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3,190,820

ELECTRODEPOSITION OF BRIGHT NICKEL

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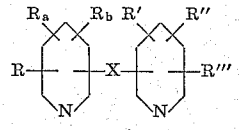
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15 Claims. (Cl. 204—49)

This invention relates to the galvanic deposition of nickel, and more particularly to the deposition of lustrous and ductile nickel deposits from electrolytes of types generally known per se, such as the so-called Watts nickel plating bath containing both nickel sulfate and nickel chloride, the nickel sulfamate, the nickel fluoroborate type electrolytes, and others.

The afore-mentioned types of nickel plating solutions normally yield dull electrodeposits, but bright deposits can be obtained by the addition of certain organic materials in small amounts. It is well established that most desirable lustrous deposits are formed from solutions which contain two addition agents, commonly referred to as primary and secondary brighteners. The secondary brighteners have little effect on the appearance of a nickel electrodeposit when employed alone, but they enhance the effect of the primary brighteners and are necessary for the fullest brightening effect of the latter. The common secondary nickel brighteners include alkyl and aryl sulfonic acids, sulfamides, and sulfimides.

The object of this invention is the provision of novel primary brighteners which permit the deposition of mirror bright deposits having good leveling characteristics, and which are effective in a broad variety of nickel plating solutions and over an unusually broad range of operating conditions.

The novel primary nickel plating brighteners of the invention have the general formula



wherein R, R_a, R_b, R', R'' and R''' are substituents attached to a carbon atom of a pyridine ring of the compound. They are selected from the group consisting of hydrogen, alkyl, lower alkylene, hydroxyalkyl, formyl, halide, alkanoyl, cyano, hydroxy, sulfo, amino, and alkylamino radicals. One substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of 2 to 5 carbon atoms. The N-addition products of the above compounds especially the lower haloalkyl N-addition compounds are also excellent primary nickel brighteners. Very good results are received with those compounds having added bromo alkyl and bromo alkylene groups to the nitrogen atom.

The brighteners of the invention thus are aliphatic hydrocarbons in which two hydrogen atoms are replaced by pyridyl, quinolyl, or isoquinolyl radicals. The heterocyclic radicals themselves carry one or more substituent groups. Substituents which do not interfere with the brightening effect include alkyl, acetyl, hydroxy, amino, cyano, sulfonate radicals, the functional formyl and carbonyl groups, and many more. The quaternary nitrogen addition compounds are as effective as the free bases. Such addition compounds include the quaternary compounds formed with alkyl and aryl halides, such as ethyl bromide, ethyl iodide, ethylene bromide ethylene iodide, allyl bromide, allyl iodide, dimethyl sulfate, choloroacetone, bromoacetophenon, benzyl chloride, a-picolyl iodide.

Representative examples of primary nickel plating brighteners of the invention are listed in Table I, but the invention is not limited to the specific examples listed since the brightening effect is characteristic of all compounds satisfying the above formulas. The brighteners of the invention are effective in very small concentrations. As little as 1 mg. per liter has the desired brightening effect. As much as 0.1 gram per liter may be employed without harmful effects. Under most practical operating conditions brightener concentrations within the range of 0.001 to 0.06 gram per liter are preferred to produce the desired mirror brightness in a nickel electrodeposit.

In this concentration range, the brighteners of the invention have a particularly favorable leveling effect. Deposits produced from electrolytes containing the brighteners of the invention tend to preferentially fill polishing scratches and other minor suface imperfections. A nickel deposit of an average thickness of 10 microns is usually sufficient to obliterate normal polishing marks. Another unusual characteristic property of bright nickel plating solutions containing the primary brighteners of the invention is the broad range of cathode current densities over which mirror bright nickel deposits are produced. Because of the lack of criticality of the current density, uniformly bright nickel deposits can be formed on objects of complex shape on the surface of which the cathode current density necessarily varies widely. Yet another distinguishing mark of nickel coatings deposited from electrolytes containing the primary brighteners of the invention in the preferred concentration range is the ductility of the deposits which usually permit the nickel plated objects to be deformed after plating without the formation of cracks.

It is preferred to provide relative movement between the electrolyte and the object being nickel plated in an electrolyte of the invention, and any conventional means for agitating the electrolyte or for moving the article being plated in the electrolyte, or both, may be employed in the usual manner. Such means include mechanical stirring of the electrolyte or passage of compressed air therethrough, cathode rod agitation, and the like. Fully bright deposits, however, are also formed from the electrolytes of the invention without any relative movement of electrolyte and article. A relatively low current density is advisable in still plating solutions as is well understood and usual in nickel plating. Nickel plating solutions useful for barrel plating produce lustrous nickel deposits on small objects plated in bulk when the brighteners of the invention are added thereto.

The temperature of the electrolyte is immaterial to the brightening effect of the brighteners of this invention, and the temperatures commonly preferred with specific types of nickel plating solutions may be employed when these solutions contain the brighteners of the invention. The brighteners are fully effective even at room temperature, and are stable at the highest temperatures that are in commercial use for nickel plating at this time. Bright deposits are obtained without difficulty from electrolytes operated at temperatures as high as 70° C.

The pH value of the electrolytes of the invention is not

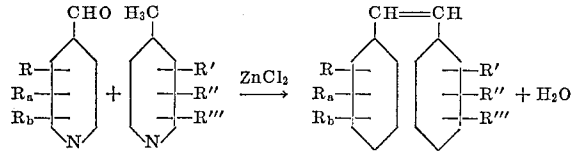
critical. The primary brighteners of the invention ensure fully bright nickel deposits over the entire range of hydrogen ion concentrations currently used in decorative nickel plating. More specifically, the brighteners are equally effective at the relatively extreme pH values of 2.0 and 5.8 and at the more usual pH values of 3.5 to 5.5.

When free of highly reactive substituent radicals, the nickel brighteners of the invention are stable in conventional nickel plating electrolytes, and do not form decomposition products which would interfere with bright plating. Nickel plating baths containing the brighteners of the invention can be operated over extended periods without requiring the usual reconditioning treatments.

As is usual with nickel plating brighteners, the brightening agents of the invention are preferably employed jointly with secondary brighteners. Representative examples of secondary brighteners useful in developing optimum deposit properties from the electrolytes of the invention are listed in Table II. These secondary brighteners include sulfonic acids derived from aliphatic and aromatic compounds, and the amides and imides of such sulfonic acids. The organic addition agents in the bright nickel plating electrolytes of the invention may further include surface active agents to prevent porosity due to hydrogen bubbles. All secondary brighteners of Table II may be combined with all primary brighteners of Table I.

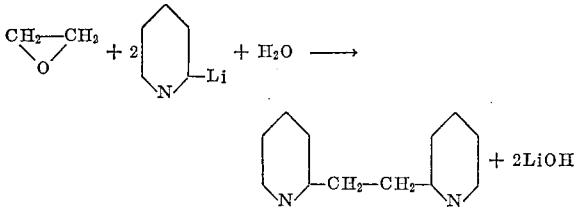
The brightening agents of the invention may be prepared by reacting the corresponding pyridyl or quinolyl aldehydes with alkyl pyridines or alkyl quinolines at elevated temperatures in the presence of a zinc chloride catalyst. The pyridyl and quinolyl alkylenes so prepared may be hydrogenated and then reacted with alkyl or aryl halides to form the nitrogen addition compounds by methods well known in themselves. In an analogous manner the substituted compounds may be prepared.

The reaction is represented by the following equation:

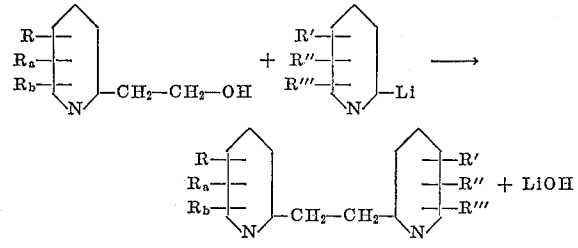


Those compounds of this invention containing a saturated hydrocarbon bridge between the two nucleus may be prepared by one of the three following methods

(1) Reaction of ethylene oxide with a lithium substituted pyridyl, quinolyl or isoquinolyl compound in the presence of water. For instance

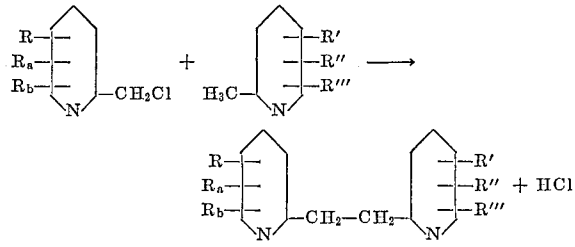


(2) Reaction of alkoxy pyridyl, alkoxy quinolyl or alkoxy isoquinolyl compounds with the respective lithium compounds:



(3) Reaction of chloro methylpyridyl, chloro methylquinolyl or chloromethyl isoquinolin compounds with the

respective chlorine free compounds, according to the following equation



Those compounds of this invention containing a hydrocarbon bridge of more than two carbon atoms between the two nucleus may be prepared by the following reaction:

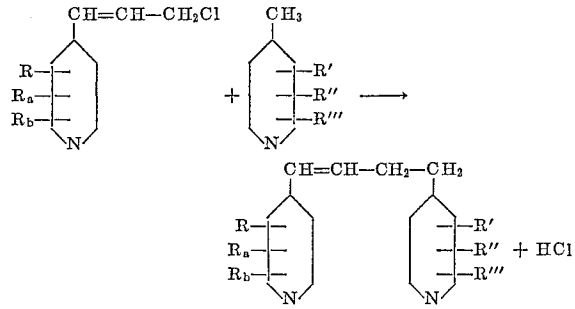


TABLE I

1,2-di-[2-pyridyl] ethylene
1,2-di-[4-pyridyl] ethylene
1-[2-pyridyl]-2-[4-pyridyl] ethylene
1,3-di-[2-pyridyl] propylene
1,5-di-[3-pyridyl]-pentadiene [1,3]
1,3-di-[4-pyridyl]-a-butylene
1,3-di-[4-pyridyl]-b-butylene
1,4-di-[4-pyridyl]-butylene
Bis-[4-chloropyridyl-[2]] ethylene
Bis-[4,6-dichloropyridyl-[2]] ethylene
Bis-[4-formylpyridyl-[2]] ethylene
Bis-[3-hydroxyethylpyridyl-[2]] ethylene
Bis-[4-chloromethylpyridyl-[2]] ethylene
Bis-[4-acetylpyridyl-[2]] ethylene
Bis-[2-ethylpyridyl-4] ethylene
Bis-[4-n-pentylpyridyl-2] ethylene
Bis-[3-cyanopyridyl-[2]] ethylene
Bis-[3-hydroxypyridyl-[4]] ethylene
Bis-[pyridyl-3-sulfonic acid-[2]] ethylene
Bis-[4-aminopyridyl-[2]] ethylene
Bis-[4-methylaminopyridyl-[2]] ethylene
1,3-di-[2,6-dimethylpyridyl-(4)] propylene
1,2-di-[2-quinolyl] ethylene
1,2-di-[3-quinolyl] ethylene
1-[3-quinolyl]-2-[4-quinolyl] ethylene
1,2-di-[4-isoquinolyl] ethylene
Bis-[4-formylquinolyl-[2]] ethylene
Bis-[4-hydroxymethylquinolyl-[2]] ethylene
Bis-[N-allyl-N-bromo-pyridine-[2]] ethylene
Bis[-N-acetonyl-N-chloro-pyridine-[2]] ethane
Bis-[N-allyl-N-bromo-4-formylpyridine-[2]] ethylene
Bis-[N-phenacyl-N-iodo-pyridine-[4]] ethylene
Bis-[N-benzothiazolyl-(2)-methyl-N-iodo-pyridine-(2)] ethylene
Bis-[N-pyridyl-(2)-methyl-N-chloro-pyridine-(2)] ethylene
Bis-[N-methyl-N-iodo-4-formylquinolyl-[2]] ethylene
1,3-di-[N-hydroxyethyl-N-bromo-pyridyl-(4)] propylene

TABLE II

Vinylsulfonic acid
Allylsulfonic acid
Benzene monosulfonic acid

Ortho-, meta-, and para-benzene disulfonic acids
Ortho-, meta-, and para-formylbenzene sulfonic acids
2,4-, 2,5-, and 2,6-formylbenzene disulfonic acids
Naphthalene mono-, di-, and trisulphonic acids
Benzene sulfonamide
Ortho- and paratoluene sulfonamides
Ortho-, meta-, and parachlorobenzene sulfonamides
Ortho-sulfimidobenzoic acid

$$HOOC—C_6H_5—SO_2—NH—SO_2—C_6H_5—COOH$$

Dibenzene sulfimide $C_6H_5—SO_2—NH—SO_2—C_6H_5$
Bis-[o-chlorobenzene] sulfimide

$$Cl—C_6H_5—SO_2—NH—SO_2—C_6H_5—Cl$$

m-Di-sulfonylbenzene-bis-N-benzene sulfimide

The soluble salts of the acids listed as secondary brighteners in Table II may equally be employed, the alkali metal salts, ammonium salts, and nickel salts being preferred for reasons which will be obvious to those skilled in this art.

The concentration of the secondary brighteners is not critical. They are effective in concentration ranging from approximately 0.2 gram per liter to the solubility limit. Concentrations between 0.5 and 5.0 grams per liter are generally preferred.

The following examples are representative of electrolytes and operating conditions employed for producing bright nickel electrodeposits in the presence of the primary brighteners of the invention, but it is to be understood that the use of the brighteners is not limited to the electrolyte compositions of the examples, nor to the specific general types of nickel plating solutions described for the purpose of the disclosure.

Example I

Nickel sulfate	grams per liter	260
Nickel chloride	do	50
Boric acid	do	40
Sodium o-formylbenzene sulfonate	do	1.0
Dibenzene sulfimide	do	1.0
Bis-[N-allyl-N-bromo-pyridyl-[2]] ethylene	grams per liter	0.007
Temperature	° C	50
pH		4.0
Cathode current density, average	amps./dm.^{2}	4.0
Cathode current density, actual	do	0.5–6.0

Example II

Nickel sulfate	grams per liter	240
Nickel chloride	do	80
Boric acid	do	40
Sodium vinyl sulfonate	do	2.0
Sodium o-sulfimidobenzoate	do	5.0
1-[3-pyridyl]-2-[4-pyridyl]-ethylene	do	0.006
Temperature	° C	60
pH		4.2
Cathode current density, average	amps./dm.^{2}	6.0
Cathode current density, actual	amps./dm.^{2}	0.5 to 8.0

Example III

Nickel fluoborate	grams per liter	340
Nickel chloride	do	20
Sodium o-formylbenzene sulfonate	do	1.0
Bis-p-chlorobenzene sulfimide	do	1.0
1,2-di-2-quinolyl ethylene	do	0.006
Temperature	° C	60
pH		3.5
Cathode current density, average	amps./dm.^{2}	15.0
Cathode current density, actual	amps./dm.^{2}	0.5–15.0

Example IV

Nickel sulfate	grams per liter	200
Sodium chloride	do	30
Boric acid	do	30
Sodium vinylsulfonate	do	1.0
p-Toluene sulfonamide	do	0.4
Bis-[4-formylpyridyl-[2]] ethylene	do	0.005
Temperature	° C	20
pH		4.6
Cathode current density, average	amps./dm.^{2}	2.0
Cathode current density, actual	amps./dm.^{2}	0.5–3.0

Example V

Nickel sulfamate	grams per liter	400
Boric acid	do	30
Sodium 1,3,6-naphthalenetrisulfonate	do	3.0
p-Chlorobenzene sulfonamide	do	1.0
1,2-di-[4-pyridyl] ethylene	do	0.01
Temperature	° C	55
pH		5.5
Current density	amps./dm.^{2}	10

In the preceding examples the primary and secondary brighteners specifically set forth may be replaced by equimolecular amounts of the primary and secondary brighteners respectively listed in Tables I and II, either singly or in combination. More specifically, the 1,2-di-4-pyridyl ethylene employed in Example VI may be replaced by an equimolecular amount of any one of the compounds listed in Table I or by an equivalent amount of a mixture composed of two or more compounds listed in Table I in any desired proportion. Similarly, the secondary brighteners of Table II may be substituted singly or in mixtures for the secondary brighteners specifically set forth in Examples I and VI.

Substantially mirror bright deposits are produced in the methods of Examples I to VI, and in methods similar to those of these examples, but modified by the substitution of primary or secondary brighteners as set forth hereinabove. The brightness of the coatings is not materially affected by the cathode current density. Objects of very complex shape on the surface of which the actual current density varies by more than one order of magnitude are uniformly coated by a lustrous nickel deposit.

Temperature, current density, pH, and other factors are relevant only as far as they influence the basic characteristics of the plating solutions in a known manner. These factors are without practical significance for the brighting effect of the primary brighteners of the invention.

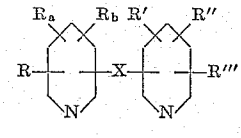
The brighteners of the invention produce lustrous nickel deposits in still tank plating, in conveyor plating on objects traveling through the electrolyte at relatively slow speeds, in high speed automatic wire plating installations, and on small objects plated in bulk in a plating barrel.

Surface active agents such as wetting agents, antifoam agents, and other addition agents conventionally employed in this art are generally compatible with the brightening agents of the invention, and those skilled in the art will find that the relatievly inert brighteners of this invention do not interfere with the normal operating characteristics of otherwise conventional electrolytes.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described:

What is claimed is:

1. A nickel plating electrolyte containing between about 0.001 and about 0.1 grams per liter of a primary brightener selected from the group consisting of compounds of the formula



wherein the substituents R, R_a, R_b, R', R'' and R''' are radicals attached to a carbon atom of a pyridine ring of said compound, and are selected from the group consisting of hydrogen, lower alkyl, lower alkylene, lower hydroxyalkyl, formyl, halide, lower haloalkyl, lower alkanoyl, cyano, hydroxy, sulfo, amino, and lower alkylamino radicals; wherein one substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms; and the lower haloalkyl N addition products of said compounds.

2. A nickel plating electrolyte according to claim 1, wherein the concentration of said primary brightner is not substantially greater than 0.06 grams per liter.

3. A nickel plating electrolyte containing as a primary brightner between about 0.001 and about 0.1 gram per liter of 1,2-dipyridyl-ethylene.

4. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of 1,2-diquinolyl-ethylene.

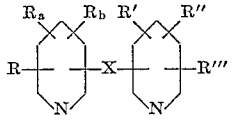
5. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of 1,2-diisoquinolyl-ethylene.

6. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of 1,2-dipyridyl-ethylene-N-lower haloalkyl addition compound.

7. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of 1,2-diquinolyl-ethylene-N-lower haloalkyl addition compound.

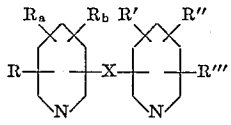
8. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of 1,2-diisoquinolyl-ethylene-N-lower haloalkyl addition compound.

9. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of a compound of the formula



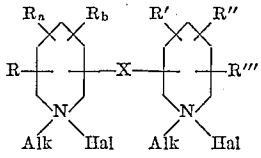
wherein the substituents R, R_a, R_b, R', R'' and R''' are radicals attached to a carbon atom of a pyridine ring of said compound, and are selected from the group consisting of hydrogen, lower alkyl, lower alkylene, lower hydroxyalkyl, formyl, halide, lower haloalkyl, lower alkanoyl, cyano, hydroxy, sulfo, amino, and lower alkylamino radicals; wherein one substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms; and the lower haloalkyl N addition products of said compounds; said nickel plating electrolyte containing a secondary brightener selected from the group consisting of viny sulfonic acid, allylsulfonic acid, benzene monosulfonic acid, ortho-, meta-, and para-benzene disulfonic acids, ortho-, meta, and paraformylbenzene sulfonic acids, 2,4-, 2,5-, and 2,6-formylbenzene disulfonic acids, naphthalene mono-, di-, and trisulfonic acids, benzene sulfonamide, ortho- and para-toluene sulfonamides, ortho-, meta-, and parachlorobenzene sulfonamides, ortho-sulfimidobenzoic acid, dibenzene sulfimide, bis-(o-chlorobenzene) sulfimide, m-di-sulfonylbenzene-bis-N-benzene sulfimide, and salts of said acids.

10. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of lower haloalkyl N-addition compound of a compound having the formula



wherein the substituents R, R_a, R_b, R', R'', and R''' are radicals attached to a carbon atom of a pyridine ring of said compound, and are selected from the group consisting of hydrogen, lower alkyl, lower alkylene, lower hydroxyalkyl, formyl, halide, lower haloalkyl, lower alkanoyl, cyano, hydroxy, sulfo, amino, and lower alkylamino radicals; wherein one substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms.

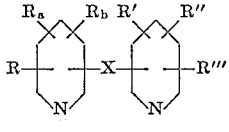
11. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of a compound of the formula



wherein the substituents R, R_a, R_b, R', R'', and R''' are radicals attached to a carbon atom of a pyridine ring of said compound and are selected from the group consisting of hydrogen, lower alkyl, lower alkylene, lower hydroxyalkyl, formyl, halide, lower haloalkyl, lower alkanoyl, cyano, hydroxy, sulfo, amino, and lower alkylamino radicals; wherein one substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms; alk is a lower alkyl radical; and Hal is a halide radical.

12. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of a compound having two pyridine rings joined by an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms and attached to respective carbon atoms of said pyridine rings.

13. A method of electrodepositing a bright nickel coating on an article which comprises making the article the cathode in a nickel plating electrolyte containing between about 0.001 and about 0.1 gram per liter of a primary brightener selected from the group consisting of compounds of the formula



wherein the substituents R, R_a, R_b, R', R'', and R''' are radicals attached to a carbon atom of a pyridine ring of said compound, and are selected from the group consisting of hydrogen, lower alkyl, lower alkylene, lower hydroxylalkyl, formyl, halide, lower haloalkyl, lower alkanoyl, cyano, hydroxy, sulfo, amino, and lower alkylamino radicals; wherein one substituent of the two groups consisting of R, R_a and R_b and R', R'' and R''' may also be a divalent radical of C_4H_4 attached to two adjacent carbon atoms of said pyridine ring, forming thus a portion of a benzene ring; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms; and the lower haloalkyl N addition products of said compounds.

14. A method according to claim 13, wherein said electrolyte has a pH value not substantially higher than 5.5.

15. A nickel plating electrolyte containing as a primary brightener between about 0.001 and about 0.1 gram per liter of a compound of the formula

A—X—A

wherein A is a radical selected from the group consisting of pyridyl, quinolyl, isoquinolyl, chloropyridyl, chloroquinolyl, chloroisoquinolyl, dichloropyridyl, dichloroquinolyl, dichloroisoquinolyl, allylpyridyl, allylquinoyl, allylisoquinolyl, formylpyridyl, formylquinonyl, formylisoquinolyl, lower alkylpyridyl, lower alkylquinolyl, lower alkylisoquinolyl, lower oxyalkypyridyl, lower oxalkylquinolyl,

lower oxyalkylisoquinolyl and the nitrogen addition compounds thereof; and wherein X is an unsubstituted olefinically unsaturated hydrocarbon chain of two to five carbon atoms.

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