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ELECTRODEPOSITION OF NICKEL

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1

This invention relates to electrodeposition of metals, and more specifically to a process, and solutions for use in a process of, electrodepositing nickel, characterized in that the resulting nickel electrodeposits is bright as it comes from the plating solution. More particularly, the present invention has to do with the discovery of cooperating brightening addition agents suitable for use in an aqueous acid nickel plating solution.

I have now discovered that excellent bright, ductile, and smooth deposits of nickel can be produced over a wide cathode current density range by electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, if such solution also contains an effective amount of each of two cooperating addition agents, one of such addition agents being a bis-pyridinium compound soluble in said solution to the extent of at least .005 gram per liter and characterized in that the two pyridinium groups are connected through a carbon chain or a carbon and oxygen chain, and the other of said addition agents being a cyclic, organic sulfate compound soluble in the acid nickel solution to the extent of at least 0.2 gm. per liter, and selected from the group consisting of organic compounds containing the group

wherein the carbon atom is nuclear carbon, and wherein which compounds each of the remaining nuclear carbon atoms carries a group of the class consisting of hydrogen, methyl, ethyl, chlorine, bromine, CIC, and phenyl. The first mentioned addition agent may be referred to as the bis-pyridinium brightener and should be maintained in the plating solution in concentration of from 0.005 to 0.05 gram per liter, preferably from 0.001 to 0.005 gram per liter, while the second mentioned addition agent, which I prefer to call a carrier or regulator, should be maintained in the solution in a concentration of from 0.2 to 15.0 gm. per liter, preferably from 1 to 7 gm. per liter.

Since the two above-mentioned classes of addition agents are intrinsically and functionally distinct, they will be separately described and identified.

2

The substances of the first addition agent class, the bis-pyridinium compounds, are soluble in the solution to the extent of at least about .005 gram per liter (for example, in a solution containing 240 grams per liter NiSO₄.6H₂O, 37.5 grams per liter of NiCl₂.6H₂O, and 37.5 grams per liter of H₃BO₃, remainder water), and should be understood to include the unsubstituted pyridinium group and also substituted pyridinium groups such as those having alkyl substituents or substituents coalesced into a ring structure so as to give, for example, isoquinolinium groups.

Addition agents of the first mentioned class are characterized by the presence of two spaced groups of the form,

the open valences being satisfied by various substituents such as hydrogen or alkyl (methyl, ethyl, propyl), chlorine, bromine, etc. The general structure may be indicated as follows:

where Z may indicate a connecting chain which may be a chain of from 1 to 5 methylene groups or a plurality of chains of from 1 to 5 methylene groups connected through oxygen or phenylene, or a chain of from 1 to 3 phenylene groups, any of the replaceable hydrogens of which may be substituted. The above indicated cyclic nitrogen group, when all the free valences are satisfied by hydrogen, is referred to as a pyridinium group. A plurality of substituents may form a ring structure, for example, isoquinolinium which has the following structure:

One or more of the hydrogens may be substituted.
by alkyl giving an alkyl pyridinium group. In general the unsubstituted pyridinium group or
the unsubstituted isoquinolinium group is preferred as being simpler, but the substituted
groups can be used. The connecting group or chain is made up of methylene and/or phenylene
and/or oxygen. It may take the form of a single methylene group, a single phenylene group, or a
more complex arrangement. If the pyridinium group, the isoquinolinium group, and substituted
pyridinium and isoquinolinium groups are indicated by P and P', the desirable compounds may
take such forms as:

\[
P - \text{CH}_2 - P' \\
P - \text{CH}_2 - \text{O} - \text{CH}_2 - P' \\
P - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - P' \\
P - \text{(CH}_2)_n - P' (n being an integer from 1-5) \\
P - \text{(CH}_2)_{2n} - P' \\
P - \text{CH}_2 \text{CH}_2 \text{OCH}_2 \text{CH}_2 - P' \\
\]

These are merely examples, and numerous other arrangements are possible.

To classify these addition agents into subclasses, most of them fall into three groups, having
general formulae as follows:

**Group 1.** \[P - [\text{CRR'}]_n - \text{O} - (\text{CRR'})_m - \text{O} - P' \]

where \(P\) and \(P'\) have the meaning indicated above, \(R\) and \(R'\) may be, independently, hydrogen, alkyl (methyl, ethyl, propyl), phenyl, etc., \(n\), \(m\), and \(n'\) may be integers from 1 to 5, and \(n''\) may be an integer from 0 to 3.

**Group 2.** \[P - [\text{CRR'}]_n - P' \]

where \(P\) and \(P'\) have the meaning indicated above, \(R\) and \(R'\) may be, independently, hydrogen, alkyl (methyl, ethyl, propyl), phenyl, etc., and \(n\) is an integer from 1 to 5.

**Group 3.** \[P - [\text{CRR'}]_n - [\text{CH}_2 - [\text{CRR'}]_m - P' \]

where \(P\) and \(P'\) have the meaning indicated above, \(R\) and \(R'\) may be, independently, hydrogen, alkyl (methyl, ethyl, propyl), phenyl, etc., \(n\) is an integer from 1 to 3, and \(n'\) is an integer from 1 to 3.

Some specific examples of the foregoing three groups are as follows:

**Group 1.** Alkyleno-ether type linkage

**a.** \(N,N'-(\text{oxydiethylene})\)-bis-isoquinolinium chloride

**b.** \(N,N'-(\text{oxydiethylene})\)-bis-pyridinium perchlorate

**c.** \(N,N'-(\text{oxydimethylene})\)-bis-pyridinium chloride

**d.** \(N,N'-(\text{oxydimethylene})\)-bis-isoquinolinium chloride

The structure is written like \((c)\) but substituting isoquinolinium groups for the pyridinium groups.

**e.** \(N,N'-(\text{oxydimethylene})\)-bis-(2-methyl-5-ethyl) pyridinium chloride

**f.** \(N,N'-(\text{oxyldy}-(\text{trimethylene})\)-bis-pyridinium chloride

**g.** \(N,N'-(\text{oxyethylene methylene})\)-bis-pyridinium chloride

**h.** \(N,N'-(\text{oxyethylene})\) isoquinolinium chloride (ethylene) pyridinium chloride

**i.** \(N,N'-(\text{dioxycarbenyl})\)-bis-pyridinium chloride
5. N,N'- (oxydiethylene) - bis-3-methylisoquinolinium chloride

k. N,N'- (oxymethylene) - pyridinium chloride - (ethylene) isoquinolinium chloride

Group 2. Alkyene linkage
a. N,N'- ethylene-bis-quinolinium bromide

b. N,N'- methylene-bis-pyridinium bromide

c. N,N' - ethylene-bis-pyridinium bromide

d. N,N'- methylene-bis-isoquinolinium bromide

e. N,N'- methylene-bis-(α-picolinium) bromide

Group 3. Alkyene aromatic linkage
a. N,N' - (o-xylene) - bis-pyridinium bromide

b. N,N' - (p-xylene) - bis-pyridinium bromide

c. N,N' - (p-xylene) - bis-(α-picolinium) bromide

d. N,N' - (p-xylene) - bis-isoquinolinium bromide
Other salts of the foregoing compounds (and others of the same types) may be used with equivalent results, e.g., the chlorides, bromides, acetates, chlorates, etc.

The carriers or regulators constituting the second addition agent class are soluble in the plating solution (for example, in a solution consisting of 240 grams of NiSO₄·6H₂O, 37.5 grams NiCl₂·6H₂O, and 37.5 grams of H₂BO₃ and water to make a liter). To the extent of at least 0.2 gram per liter. These include such materials as benzene, naphthalene and thiophene sulfuric acids and salts thereof, and halogenated ethylene, CHO, and phenyl substituent products of the foregoing, such as, for example:

**CARRIERS OR REGULATORS**

1. Benzene mono-sulfonic acid (C₆H₅SO₂H)
2. Benzene disulfonic acids (C₆H₅SO₄H₂)
3. Monochlorobenzene monosulfonic acids (ClC₆H₅SO₂H)
4. Dichlorobenzene disulfonic acids (Cl₂C₆H₄(SO₂H)₂)
5. 2,5-dibromobenzensulfonic acid (Br₂C₆H₄(SO₂H)
6. Toluene sulfonic acids (C₆H₅CH₃SOH)
7. Benzaldehydesulfonic acids (C₆H₅(CH=O)SO₂H)
8. Diphenylsulfonic acids (C₆H₅C₆H₄(SO₂H)₂)
9. Thiophenesulfonic acids (C₅H₄SO₂H)
10. Diphenyl sulfonyl sulfonic acids (C₆H₅SO₂C₆H₄SO₂H)
11. Naphthalene disulfonic acids
12. Naphthalene monosulfonic acids
13. Chloronaphthalene disulfonic acids
14. Dibenzensulfonamide (C₆H₅SO₂NH₂)
15. Dichloro dibenzensulfonamides (ClC₆H₅SO₂NH₂)
16. N-ethane sulfonyl benzene sulfonamide (C₆H₅SO₂NH₂CH₂H)

Potassium, sodium, nickel and cobalt salts of the foregoing

17. Benzenemono-sulfonamide (C₆H₅SO₂NH₂)
18. Saccharine, sodium salt (C₆H₅SO₂CONa) or anhydride (C₆H₅SO₂CONH₂)
19. Benzenebenzyl chloride (C₆H₅SO₂Cl)
20. Benzenebenzyl sulfonamide (C₆H₅SO₂NH₂)
21. Xylenesulfonamides (C₆H₅SO₂NH₂)
22. Toluene sulfonamides (C₆H₅SO₂NH₂)
23. Sulfunated naphthalene. (Mixtures of naphthalene sulfuric acids, produced by treating naphthalene with oleum, preferably two parts of 20% oleum on one part of naphthalene at 160° C. for two hours.)

From these examples it becomes clear that numerous single ring compounds containing the effective group can be used, whether aromatic, such as the benzene sulfonic acids, or heterocyclic with aromatic characteristics, such as thiophene sulfonic acid. Various substituents on the ring structure are exemplified.

It is to be understood that all statements made herein concerning the capabilities of the addition agents presuppose the use of one or a mixture of two or more from each class, i.e., one or a mixture from the bis-pyridinium class and one or a mixture from the class of aromatic sulfur compounds containing the

**-SO₂-**

group. The carrying agents produce a degree of brightness without any brightener, but not enough to yield full brightness alone. I prefer the use of the more common and readily available compounds, and prefer to employ in each addition agent class only compounds devoid of the group which characterizes the other addition agent class.

The constituents of the bath according to the preferred practice of the invention are (1) water, (2) nickel sulfate, nickel chloride or nickel sulfamate with nickel chloride, (3) an aromatic sulfonamide compound such as an aromatic sulfonic acid or a nickel, alkali metal, or cobalt salt thereof, an aromatic sulfonamide, or sulfamide, or a mixture of a plurality thereof, (4) a wetting agent (optional), and (5) a bis-pyridinium compound or a mixture of bis-pyridinium compounds. An additional ingredient of the solution which is desirable is a buffering agent such as boric acid, formic acid, ammonium sulfate, or the like.

It will be noted that in respect to major constituents, the solutions are similar to the well-known "all sulfate," "all chloride," and "sulfate-chloride" or Watts type nickel plating solutions. It will be noted also that as to the aromatic sulfonamide type of addition agent or "carrier," as it is often called, the group of suitable materials are of the type which is represented by well-known carriers in the bright nickel plating industry. The essential novel feature of the present invention is the use in such solutions containing the aromatic sulfonamide group of a small amount of a bis-pyridinium compound or a mixture of bis-pyridinium compounds.

The preferred basic solutions in connection with which my invention is realized are as follows:

**ALL SULFATE**

| NiSO₄·7H₂O | 100 to 400 g., preferably 100 to 200 g. |
| Boric acid | 0 to 60 g., preferably 10 to 30 g. |
| Wetting agent (e.g., sodium 0 to 0.5 g., preferably 0.05 to 0.25 g.) |
| H₂O to make | 1000 cc. |

**ALL CHLORIDE**

| NiCl₂·6H₂O | 50 to 250 g., preferably 100 to 200 g. |
| Boric acid | 0 to 60 g., preferably 10 to 30 g. |
| Wetting agent (e.g., sodium 0 to 0.5 g., preferably 0.05 to 0.15 g. lauryl sulfate) |
| H₂O to make | 1000 cc. |

SULFATE-CHLORIDE (WATTS TYPE)

| NiSO₄·7H₂O | 100 to 400 g., preferably 100 to 200 g. |
| NiCl₂·6H₂O | 10 to 60 g., preferably 30 to 40 g. |
| Boric acid | 0 to 50 g., preferably 15 to 25 g. |
| Wetting agent (e.g., sodium 0 to 0.5 g., preferably 0.025 to 0.2 g. lauryl sulfate) |
| H₂O to make | 1000 cc. |

To each of the foregoing basic solutions I add a suitable quantity of each, or a mixture of two or more of each, of the two co-operating addition agents. One of said addition agents or mixtures is one of the aromatic sulfonic type, and the other is of the bis-pyridinium type described above. The solution should, for plating results, contain an anti-pit agent, although the deposits may be suitable for some purposes without eliminating the pitting, and under some conditions the deposits may not be objectionably pitted even in the absence of an addition agent for control of pitting. Sodium lauryl sulfate and other alkyl sulfate having 8 to 18 carbon atoms may be used as an anti-pit agent, although, as stated, its use is not essential, and other wetting agents or mixtures of wetting agents may be used for control of pitting.

The specific examples in the following table will serve to illustrate the invention, values therein being grams per liter except as otherwise indicated, the balance being water.
Having thus described my invention, what I claim is:

1. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolysing an aqueous acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a compound of the formula,

\[ P(-\text{C})_n-P' \]

where \( P \) and \( P' \) are radicals of the formula

\[
\begin{align*}
\text{P} & \quad \text{O} \\
\quad \quad \quad \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

and the other of said addition agents being an aromatic compound containing the

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

group, and being soluble in said solution to the extent of at least 0.2 gram per liter, the carbon atom is said

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

group being nuclear carbon, said first mentioned addition agent being present in concentration from 0.005 to 0.01 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

2. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolysing an aqueous acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a compound of the formula,

\[ P(-\text{C})_n-P' \]

where \( P \) and \( P' \) are radicals of the formula

\[
\begin{align*}
\text{P} & \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

and the other of said addition agents being an aromatic compound containing the

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\quad \quad \quad \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

group, and being soluble in said solution to the extent of at least 0.2 gram per liter, the carbon atom in said

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]

group being nuclear carbon, said first mentioned addition agent being present in concentration from 0.005 to 0.01 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

3. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolysing an aqueous acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a compound of the formula,

\[ P(-\text{C})_n-P' \]

where \( P \) and \( P' \) are radicals of the formula

\[
\begin{align*}
\text{P} & \quad \text{O} \\
\quad \quad \quad \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\quad \quad \quad \quad \text{C} \\
\quad \quad \quad \quad \text{O} \\
\end{align*}
\]
and the other of said addition agents being an aromatic compound containing the group, and being soluble in said solution to the extent of at least 0.2 gram per liter, the carbon atom in said

and being nuclear carbon, said first mentioned addition agent being present in concentration from 0.005 to 0.01 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

4. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a compound of the formula,

\[
P(-\text{CH}_2\text{CH}_2\text{-N})_p\cdot\text{R}
\]

where \( P \) and \( P' \) are radicals of the formula

and the other of said addition agents being an aromatic compound containing the group, and being soluble in said solution to the extent of at least 0.2 gram per liter, the carbon atom in said

and being nuclear carbon, said first mentioned addition agent being present in concentration from 0.005 to 0.01 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

5. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being oxydi-
ethylene-bis-isoquinolinium chloride, and the other of said addition agents being sulfonated naphthalene, said first mentioned addition agent being present in concentration from 0.005 to 0.01 gram per liter, and said second mentioned addition agent being present in concentration from 0.3 to 15 grams per liter.

7. The invention as defined in claim 6 further characterized in that there is included as a third addition agent, 2,5-dichloro dibenzenesulfonamide in quantity such that the combined concentrations of the sulfonated naphthalene and 2,5-dichloro dibenzenesulfonamide are within the range from 0.2 to 15 grams per liter.

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References Cited in the file of this patent

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