United States Patent Office

3,261,840

Patented July 19, 1966

3,261,840

BRIGHT NICKEL PLATING BATHS

Harry Kroll, Warwick, R.I., assignor to Sarki Research and Development Corporation, a corporation of Rhode Island

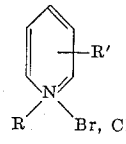
No Drawing. Original application Mar. 18, 1963, Ser. No. 266,032, now Patent No. 3,170,853, dated Feb. 23, 1965. Divided and this application Apr. 14, 1964, Ser. No. 359,762

9 Claims. (Cl. 260—290)

This application is a division of application Serial No. 266,032, now Patent No. 3,170,853, filed March 18, 1963.

This invention relates to a composition of organic bromides and chlorides useful for addition to electroplating baths, i.e. solutions of water-soluble nickel salts to improve the brightness of nickel electrodeposited from such solutions. The organic bromide and chloride additives produce electro-deposits of nickel on base metals which are highly lustrous, adherent and ductile.

The subject compounds are nitrogen heterocyclic derivatives belonging to the 2- and 4-vinyl pyridine groups, reacted with allyl and methallyl bromide or chloride to yield corresponding vinyl pyridinium compounds. These compounds can be represented by the following:



Pyridinium compounds

In the above representation, R is an allyl or methallyl group, R' is vinyl, and may be substituted in the 2 or 4 position of the pyridine. Of outstanding utility are the N-allyl-2-vinyl pyridinium bromide, N-allyl - 4 - vinyl pyridinium bromide, and mixtures thereof; the corresponding chlorides are also useful; and, also, the corresponding N-methallyl-2-vinyl pyridinium bromide and chloride as well as the N-methallyl-4-vinyl pyridinium bromide and chloride are useful.

The organic derivatives which are the basis of this invention and the preferred concentration at which they are used in electroplating baths are listed in Table I. They are used jointly with the sulfur compounds described in Table II. The sulfur compounds listed are a representative group useful for the purpose.

Although quaternary ammonium salts of nitrogen heterocyclics have been previously identified as useful additives to bright nickel plating baths, allyl bromide and chloride salts of 2 and 4 vinyl pyridine are unique for this application.

I have found that if the acid anion is a bromide or chloride, and if the nitrogen in the cation is quaternized with an allyl or methallyl group, a product is obtained which is water dispersible and produces a superior brilliant adherent nickel deposit when added to a nickel electroplating bath containing the organic additives described in Table II.

The use of the compounds in accordance with this invention for producing bright nickel deposits is based on electro-depositing nickel from a solution of one or more nickel salts to which there has been added 0.001 to 0.30 gram per liter of an allyl or methallyl 2- or 4-vinyl pyridinium halide as listed in Table I herein, together with 0.1 to 80 grams per liter of a sulfur compound in which the sulfur atom has a valence of 4 or 6, and is selected from the group of aliphatic unsaturated sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, aromatic sulfonamides and sulfonimides (see

Table II herein). The water soluble alkali metal, ammonium magnesium, and nickel salts of the above compounds are used in combination with the quaternary 2- and 4-vinyl pyridinium compounds in accordance with this invention.

The brightener additives used in the method of this invention were evaluated in a Hull cell using a standard Watt's type bath containing 330 grams of nickel sulfate hexahydrate/liter, 45 grams of nickel chloride per liter, 37.5 grams per liter of boric acid, operated at a pH of 3.5, and a temperature of 50° C. The nickel deposits were made on brass Hull cell panels 2" by 3" by plating for five minutes at three amperes. The concentrations and combination of organic additives which gave brilliant mirror-like deposits of nickel over a wide current density range are listed in Table III.

Lustrous and adherent nickel deposits were also obtained from baths having the following composition:

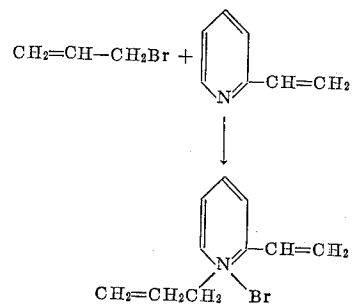
	Grams/liter
Nickel sulfate·$6H_2O$	330
Sodium chloride	30
N-allyl 2-vinyl pyridinium bromide	0.01
Naphthalene trisulfonic acid	2.0–8.0
Nickel fluoborate	225
Nickel chloride·$6H_2O$	30
Boric acid	30
N-allyl 4-vinyl pyridinium bromide	0.005–.10
2,5-naphthalene disulfonic acid	2.8–8.0

The above plating bath compositions are illustrative of the ranges of bath compositions which have been tested successfully and do not indicate any limit of the bath composition which can be employed in accordance with the invention. Actually, useful ranges of nickel concentration are from 200–400 grams per liter; whether the nickel be present as sulfate, chloride, nitrate or fluoborate. The concentrations of the organic sulfur additives and the vinyl pyridinium additives listed in the tables are by no means limiting. Preferred operative ranges are given. A considerable variation in concentration of these agents is permissible depending on what the specification requires of the electro-deposited nickel; i.e. brightness, ductility, thickness, speed of build-up, etc.

It is also well understood in the process of bright nickel electroplating that in order to obtain pit-free nickel deposits, it is advantageous to employ agitated, well-filtered solutions. The use of a wetting agent such as sodium lauryl sulfate at concentrations up to 0.25 gram per liter also permits the electroplating of pit-free nickel deposits.

The synthesis of these novel brighteners is readily carried out in accordance with the following procedure:

EXAMPLE I.—ALLYL 2-VINYL PYRIDINIUM BROMIDE



Reagents:

	Weight (grams)
Allyl bromide (1 mol)	1260
2-vinyl pyridine (1 mol)	1434

The allyl bromide and vinyl pyridine are mixed with an equal weight of isopropyl alcohol, and the solution is re-

fluxed for 6–8 hours. Reflux temperature is 78–83° C. The end-point of the reaction is determined by titrating for ionic bromide with silver nitrate.

The pyridine compounds are all synthesized in the same fashion. The allyl bromide or chloride is reacted with the appropriate pyridine or quinoline in stoichiometric proportions and the quaternized compound recovered. Thus, allyl bromide is reacted, as in Example I, in a 1:1 molar ratio with quinoline, methyl quinoline and vinyl quinolines.

EXAMPLE II

To synthesize the N-methallyl 2-vinyl pyridinium bromide, the methallyl bromide is reacted with 2-vinyl pyridine under the conditions described in Example I.

EXAMPLE III

To make the N-allyl 4-vinyl pyridinium bromide, the phosphate is reacted with the quinoline as in Example I.

EXAMPLE IV

Similarly, for making the allyl and methallyl chloride compounds of 2- and 4-vinyl pyridine, the corresponding allyl and methallyl chlorides are reacted with the corresponding 2- and 4-vinyl pyridines.

The synthesis is the direct stoichiometric reaction carried out carefully with stoichiometric amounts, so that a good yield is obtained.

Referring to the following tables, in Table I, I have listed the quaternized 2- and 4-vinyl pyridine compounds useful for addition to conventional plating baths as brighteners. I have also indicated the preferred range of concentration.

In Table II, I have listed a group of preferred sulfur compounds which are commonly referred to in the trade as primary brighteners. By this is meant that they are added to the plating bath as brighteners and with the cyclic nitrogen compounds give a net result which is a substantial improvement over the effect obtained with either one alone. The preferred concentration ranges are also indicated.

Any of the primary brighteners listed in Table II as being typical may be combined with any of the secondary brighteners of Table I in the conventional acid nickel plating baths. I have tested a large variety of combinations, virtually exhausting the possibilities, and have found that, in all cases, an improvement in the brightening effect is obtained. It is also accompanied by an improvement in ductility of the nickel plate. In Table III, I have listed certain of the preferred combinations, indicating that in any of the conventional Watt's type baths used in the art, or conforming to those indicating herein, the combination will produce optimum results. Here, it will be noted that in some cases there are two sulfur compounds where the quaternized pyridine components are used. In all cases, the results are characterized by the fact that improvements in brightness, adherence, ductility are obtained under ordinary nickel plating conditions.

Table I

Compound	Concentration range, grams/liter
1. N-allyl 2-vinyl pyridinium bromide	0.30
2. N-2-methallyl 2-vinyl pyridinium bromide	0.30
3. N-allyl 4-vinyl pyridinium bromide	0.30
4. N-allyl 2-vinyl pyridinium chloride	0.30
5. N-methallyl 4-vinyl pyridinium bromide	0.30
6. N-allyl 2-vinyl pyridinium chloride	0.30
7. N-allyl 4-vinyl pyridinium chloride	0.30
8. N-2-methallyl 4-vinyl pyridinium chloride	0.30

0.001

Table II

ORGANIC SULFUR ADDITIVES

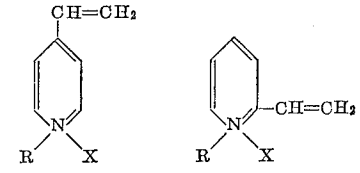
Compound:	Concentration range, grams/liter
Benzene sulfonamide	0.1–3
p-Toluenesulfonamide	0.1–2
O-benzoylsulfonimide	0.1–1.5
O-carboxybenzenesulfonamide	0.1–2.0
Benzene sulfohydroxamic acid	0.1–2.0
N-benzenesulfonyl iminodiacetic acid	0.1–2.0
N-benzenesulfonyl iminodipropionic acid	0.1–2.0
Allyl sulfonic acid	1–10
Vinyl sulfonic acid	1–10
Sodium benzenesulfonate	1–10.0
Sodium metabenzenedisulfonate	1–10.0
1,5-naphthalene disulfonic acid	1–8
2,7-naphthalene disulfonic acid	1–8
Naphthalene trisulfonic acid	1–8

Table III

Bath No.	Addition Agents	Grams/liter
1	N-allyl 2-vinyl pyridinium chloride	.005
	o-Benzoyl sulfonamide	1.0
	Para toluenesulfonamide	0.6
2	N-allyl 4-vinyl pyridinium chloride dibutyl phosphate.	.009
	o-Benzoyl sulfonimide	0.90
3	N-2-methallyl 4-vinyl pyridinium bromide	.009
	Benzenesulfonamide	1.0
	o-Benzoylsulfonimide	1.0
4	N-allyl 2-vinylpyridinium bromide	0.01
	Benzenesulfonamide	1.0
	o-Benzoylsulfonimide	1.0
5	N-allyl 4-vinyl pyridinium bromide	.006
	o-Benzoylsulfonimide	1.0
	Para toluenesulfonamide	0.6
6	N-2-methallyl 2-vinyl pyridinium bromide	0.01
	Para toluenesulfonamide	1.0
	o-Benzoyl sulfonimide	1.0
7	N-allyl 2-vinyl pyridinium chloride	0.05
	o-Benzoyl sulfonimide	1.5
8	N-allyl 4-vinyl pyridinium chloride	.009
	Allyl sulfonic acid	8.0

What is claimed is:

1. A compound having a formula given by the following:



where R is selected from the group consisting of allyl and methallyl radicals, R' is a vinyl group, and X is selected from the group consisting of bromide and chlorine.

2. N-2-methallyl 2-vinyl pyridinium bromide.
3. N-allyl 2-vinyl pyridinium bromide.
4. N-allyl 4-vinyl pyridinium bromide.
5. N-2-methallyl 4-vinyl pyridinium bromide.
6. N-2-methallyl 2-vinyl pyridinium chloride.
7. N-allyl 2-vinyl pyridinium chloride.
8. N-allyl 4-vinyl pyridinium chloride.
9. N-2-methallyl 4-vinyl pyridinium chloride.

No references cited.

WALTER A. MODANCE, *Primary Examiner.*
A. L. ROTMAN, *Assistant Examiner.*