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ELECTRODEPOSITION OF NICKEL

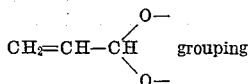
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10 Claims. (Cl. 204—49)

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 vinyl substituted m-dioxane compounds, such as those illustrated in Table I, containing the

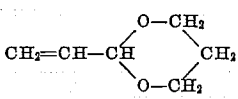
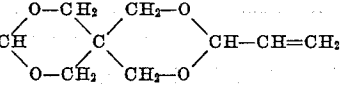
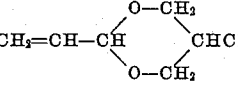
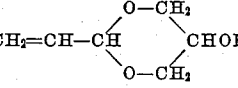
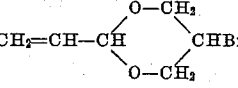


when used in very small concentrations in aqueous acidic nickel baths in conjunction with the well-known organic sulfon-compounds (as illustrated in Table II) make possible the production of brilliant ductile nickel plate.

While numerous unsaturated compounds have been used in the art in conjunction with sulfon-compounds to obtain bright ductile nickel plate, the number of highly satisfactory unsaturated vinyl substituted compounds have been very few. For example, 2-vinyl pyridine is actually far inferior to pyridine as a nickel brightener when used in conjunction with an aryl sulfon-compound and vinyl benzene is insoluble in a Watts-type nickel bath.

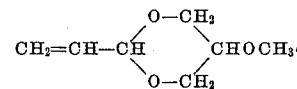
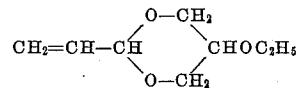
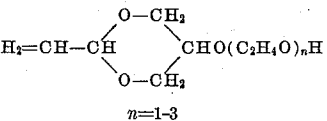
The vinyl substituted saturated ring, m-dioxane, compounds of Table I give far superior brightening results than when the vinyl group is attached to an aromatic-type ring such as benzene or pyridine. This is thought to be due to the fact that in the compounds of Table I the vinyl group is, in fact, an allylic group with the terminal, i. e. farthest from the double bond carbon atom of the allylic group as part of the dioxane ring.

TABLE I

	Optimum Conc., Grams/liter
1. 	0.01 to 0.06
2. 	0.01 to 0.06
3. 	0.01 to 0.06
4. 	0.01 to 0.06
5. 	0.01-0.06

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TABLE I.—Continued

	Optimum Conc., Grams/liter
5. 	0.01 to 0.06
10 7. 	0.01 to 0.06
15 8. 	0.01 to 0.06

The compounds of Table I are effective in very low concentrations, and when fast agitation is used (air or mechanical, or hydraulic), concentrations as low as about two or three milligrams per liter show beneficial brightening effects. In general, however, concentrations of about 0.01 to 0.06 gram/liter are preferred, though much higher concentrations can be used, for example, up to about 0.2 gram/liter and in some cases as high as 0.5 gram/liter.

TABLE II

Sulfur-Containing Brighteners	Optimum Conc., grams/liter
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
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
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
23. Diphenyl sulfonic acid.....	1-5
24. m-Diphenyl benzene sulfonic acid.....	1-4
25. 2-Chloro-5-sulfo benzaldehyde.....	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
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.....	.05-5
36. 2-chloro butene-4-sulfonic acid.....	0.3-5
37. 2-chloro propene sulfonic acid.....	0.1-1.5
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

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 without the additives, 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 per 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.-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, it is usually not necessary to use a surface-active agent but if desired, sodium 2-ethyl sulfate can be used which does not foam excessively, or otherwise a more powerful surface-active agent such as sodium lauryl sulfate can be used in conjunction with an anti-foam such as a silicone oil or a tallow alcohol.

The compounds of Table II can be used in amounts between about 0.1 gram/liter and saturation and the preferred organic sulfon-compounds to be used with the compounds of Table I are the benzene sulfonamides and sulfonimides (0.1 gram/liter to saturation) especially when used in conjunction with allyl sulfonic acid (0.6-2 grams/liter) or 2-butyne disulfonic acid (3-10 grams/liter). The preferred compound of Table I is Example 2, which is 3,9-divinyl spirobi (m-dioxane), in a concentration of 0.01 to 0.05 gram/liter.

The baths containing compounds of Table I and Table II are not very sensitive to giving poor adhesion due to broken electrical contacts or to small excesses of these compounds, and therefore these compounds do not readily cause double or laminated plates. For these reasons, the compounds of Table I in conjunction with those of Table II give excellent results in bulk, tumble or barrel plating, as well as in the rack plating of steel, zinc die-cast, aluminum and brass articles. Especially superior results (brightness and ductility) are obtained with rapid agitation (air agitation or hydraulic agitation).

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 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. Furthermore, the conjunctive use of the compounds of Table I with the compounds of Table II does not greatly reduce the excellent properties which are characteristic of all of the organic sulfon-compounds of Table II with respect to the low sensitivity of nickel baths containing the latter organic sulfon-compounds to poor adhesion from broken electrical contacts or delayed electrical contacts or from reverse or anodic currents as in periodic current reversals, or in anodic activation of the nickel plate for re-plate. Delays of as long as one minute before electrical contact is made, or anodic currents for as long as one minute in many cases, do not cause poor adhesion. Zinc ions or cadmium ions can be present in most of the nickel baths, especially in high chloride baths, in concentrations of at least 0.05 to 0.1 gram per liter and also not affect the adhesion during delayed electrical contacts or periodic current reversals. As a matter of fact, the zinc or cadmium present in the nickel plate causes a more shallow type of corrosion pit to occur in the nickel when chromium plated and exposed to a corrosive atmosphere (for example the atmosphere in industrial areas). The relative insensitivity of such baths to passivity from anodic current, makes possible the use of periodic current reversal in its sacrificial form which tends to promote leveling and to improve the corrosion protection afforded to the underlying metal. For

example, after the initial deposition of a thin nickel plate (0.1 to 0.2 mil), a sacrificial periodic current reversal cycle of ten or more seconds anodic current preferably at low anodic current (5 to 10 amps./sq. ft.) with about 1 to 5 seconds cathodic current can be used for periods of about 1 to 2 or more minutes and then the procedure repeated until the desired thickness of plate is obtained. The benzene sulfonamides and sulfonimides and o-benzoyl sulfimide together with small concentrations of the compounds of Table I represent preferred combinations of the compounds of this invention for the periodic current reversal treatments.

Example I

15	NiSO ₄ ·6H ₂ O	-----grams/liter--	200-300
	NiCl ₂ ·6H ₂ O	-----do-----	30-80
	H ₃ BO ₃	-----do-----	30-50
	NaBF ₄	-----do-----	0-0.5
	Example 2 of Table I (3,9-divinyl spirobi (m-dioxane))		
20	Sodium allyl sulfonate	-----grams/liter--	0.01-0.04
	Benbene sulfonamide	-----do-----	0.6-2
	o-Benzoyl sulfimide	-----do-----	1-2
	Temperature	-----° F--	0-2
	pH	-----	120-160
25			3.2-4.8

Example II

	NiCl ₂ ·6H ₂ O	-----grams/liter--	100-200
	NiSO ₄ ·6H ₂ O	-----do-----	0-50
	H ₃ BO ₃	-----do-----	30-50
30	Example 2 of Table I (3,9-divinyl spirobi (m-dioxane))		
	Sodium allyl sulfonate	-----grams/liter--	0.01-0.04
	o-Benzoyl sulfimide	-----do-----	0.6-2
	Benzene sulfonamide	-----do-----	1-2
35	Temperature	-----° F--	1-2
	pH	-----	120-160
			3.2-4.8

Example III

	NiSO ₄ ·6H ₂ O	-----grams/liter--	200-300
40	NiCl ₂ ·6H ₂ O	-----do-----	30-100
	H ₃ BO ₃	-----do-----	30-50
	Example I of Table I (vinyl-m-dioxane)		
	o-Benzoyl sulfimide	-----grams/liter--	0.01-0.05
45	Temperature	-----do-----	0.1-2
	pH	-----° F--	120-160
			3.2-4.8

Example IV

	NiSO ₄ ·6H ₂ O	-----grams/liter--	200-300
50	NiCl ₂ ·6H ₂ O	-----do-----	30-80
	H ₃ BO ₃	-----do-----	30-50
	NaBF ₄	-----do-----	0-0.5
	Example 2 of Table I (3,9-divinyl spirobi (m-dioxane))		
55	2-Butyne 1,4-disulfonic acid Na, K, or Ni salt)	-----grams/liter--	0.01-0.04
	Benzene sulfonamide	-----do-----	3-10
	o-Benzoyl sulfimide	-----do-----	1-2
	Temperature	-----do-----	0-2
60	pH	-----° F--	120-160
			3.2-4.8

The above baths gave brilliant ductile nickel deposits that were remarkably adherent even when electrical contact was not instantly made. Exceptionally good results were obtained with air agitation, especially in baths of Examples I, II and IV.

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

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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 0.002 to about 0.5 gram/liter of a compound selected from the group consisting of vinyl substituted m-dioxane, and di-vinyl substituted bi(m-dioxane), and derivatives thereof, in which derivatives the m-dioxane ring is substituted with a radical selected from the group consisting of chloro, bromo, hydroxy, methoxy, ethoxy and hydroxy-ethoxy radicals.

2. A bath in accordance with claim 1 wherein said vinyl substituted m-dioxane compound is 3,9-divinyl spirobi (m-dioxane) and is present in a concentration in the bath of 0.005 to about 0.2 gram/liter.

3. A bath in accordance with claim 1 wherein the vinyl substituted m-dioxane is 3-vinyl m-dioxane and is dissolved in the said nickel bath in a concentration of 0.005 to about 0.2 gram/liter.

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

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

6. 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

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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 tetrasulfonimides 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 0.002 to about 0.5 gram/liter of a compound selected from the group consisting of vinyl substituted m-dioxane, and di-vinyl substituted bi(m-dioxane), and derivatives thereof, in which derivatives the m-dioxane ring is substituted with a radical selected from the group consisting of chloro, bromo, hydroxy, methoxy, ethoxy and hydroxy-ethoxy radicals.

7. A method in accordance with claim 6 wherein said vinyl substituted m-dioxane compound is 3,9-divinyl spirobi (m-dioxane) and is present in a concentration in the bath of 0.005 to about 0.2 gram/liter.

8. A method in accordance with claim 6 wherein the vinyl substituted m-dioxane is 3-vinyl m-dioxane and is dissolved in the said nickel bath in a concentration of 0.005 to about 0.2 gram/liter.

9. A method in accordance with claim 6 wherein said organic sulfon-compound is allyl sulfonate.

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

No references cited.