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2,882,208

ELECTRODEPOSITION OF NICKEL

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This invention relates to the electrodeposition of nickel, and more particularly it relates to the electrodeposition of bright ductile nickel from aqueous acidic nickel electroplating baths.

In accordance with this invention, it has been found that certain unsaturated organic compounds containing both the triple bonded $\text{—C}\equiv\text{C—}$ unsaturated group and the triple bonded unsaturated $\text{—C}\equiv\text{N}$ group in the same molecule, as exemplified by the compounds of Table I, give brilliant ductile plate when used in aqueous acidic nickel baths in unusually small concentrations in conjunction with the well-known organic sulfon-compounds as exemplified in Table II.

While it is old to use compounds containing the cyano group (nitriles), (U.S. Patent 2,524,010, September 26, 1950), in conjunction with the organic sulfon-compounds, nevertheless the concentrations necessary to obtain bright plate have been between 0.1 gram to 1 gram per liter. It has been found that on continued electrolysis of nickel baths using concentrations of 0.1 g./l. to 1 g./l. of cyano compounds such as cyanoacetamide, lactonitrile, etc. not containing a sulfonic acid in the same molecule, that there accumulates hydrolytic and electrolytic degradation products which cause increasing brittleness in the bath with the continued additions necessary to maintain brightness during continuous plating. It has also been found that the harmful "break-down" products formed during continuous electrolysis in the case of such aliphatic nitriles as cyanoacetamide, lactonitrile and others are not readily removed by activated carbon or absorptive clays, and the nickel baths give increasingly brittle plate and become exceedingly difficult to purify. These serious embrittling defects are not encountered with the compounds of Table I which contain both the $\text{—C}\equiv\text{N}$ and $\text{—C}\equiv\text{C—}$ unsaturated groups. It will be noted that in each of the compounds of Table I, the $\text{C}\equiv\text{N}$ group is separated by an ether linkage from the $\text{C}\equiv\text{C}$ group. This linkage is considered to be an important contributor to the effectiveness of these compounds. The concentrations that are necessary for high brilliance without excessive brittleness are very low, 0.001 to 0.01 gram per liter, much lower than the recommended concentrations for compounds carrying separately either the $\text{—C}\equiv\text{C—}$ group or the $\text{—C}\equiv\text{N}$ group. The presence of both types of triple bonds in the same molecule exerts an enhanced brightening effect over either one alone.

The compounds of Table I are preferably used in concentrations of 0.001 to 0.005 gram/liter in conjunction with the organic sulfon-compounds illustrated in Table II. The compounds of Table I can be used in conjunction with other nickel brighteners such as those containing the



bond (U.S. Patent 2,647,866, August 4, 1953), using lower concentrations of the compounds of Table I together with lower concentrations of



compounds giving improved results. This use is illustrated in Example D below.

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TABLE I

		Optimum Conc., grams/liter
5		
(1)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{CH}_3 \end{array}$	0.001-0.005
10	3-(beta-cyanoethoxy)-3-methyl-butyn-1	
(2)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{CH}_3 \end{array}$	0.001-0.008
15		
(3)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{CH}_3 \end{array}$	0.001-0.008
20		
(4)	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{CH}_3 \end{array}$	0.001-0.005
(5)	$\text{HC}\equiv\text{C—CH}_2\text{O C}_2\text{H}_4\text{C}\equiv\text{N}$	0.001-0.003
(6)	$\text{HC}\equiv\text{C—CH}_2\text{O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{C}\equiv\text{N}$	0.001-0.005
25		
(7)		0.001-0.003
30	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{CH}_3 \end{array}$	
(8)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}\equiv\text{C—C—O C}_2\text{H}_4\text{C}\equiv\text{N} \\ \\ \text{H} \end{array}$	0.001-0.005
35		
(9)	$\text{CH}_3\text{O CH}_2\text{C}\equiv\text{C—CH}_2\text{O C}_2\text{H}_4\text{C}\equiv\text{N}$	0.001-0.01
(10)	$\text{HO CH}_2\text{—C}\equiv\text{C—CH}_2\text{O C}_2\text{H}_4\text{C}\equiv\text{N}$	0.003-0.015
(11)	$\text{N}\equiv\text{C—C}_2\text{H}_4\text{O CH}_2\text{C}\equiv\text{C—CH}_2\text{O C}_2\text{H}_4\text{C}\equiv\text{N}$	0.001-0.01

TABLE II

Sulfur-Containing Brighteners	Optimum Conc., grams/liter
45	
1. Benzene sulfonamide.....	0.1-3
2. Toluene sulfonamides (o- and p-).....	0.1-2
3. o-Benzoyl sulfimide.....	0.1-2
4. N-Benzoyl benzene sulfonimide.....	0.1-1
5. p-Toluene sulfonchloramide.....	0.1-1
6. p-Brom benzene sulfonamide.....	0.1-1
7. 6-Chlor o-benzoyl sulfimide.....	0.1-1
50	
8. m-Aldehyde benzene sulfonamide.....	0.1-1
9. Sulfomethyl benzene sulfonamide.....	0.1-6
10. Benzene sulfonamide m-carboxylic amide.....	0.1-3
11. 7-Aldehyde o-benzoyl sulfimide.....	0.1-3
12. N-acetyl benzene sulfonimide.....	0.1-2
13. Methoxy benzene sulfonamides.....	0.1-1
14. Hydroxymethyl benzene sulfonamide.....	0.1-2
15. Allyl sulfonamide.....	0.4-12
55	
16. Benzene sulfonic acids (mono-, di-, and tri-).....	1-15
17. p-Brom benzene sulfonic acid.....	3-6
18. Benzaldehyde sulfonic acids (o, m, p).....	2-6
19. Diphenyl sulfone sulfonic acid.....	1-8
20. Naphthalene sulfonic acids (mono-, di-, and tri-).....	1-8
21. Benzene sulfohydroxamic acid.....	1-5
22. p-Chlor benzene sulfonic acid.....	1-15
60	
23. Diphenyl sulfonic acid.....	1-5
24. m-Diphenyl benzene sulfonic acid.....	1-4
25. 2-Chloro-5-sulfobenzaldehyde.....	1-5
26. m-Benzene disulfonamide.....	0.5-1
27. Allyl sulfonic acid.....	0.4-12
28. Dichlorobenzene sulfonic acids.....	0.5-8
29. Di-benzene sulfonimide.....	0.1-3
30. Di-toluene sulfonimide.....	0.1-3
65	
31. 2-Butyne-1, 4-disulfonic acid.....	5-20
32. 4-Hydroxy-2-butyne-1-sulfonic acid.....	0.2-2
33. 2-Butyne-1-sulfonic acid.....	0.05-1.5
34. 3-Chloro-2-propyne-1-sulfonic acid.....	0.05-1.5
35. 2-butene-1,4-disulfonic acid.....	0.3-5
36. 2-chloro butene-4-sulfonic acid.....	0.3-5
37. 2-chloro propene sulfonic acid.....	0.1-1.5
70	
38. Cinnamyl sulfonic acid.....	0.1-3.0
39. 3-Phenyl-2-propyne-1-sulfonic acid.....	0.3-3.0
40. 4-Methoxy-2-butyne-1-sulfonic acid.....	0.2-2

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The more rapid the rate of cathode or solution agitation, the lower the concentration of the compounds of Table I that are necessary for high brilliance. For example, with strong air agitation of the bath, the lower concentrations of the compounds of Table I are used.

The combination of the compounds of Table I with those of Table II can be used in all types of acidic nickel baths that give good ductile gray nickel deposits, such as Watts nickel baths, high chloride, fluoborate, and sulfamate baths and mixtures of these various nickel salts. Sodium, potassium, and lithium ions may be present, also ammonium ions, though the latter should preferably be kept below about 7 grams/liter for maximum ductility and brightness. Boric acid is the preferred buffer.

The best pH range is from about 2.8 to 4.5, though pH values of 2 to 6 may be used. The temperature of the bath may be from room to 190° F., though in general 120° F. to 160° F. is preferred.

When no air agitation or strong mechanical or hydraulic agitation is used, it is preferred to use a suitable surface-active agent such as sodium lauryl sulfate, sodium 2-ethyl hexyl sulfate or sulfonate, octyl sulfonic acid, etc., to prevent gas-pitting. With air agitation a surface-active agent such as sodium 2-ethyl hexyl sulfate or sulfonate can be used which does not foam excessively, or else an anti-foam such as a silicone oil can be used with a more powerful surface-active agent, such as sodium lauryl sulfate.

The preferred organic sulfon-compounds to be used with the compounds of Table I are o-benzoyl sulfimide and the benzene sulfonamides and sulfonimides (0.1 gram/liter to saturation) especially when used in conjunction with allyl sulfonic acid (0.6-2 grams per liter) or 2-butyne-1,4-disulfonic acid (2-10 grams/liter).

In the following examples typical bath compositions and conditions are illustrated for obtaining the bright nickel deposits in accordance with this invention, but it is to be understood that they are representative only, and that the compounds of Table I can be used in such bath compositions in combination with each compound or combinations of the compounds of Table II or other organic sulfon-compounds similar to those of Table II such as those carrying di-, tri-, or tetra-sulfonimide groups of phenyl, biphenyl, naphthyl, or mixed phenyl, biphenyl etc., di-, tri-, and tetra-sulfonimides, such as



in the approximate proportions indicated in Table II.

Example A

	Grams/liter
NiSO ₄ ·6H ₂ O	200-300
NiCl ₂ ·6H ₂ O	30-80
H ₃ BO ₃	30-50
NaBF ₄	0-0.5
Example 1 of Table I: 3-(beta cyanoethoxy)-3-methyl-butyne-1	0.001-0.004
Sodium allyl sulfonate	0.6-2
Benzene sulfonamide	1-2
o-Benzoyl sulfimide	0-2
Temperature, 120° F.-160° F.	
pH, 3.2-4.8.	

Example B

	Grams/liter
NiCl ₂ ·6H ₂ O	100-200
NiSO ₄ ·6H ₂ O	0-50
H ₃ BO ₃	30-50
Example 2 of Table I	0.002-0.005
Sodium allyl sulfonate	0.6-2
o-Benzoyl sulfimide	1-2
Benzene sulfonamide	1-2
Temperature, 120° F.-160° F.	
pH, 3.2-4.8.	

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Example C

	Grams/liter
NiSO ₄ ·6H ₂ O	200-300
NiCl ₂ ·6H ₂ O	30-100
H ₃ BO ₃	30-50
Example 10 of Table I	0.005-0.015
2-butyne-1,4-disulfonic acid (Na, K or Ni salt)	2-10
o-Benzoyl sulfimide	0.2-2
Temperature, 120° F.-160° F.	
pH, 3.2-4.8.	

Example D

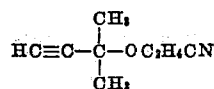
	Grams/liter
NiSO ₄ ·6H ₂ O	200-300
NiCl ₂ ·6H ₂ O	30-80
H ₃ BO ₃	30-50
NaBF ₄	0-0.5
Example 5 of Table I	0.001-0.002
N-allyl quinaldinium bromide	0.001-0.004
2-butyne 1,4-disulfonic acid (Na, K, or Ni salt)	2-10
Benzene sulfonamide	1-2
o-Benzoyl sulfimide	0.2-2
Temperature, 120° F.-160° F.	
pH, 3.2 to 4.8.	

The above baths give brilliant ductile nickel deposits with very good rate of brightening or leveling.

What is claimed is:

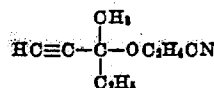
1. A bath for electrodepositing bright, ductile nickel plate which comprises an aqueous acidic solution containing at least one electrolyte selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, and having dissolved therein about 0.1 gram/liter to saturation of at least one organic sulfon-compound selected from the class consisting of benzene, biphenyl and naphthalene sulfonic acids, sulfonamides and sulfonimides and the mixed phenyl, biphenyl and naphthyl sulfonamides and the mono-, di-, tri-, and tetra-sulfonimides thereof, and dibenzene sulfonimides and the halogen, methyl, and aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene and alkyne sulfonic acids having 4-2 carbon atoms, and about 0.001 to about 0.015 gram/liter of a nitrile having the elements hydrogen, nitrogen, oxygen and 6-17 carbon atoms inclusive and containing a $\text{—C}\equiv\text{C}$ group, which $\text{—C}\equiv\text{C}$ group is separated from the $\text{—C}\equiv\text{N}$ group by at least one ether linkage.

2. A bath in accordance with claim 1 wherein the said nitrile is the compound



and is present in a concentration in the bath of 0.001 to about 0.008 gram/liter.

3. A bath in accordance with claim 1 wherein the said nitrile is the compound



and is dissolved in the said nickel bath in a concentration of 0.001 to about 0.01 gram/liter.

4. A bath in accordance with claim 1 wherein the said nitrile is the compound $\text{HC}\equiv\text{C}-\text{CH}_2\text{OC}_2\text{H}_4\text{CN}$ and is dissolved in the said nickel bath in a concentration of 0.001 to about 0.01 gram/liter.

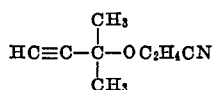
5. A bath in accordance with claim 1 wherein said organic sulfon-compound is allyl sulfonate.

6. A bath in accordance with claim 1 wherein said organic sulfon-compound is 2-butyne-1,4-disulfonate.

7. A method of electrodepositing bright, ductile nickel plate which comprises electrolyzing an aqueous acidic solution comprising at least one nickel salt selected from

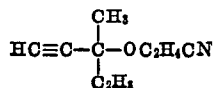
the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said bath containing dissolved therein about 0.1 gram/liter to saturation of at least one organic sulfon-compound selected from the group consisting of benzene, biphenyl and naphthalene sulfonic acids, sulfonamides and sulfonimides and the mixed phenyl, biphenyl and naphthyl sulfonamides and the mono-, di-, tri-, and tetra-sulfonimides thereof, and dibenzene sulfonimides and the halogen, methyl, and aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene and alkyne sulfonic acids having 4-2 carbon atoms, and about 0.001 to about 0.015 gram/liter of a nitrile having the elements hydrogen, nitrogen, oxygen and 6-17 carbon atoms inclusive and containing a $\text{—C}\equiv\text{C}$ group, which $\text{—C}\equiv\text{C}$ group is separated from the $\text{—C}\equiv\text{N}$ group by at least one ether linkage.

8. A method in accordance with claim 7 wherein the said nitrile is the compound



and is present in a concentration in the bath of 0.001 to about 0.008 gram/liter.

9. A method in accordance with claim 7 wherein the said nitrile is the compound



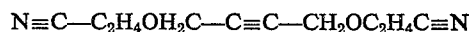
and is present in the said nickel bath in a concentration of 0.001 to about 0.01 gram/liter.

10. A method in accordance with claim 7 wherein the said nitrile is the compound $\text{HC}\equiv\text{C}-\text{CH}_2\text{OC}_2\text{H}_4\text{CN}$ and is present in the said nickel bath in a concentration of 0.001 to about 0.01 gram/liter.

11. A method in accordance with claim 7 wherein said organic sulfon-compound is allyl sulfonate.

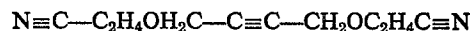
12. A method in accordance with claim 7 wherein said organic sulfon-compound is 2-butyne-1,4-disulfonate.

13. A bath in accordance with claim 1 wherein the said nitrile is the compound



and is present in a concentration in the bath of about 0.001 to about 0.01 gram/liter.

14. A method in accordance with claim 7 wherein the said nitrile is the compound



and is present in a concentration in the bath of about 0.001 to about 0.01 gram/liter.

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