 0.06 g./l. Especially suitable have proved amounts between about 0.004 g./l. and about 0.035 g./l. It is, of course, understood that the compounds involved must be soluble in the electrolyte bath.

The heterocyclic compounds which are added to the electrolyte bath according to the present invention are readily available by reaction of halogen derivatives of the acetylene series, for instance, a propyne-1-bromide-3, with heterocyclic compounds containing a heterocyclic nitrogen atom in their heterocyclic ring, for instance, with pyridine, quinoline, isoquinoline, acridine compounds, and especially their methyl and ethyl homologues.

A number of such quaternary heterocyclic compounds which are substituted at their quaternary heterocyclic nitrogen atom by alkynyl radicals, as they are used in electrolyte composition according to the present invention are given in the following table. It is, of course, understood that the invention is by no means limited to such compounds which are merely given as examples.

N-2-propyne quinolinium bromide,
N-2-propyne isoquinolinium bromide,
N-2-propyne acridinium bromide,
N-2-butyne quinolinium bromide,
N-2-butyne isoquinolinium bromide,
N-2-butyne acridinium bromide,
N-(2-propyne)-2-methyl pyridinium bromide,
N-(2-butyne)-2,6-dimethyl quinolinium chloride,
N-(2-propyne)-3-methyl isoquinolinium bromide,
N-(2-propyne)-3-chloro-2-methyl quinolinium chloride.

According to a preferred embodiment of the present invention electrolyte baths which yield exceedingly well levelled, ductile nickel deposits of mirror-like luster are obtained when adding to said acid aqueous nickel electrolyte baths, in addition to said N-alkynyl substituted heterocyclic compounds containing a pyridinium ring as they are illustrated by the above given Formula I, specific brightening agents which represent alkynyl sulfonic acids of the Formula III:

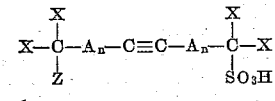
$$R_1—C\equiv C—R_2 \qquad \text{(III)}$$

In said Formula III:

R_2 indicates a saturated or double bond or triple bond

unsaturated organic radical carrying a sulfonic acid group (—SO_3H) or the sulfonic acid group directly attached to one of the acetylene carbon atoms, while R_1 is a saturated or double bond or triple bond unsaturated organic radical, hydrogen, a saturated or double bond or triple bond unsaturated organic radical carrying a sulfonic acid group, or the sulfonic acid group directly attached to the other one of the acetylene carbon atoms.

The preferred compounds of this type correspond to the following Formula IV:



(IV)

In said formula:

A indicates a saturated or double bond or triple bond unsaturated hydrocarbon chain having 0 to 6 carbon atoms, i.e., wherein *n* indicates the numerals 0 to 6,
X indicates hydrogen, an organic radical or another substituent, and
Z indicates hydrogen, an organic radical, or the sulfonic acid group.

Such a triple bond unsaturated aliphatic sulfonic acid is added to the electrolyte bath in an amount between about 0.01 g./l. and about 15 g./l. and preferably in an amount between about 0.20 g./l. and about 0.50 g./l.

As stated hereinabove, the additives according to the present invention can, of course, also be used in combination with known brightening agents of the type of organic sulfoxy compounds, for instance, with aromatic sulfonamides, sulfonimides, and sulfonic acids, or, respectively, with saturated and unsaturated aliphatic sulfonic acids, or with mixtures of such organic sulfoxy compounds with each other or with triple bond unsaturated aliphatic sulfonic acid. Organic sulfoxy compounds as they are used in electrolyte compositions according to the present invention are given in the following table. The invention is, of course, not limited to such compounds which are merely given as examples.

Naphthalene trisulfonic acid,
Naphthalene disulfonic acid,
Naphthalene sulfonic acid,
Benzaldehyde sulfonic acid,
Benzene sulfonamide,
Toluene sulfonamide,
o-Benzoyl sulfimide,
Allyl sulfonic acid,
Vinyl sulfonic acid,
m-Benzene disulfonic acid,
Propyne-1-sulfonic acid-3,
Butyne-2-disulfonic acid-1,4,
p-Toluene Sulfinic acid,
Benzene sulfinic acid,
Pyrocatechol disulfonic acid,
and others, and the alkali metal, ammonium, nickel, and magnesium salts of such sulfonic and sulfinic acids.

It is, of course, understood that the electrolyte composition according to the present invention may also contain wetting agents, brightening metal salts, conducting salts, inhibitors, and other additives as they are conventionally used in nickel plating baths.

The following example serves to illustrate the present invention without, however, limiting the same thereto:

Example 1

The composition of an excellent electrolyte bath according to the present invention is as follows:

	G./l.
Nickel sulfate ($NiSO_4.7H_2O$)	280
Nickel chloride ($NiCl_2.6H_2O$)	45
Boric acid	32
Butyne-2-disulfonic acid-1,4	13.5

	G./l.
N-2-propyne quinolinium bromide	0.015
Sodium lauryl sulfate	0.2

The pH-value of the bath is about 4.5.

Electroplating is effected at a temperature between about 40° C. and about 70°° C. whereby the goods to be electroplated are kept in constant motion in the bath.

The electrolyte bath as given in Example 1 yields excellently levelled, ductile nickel deposits of mirror-like luster when operating at a range of current density between about 0.1 amp./sq. dm. and about 12.0 amp./sq. dm.

In place of the above given acid nickel plating bath any other nickel plating bath containing, in acid aqueous solution, one or several nickel salts can be employed. Not only nickel sulfate and nickel chloride can be used as salts containing the nickel ion or radical to be deposited and/or serving as salt for increasing the conductivity of the bath, but also other nickel compounds such as nickel sulfamate, nickel fluoborate, and others may be employed for said purpose.

As additives to maintain the desired pH-value of the electrolyte bath there can be used, in place of boric acid, oxalic acid, borax, and others.

In place of sodium lauryl sulfonate, there can be employed other wetting agents such as other sodium alkyl sulfonates, sodium higher alkanol sulfates, fatty acid amides, and others.

The bath composition given in the preceding example, however, has proved to be especially suitable and to yield an especially valuable ductile, well levelled nickel coating of high luster.

I claim:

1. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of a nickel salt, between about 0.01 g./l. and about 15.0 g./l. of an organic sulfoxy compound serving as brightening agent, said organic sulfoxy compound being selected from the group consisting of an aromatic sulfonamide, an aromatic sulfonimide, an aliphatic saturated sulfonic acid, an aliphatic unsaturated sulfonic acid, and an aromatic sulfonic acid, and between about 0.001 g./l. and about 0.06 g./l. of an organic heterocyclic compound soluble in said aqueous nickel salt solution and containing a pyridinium ring free of sulfonic acid substituents, said heterocyclic compound being selected from the group consisting of pyridinium, quinolinium, isoquinolinium, and acridinium compounds, the heterocyclic nitrogen atom of said pyridinium ring being substituted by the anion of a water soluble acid and an alkynyl radical with 2 to 6 carbon atoms, said pyridinium ring containing attached to its carbon atoms substituents R_a and Y_b, wherein R is lower alkyl; Y is halogen; *a* is a numeral between 0 and 2; *b* is a numeral between 0 and 1; the sum of $a+b$ is one when said heterocyclic compound is a pyridinium compound; the sum of $a+b$ is not greater than 2 when said heterocyclic compound is a quinolinium or isoquinolinium compound; and the sum of $a+b$ is zero when said heterocyclic compound is an acridinium compound.

2. The electrolyte composition according to claim 1, wherein the heterocyclic compound containing a pyridinium ring is substituted at the heterocyclic nitrogen atom by an alkynyl radical selected from the group consisting of the ethynyl, propynyl, butynyl, pentynyl, and hexynyl radical.

3. The electrolyte composition according to claim 1, wherein the anion attached to the quaternary heterocyclic nitrogen atom of the pyridinium compound is an anion selected from the group consisting of the chlorine, bromine, iodine, and sulfate anion.

4. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of

a nickel salt, between about 0.01 g./l. and about 15 g./l. of an organic sulfoxy compound serving as brightening agent, said organic sulfoxy compound being selected from the group consisting of an aromatic sulfonamide, an aromatic sulfonimide, an aliphatic saturated sulfonic acid, an aliphatic unsaturated sulfonic acid, and an aromatic sulfonic acid, and between about 0.004 g./l. and about 0.035 g./l. of an organic heterocyclic compound soluble in said aqueous nickel salt solution and containing a pyridinium ring free of sulfonic acid substituents, said heterocyclic compound being selected from the group consisting of pyridinium, quinolinium, isoquinolinium, and acridinium compounds, the heterocyclic nitrogen atom of said pyridinium ring being substituted by the anion of a water soluble acid and an alkynyl radical with 2 to 6 carbon atoms, said pyridinium ring containing attached to its carbon atoms substituents R_a and Y_b, wherein R is lower alkyl; Y is halogen; a is a numeral between 0 and 2; b is a numeral between 0 and 1; the sum of $a+b$ is one when said heterocyclic compound is a pyridinium compound; the sum of $a+b$ is not greater than 2 when said heterocyclic compound is a quinolinium or isoquinolinium compound; and the sum of $a+b$ is zero when said heterocyclic compound is an acridinium compound.

5. The electrolyte composition according to claim 1, wherein the organic sulfoxy compound serving as brightening agent is a triple bond unsaturated aliphatic sulfonic acid of the formula

$$R_1—C\equiv C—R$$

wherein

R is a member selected from the group consisting of the sulfonic acid group, a saturated alkyl radical carrying a sulfonic acid group, and an unsaturated alkyl radical carrying a sulfonic acid group, while

R_1 is a member selected from the group consisting of hydrogen, the sulfonic acid group, a saturated alkyl radical, an unsaturated alkyl radical, a saturated alkyl radical carrying a sulfonic acid group, and an unsaturated alkyl radical carrying a sulfonic acid group.

6. The electrolyte composition according to claim 5, wherein the amount of brightening agent is between about 0.20 g./l. and about 0.50 g./l.

7. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of a nickel salt, between about 0.01 g./l. and about 15.0 g./l. of propyne-1-sulfonic acid serving as brightening agent, and between about 0.001 g./l. and about 0.06 g./l. of N-2-propyne quinolinium bromide.

8. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of a nickel salt, between about 0.01 g./l. and about 15.0 g./l. of butyne-2-disulfonic acid-1,4 serving as brightening agent, and between about 0.001 g./l. and about 0.06 g./l. of N-2-propyne quinolinium bromide.

9. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of a nickel salt, between about 0.01 g./l. and about 15.0 g./l. of propyne-1-sulfonic acid serving as brightening agent, and between about 0.001 g./l. and about 0.06 g./l. of N-2-propyne isoquinolinium bromide.

10. Electrolyte composition for electrolytic deposition of well levelled, ductile nickel coatings of mirror-like luster, said composition comprising an acid aqueous solution of a nickel salt, between about 0.01 g./l. and about 15.0 g./l. of butyne-2-disulfonic acid-1,4 serving as brightening agent, and between about 0.001 g./l. and about 0.06 g./l. of N-2-propyne isoquinolinium bromide.

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