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ELECTROPLATING

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This invention relates to electroplating and, more particularly, to electrodepositing nickel from an aqueous acidic nickel plating bath. The invention is based on our discovery that bis-pyridyl compounds, when incorporated in a nickel electroplating bath, particularly in conjunction with various sulfo-oxygen compounds, are capable of promoting the formation of excellent bright and ductile electrodeposits of nickel over a wide current density range.

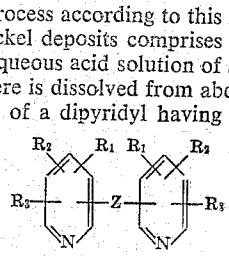
The electrodeposition of nickel from a plating bath containing a sulfo-oxygen "carrier" brightener additive yields deposits of limited intensity. Moreover, such brightness as is produced using such agents is obtained only over a limited current density range. When, however, a small quantity of a bis-pyridyl compound is incorporated in the plating bath together with a sulfo-oxygen compound, the brightness capacity of the bath is extended, and the electrodeposit is ductile and bright over a very wide current density range.

The common structural feature of these bis-pyridyl compounds is the presence of the two heterocyclic rings, which are joined together by a carbon-carbon covalent bond or by a carbon linkage containing up to two carbon atoms. The position of the ring nitrogen atoms is either alpha, beta, or gamma to the carbon-carbon linkage joining the rings, and hence the approach of the bis-pyridyl compounds to the cathode during electrolysis is not substantially impeded by steric hindrance of the highly polarized ring nitrogen atoms.

Only relatively small quantities of the bis-pyridyl compounds are required in the plating bath, especially when they are used in conjunction with a sulfo-oxygen "carrier" brightener, for we have found that the spatial configuration of a bis-pyridyl compound appears to exert a pronounced synergistic effect on the brightening capacity of the sulfo-oxygen compound. In general, concentrations of the bis-pyridyl compound as low as 0.001 gram per liter are effective, though for optimum results it is usually preferable to employ at least 0.004 gram per liter. There appears to be no critical upper limit to the concentration of the bis-pyridyl compound, but there is no great advantage in using more than about 1 gram per liter, and in most plating baths substantially the full benefit of its presence is achieved with 0.04 gram per liter or even less.

Any bis-pyridyl compound which is capable of being dissolved by acid and does not undergo decomposition upon protonation may be selected for inclusion in the plating solution. We have obtained particularly satisfactory results by using the isomeric dipyridyls and the bis-picolines in the plating bath in combination with various sulfo-oxygen compounds.

A preferred process according to this invention for producing bright nickel deposits comprises electro-depositing nickel from an aqueous acid solution of at least one nickel salt, in which there is dissolved from about 0.001 to about 1 gram per liter of a dipyridyl having the structure



in which Z is a linkage of the group consisting of a carbon-carbon covalent bond, methylene, hydroxymethylene, ethylene, hydroxyethylene, and dihydroxyethylene, and R_1,

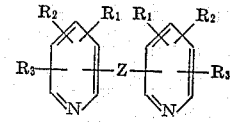
R_2, and R_3 are substituents selected from the group consisting of hydrogen, methyl, ethyl, and propyl radicals. It is especially advantageous to employ these compounds in conjunction with ¼ to 80 grams per liter of one or more water soluble sulfo-oxygen compounds of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, ammonium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides.

Preparation of the bis-pyridyl compounds may be effected by a variety of standard organic reactions. For example, a mixture of 2,2'-dipyridyl,2,3'-dipyridyl,2,4'-dipyridyl, and 4,4'-dipyridyl is formed when pyridine is heated with molten sodium at 115° C. A specific dipyridyl, such as 2,2'-dipyridyl, may be prepared by heating bromopyridine with copper powder. Other bis-pyridyls, in which the heterocyclic rings are joined through a carbon linkage having up to two carbon atoms, such as hydroxymethylene, may be synthesized from pyridinelithium via the Grignard reaction.

Examples of the bis-pyridyl compounds which may be used successfully in embodiments of this invention are listed in Table I. Although these bis-pyridyl compounds may be used in concentrations as high as 1 or even 2 or more grams per liter, they are quite expensive and no particular advantage is to be gained from the higher concentrations, and hence they are preferably used in the range of concentrations from about 0.004 to about 0.04 gram per liter.

TABLE I

Dipyridyl compounds



Compound	R_1	R_2	R_3	Z
2,2'-Dipyridyl	H	H	H	Covalent bond.
2,3'-Dipyridyl	H	H	H	Do.
3,3'-Dipyridyl	H	H	H	Do.
4,4'-Dipyridyl	H	H	H	Do.
2,4'-Dipyridyl	H	H	H	Do.
2,2'-bis(4-Picoline)	CH_3	H	H	Do.
4,4'-bis(2-Picoline)	H	CH_3	H	Do.
6,6'-bis(2-Picoline)	H	H	CH_3	Do.
4,4'-bis(3-Picoline)	CH_3	H	H	Do.
2,2'-bis(3-Methylpyridine).	CH_3	H	H	Do.
2,2'-bis(5-Methylpyridine).	H	CH_3	H	Do.
4,4'-bis(2,6-Lutidine)	CH_3	CH_3	H	Do.
3,3'-bis(2,4,6-Trimethylpyridine).	CH_3	CH_3	CH_3	Do.
5,5'-bis(2-Methyl-4-ethylpyridine).	CH_3	C_2H_5	H	Do.
3,3'-bis(4,5,6-trimethylpyridine).	CH_3	CH_3	CH_3	Do.
Di-2-pyridyl carbinol	H	H	H	CHOH.
Di-4-pyridyl carbinol	H	H	H	CHOH.
Di-2-pyridyl methane	H	H	H	CH_2.
1-(2-Pyridyl)-2-(3-pyridyl)-ethane-1-ol.	H	H	H	$CH(OH)CH_2$.
1,2-di-[4-(2-n-Propylpyridyl)]-ethane.	H	C_3H_7	H	CH_2CH_2.
1,2-di-(4-Pyridyl)-ethane.	H	H	H	CH_2CH_2.
1,2-di-[4-(2-Methylpyridyl)]-ethane.	CH_3	H	H	CH_2CH_2.
1,2-di-(2-Pyridyl)-ethane-1,2-diol.	H	H	H	CH(OH)CH(OH).
1,2-di-(4-Pyridyl)-ethane-1,2-diol.	H	H	H	CH(OH)CH(OH).

The compounds listed in Table II are examples of sulfo-oxygen compounds which, when used in the plating bath in combination with the bis-pyridyl compounds, extend the current density range over which the formation of bright and ductile nickel deposits may be obtained.

These sulfo-oxygen compounds may be used over a very wide range of concentrations (¼ to 80 grams per liter), but preferably are used in an amount in the range from about 2 to 30 grams per liter.

TABLE II

Organic sulfo-oxygen compounds

(1) Unsaturated aliphatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Sodium vinyl sulfonate, $H_2C{=}CHSO_3Na$
Sodium allyl sulfonate, $H_2C{=}CHCH_2SO_3Na$

(2) Mononuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Benzene monosulfonic acid, $C_6H_5SO_3H$
Sodium benzine monosulfonate, $C_6H_5SO_3Na$
Nickel benzene monosulfonate, $(C_6H_5SO_3)_2Ni$
Sodium p-toluene monosulfonate, $CH_3C_6H_4SO_3Na$
p-Chlorobenzene sulfonic acid, $ClC_6H_4SO_3H$
Sodium p-chlorobenzene sulfonate, $ClC_6H_4SO_3Na$
Sodium p-bromobenzene sulfonate, $BrC_6H_4SO_3Na$
1,2-dichlorobenzene sulfonic acid, $Cl_2C_6H_3SO_3H$
1,2- or 2,5-dichlorobenzene sulfonate sodium salt

$$Cl_2C_6H_3SO_3Na$$

Sodium m-benzene disulfonate, $C_6H_4(SO_3Na)_2$
m-Benzene disulfonic acid, $C_6H_4(SO_3H)_2$
Nickel m-benzene disulfonate, $C_6H_4(SO_3)_2Ni$
o-Sulfobenzoic acid monoammonium salt,

$$HOOC{-}C_6H_4SO_3NH_4$$

1-amino-2,5-benzene disulfonic acid, $H_2NC_6H_3(SO_3H)_2$
o-Aminobenzene sulfonic acid, $H_2NC_6H_4SO_3H$

(3) Mononuclear aromatic sulfinic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Sodium benzene sulfinate, $C_6H_5SO_2Na$
Sodium p-toluene sulfinate, $CH_3C_6H_4SO_2Na$

(4) Mononuclear aromatic sulfonamides and sulfonimides

Benzene sulfonamide, $C_6H_5SO_2NH_2$
p-Toluene sulfonamide, $CH_3C_6H_4SO_2NH_2$
o-Sulfobenzoic imide

Benzyl sulfonamide, $C_6H_5CH_2SO_2NH_2$
Benzene sulfhydroxamic acid, $C_6H_5SO_2NHOH$
N,N-dimethyl-p-toluene sulfonamide,

$$CH_3C_6H_4SO_2N(CH_3)_2$$

N,N-dicarboxyethyl benzene sulfonamide,

$$C_6H_5SO_2N(C_2H_4COOH)_2$$

(5) Binuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

2-naphthalene monosulfonic acid, $C_{10}H_7SO_3H$
1,5- or 2,7-naphthalene disulfonic acid, $C_{10}H_6(SO_3H)_2$
Nickel 1,5- or 2,7-naphthalene disulfonate, $C_{10}H_6(SO_3)_2Ni$
Sodium naphthalene trisulfonate, $C_{10}H_5(SO_3Na)_3$
Naphthalene trisulfonic acid, $C_{10}H_5(SO_3H)_3$
Diphenyl p,p'-disulfonic acid, $HSO_3C_6H_4{-}C_6H_4SO_3H$
2-naphthol-3,6-disulfonic acid, $HOC_{10}H_5(SO_3H)_2$
Sodium 2-naphthol-3,6-disulfonate, $HOC_{10}H_5(SO_3Na)_2$
1-naphthylamine-3,6,8-trisulfonic acid,

$$H_2N.C_{10}H_4(SO_3H)_3$$

(6) Heterocyclic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Thiophene sulfonic acid, $C_4H_3S.SO_3H$
Sodium thiophene sulfonate, $C_4H_3S.SO_3Na$
2-(4-pyridyl)ethyl sulfonic acid, $C_5H_4N.C_2H_4SO_3H$

For the most part, only free sulfonic acids are listed in Table II. However, the alkali metal, ammonium, magnesium, and nickel salts are in all cases the full equivalent of the acids, and may be used in their place in carrying out the process of the invention.

Brightener additions according to this invention have, of course, been used successfully in the standard Watts nickel electroplating bath. However, these brightener additions are also effective in all other nickel electroplating baths, and consequently the invention is applicable to electrodeposition from any aqueous acidic plating solution of one or more nickel salts.

To illustrate the applicability of using the bis-pyridyl compounds in different nickel electroplating baths under a variety of conditions, Table III lists the basic compositions of several types of plating baths which were employed in carrying out the examples of the invention that are set forth below.

TABLE III

Bath concentrations in grams per liter

	Bath A	Bath B	Bath C
Nickel sulfate	300		
Nickel chloride	45	30	
Nickel sulfamate		300	
Nickel fluoborate			220
Boric acid	37.5	30	15

In each of the following examples of the invention, the electrodeposit was formed in a Hull test cell on brass cathodes so that the effect of a wide range of current densities could be observed. The pH of the bath was adjusted to about 3.5 in each case, and the electrodeposit was formed at a temperature of 50° C. Mild agitation of the bath was provided in each case.

Table IV summarizes the results achieved when nickel is electrodeposited from a standard Watts bath (bath A) containing varying concentrations of a representative sulfo-oxygen compound alone and in combination with 2,2'-dipyridyl. Bright deposits also are obtained when the dipyridyl compound is used alone, but in such cases the current density range of maximum brightness is somewhat restricted.

TABLE IV

Sulfo-Oxygen Compound		2,2'-Dipyridyl (gm./l.)	Character of Deposit
Name	Conc. (gm./l.)		
Sodium naphthalene-1,3,6-trisulfonate.	8	0.0	Semi-bright, hazy.
	8	0.004	Bright, ductile.
	15	0.004	Do.
	30	0.01	Do.
Sodium benzene-1,5-disulfonate.	4	0.0	Fairly bright, matted.
	4	0.004	Very bright, ductile.
	4	0.008	Do.
Sodium benzenesulfonate	8	0.004	Very bright.
	16	0.008	Do.
Sodium allylsulfonate	2	0.0	Semi-bright.
	2	0.004	Very bright.
	2	0.008	Do.
o-Sulfobenzoic imide	2	0.004	Brilliant, ductile.
	2	0.012	Do.
Benzene sulfonamide	2	0.004	Very bright, ductile.
	2	0.012	Do.
Benzyl sulfonamide	2	0.004	Do.
	2	0.012	Do.

Excellent results were also obtained when the bis-pyridyl compounds were used in a sulfamate bath (bath B) containing 15 grams per liter of sodium naphthalene-1,3,6-trisulfonate and 0.016 gram per liter of 2,2'-dipyridyl in a Hull test cell. The deposit formed from such bath was bright and ductile over a very wide current density range. Increasing the concentration of 2,2'-

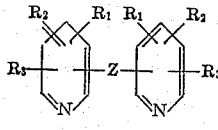
dipyridyl to 0.024 gram per liter did not substantially increase the brightness. Substitution of 2 grams per liter of o-sulfobenzoic imide (saccharin) in the sulfamate bath in place of sodium naphthalene-1,3,6-trisulfonate yielded brilliant electrodeposits when used in conjunction with 0.016 to 0.024 gram per liter of 2,2'-dipyridyl.

A nickel electrodeposit formed on the test panel from a nickel fluoborate bath (bath C) containing 15 grams per liter of sodium naphthalene-1,3,6-trisulfonate, but no dipyridyl compound, was hazy and only semi-bright in the low and middle current density ranges. Upon the addition of from 0.016 to 0.024 gram per liter of 2,2'-dipyridyl to this bath, the resultant deposits were very bright and ductile over the entire current density range of the Hull cell panel. Identical results were obtained when 2 grams per liter of o-sulfobenzoic imide were added to the bath as a substitute for the trisulfonate. Only upon the addition of the bis-pyridyl compound could a brilliant deposit be obtained over a wide current density range.

The brightening effect of the bis-pyridyls generally increases with increasing concentrations in the plating bath of the bis-pyridyl compound. The test panel of a Hull cell received a nickel electroplate from bath A, which contained 2 grams per liter of o-sulfobenzoic imide and 0.01 gram per liter of 1,2-di-(4-pyridyl)-ethane-1,2-diol. The nickel deposit from this solution was bright over the entire current density range of the panel. Increasing the concentration of 1,2-di-(4-pyridyl)-ethane-1,2-diol to 0.04 gram per liter made the deposit even brighter. Upon further increase of the concentration of the bis-pyridyl compound to 0.08 gram per liter, an even more brilliant deposit was obtained; but this deposit showed some slight loss in ductility.

We claim:

1. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.001 to about 1 gram per liter of a bis-pyridyl having the structure

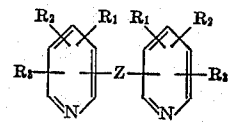


in which Z is a linkage of the group consisting of a carbon-carbon covalent bond, methylene, hydroxymethylene, ethylene, hydroxyethylene, and dihydroxyethylene, and R_1, R_2 and R_3 are substituents selected from the group consisting of hydrogen, methyl, ethyl, and propyl radicals.

2. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 2 to about 30 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.004 to about 0.04 gram per liter of 2,2'-dipyridyl.

3. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 2 to about 30 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.004 to about 0.04 gram per liter of 1,2-di-(4-pyridyl)-ethane-1,2-diol.

4. An aqueous acidic electroplating solution of at least one nickel salt in which there is dissolved from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.001 to about 1 gram per liter of a bis-pyridyl having the structure



in which Z is a linkage of the group consisting of a carbon-carbon covalent bond, methylene, hydroxymethylene, ethylene, hydroxyethylene, and dihydroxyethylene, and R_1, R_2 and R_3 are substituents selected from the group consisting of hydrogen, methyl, ethyl, and propyl radicals.

5. An aqueous acidic electroplating solution of at least one nickel salt in which there is dissolved from about 2 to about 30 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.004 to about 0.04 gram per liter of 2,2'-dipyridyl.

6. An aqueous acidic electroplating solution of at least one nickel salt in which there is dissolved from about 2 to about 30 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.004 to about 0.04 gram per liter of 1,2-di-(4-pyridyl)-ethane-1,2-diol.

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