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ELECTRODEPOSITION OF NICKEL FROM AN ACID BATH

Henry Brown, Detroit, Mich., assignor to The Udylite Corporation, Detroit, Mich., a corporation of Delaware

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This invention relates to the electrodeposition of nickel from aqueous acidic nickel baths.

The object of this invention is to decrease the grain size and increase the luster and brightness of the nickel deposit without decreasing appreciably the ductility of the plate or the current density range of the nickel bath.

This object can be accomplished by the addition of certain unsaturated aliphatic sulfonamides and sulfonimides such as the alpha and/or beta unsaturated aliphatic sulfonamides and sulfonimides as exemplified by vinyl (ethylene) sulfonamide (CH_2=$CHSO_2NH_2$) and allyl sulfonamide (CH_2=CH—$CH_2SO_2NH_2$). In Table I are listed a number of alpha and beta unsaturated aliphatic sulfonamides and sulfonimides and their optimum concentrations in the nickel baths. Actually they all can be used up to saturation in the baths, that is, they do not have critical upper concentration limits.

The brighteners listed in Table I can be used in any type of operating acidic nickel baths with beneficial effects. In Table II are listed by way of illustration a number of such acidic nickel baths.

The nickel plate obtained with the alpha and beta unsaturated aliphatic sulfonamides and sulfonimides present in the acidic baths is very fine-grained, of good color and ductility, and remarkably free from pitting. On buffed surfaces the plate obtained is at least as good in reflectivity and brightness as the base.

It is a remarkable fact, for example, that in a warm nickel chloride bath (bath No. 2—300 g./l. $NiCl_2 \cdot 6H_2O$ and 35 g./l. H_3BO_3) which gives very brittle darkish plate (evidently due to basic salt inclusions) at pH values of 4–5, the addition of about 4 g./l. of vinyl sulfonamide or allyl sulfonamide (added as the Ni salt) will produce very ductile fine-grained plate of good luster, brightness, and color, under otherwise the same conditions, i. e., temperatures, pH values, and current densities whereas 1,5 naphthalene disulfonic acid or m-benzene disulfonic acid will not accomplish this, and the plate is still very brittle and of poor darkish color, even though finer grained than the plain nickel chloride bath. These facts also hold true in other high speed plating baths containing high nickel chloride concentrations, for example, 150 g./l. of nickel

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sulfate and 150 g./l. of nickel chloride. It is also interesting to note that formaldehyde at about 1 g./l. also gives brittle, darkish, fine-grained, frosty plate in the high nickel chloride baths.

If other nickel brighteners such as, for example, zinc or cadmium in a concentration of about 0.1–0.5 g./l. are present in acidic nickel baths besides a sufficient concentration of a compound (or compounds) of Table I, the plate obtained is brighter than with either material alone in the bath. Also, the bath can tolerate larger concentrations of the zinc and cadmium than the plain bath without getting brittle, darkish, poorly adherent plate. This is also true with respect to thallous and mercuric salts in about the same concentrations. It is also true with respect to the impurity, copper, which does not produce any significant brightness when present in small concentrations, but tends, instead to very readily produce dark deposits, first appearing at the lowest current densities and extending upward as the concentration of copper is increased. In fact with respect to increasing the tolerance of the nickel bath to such materials which plate out preferentially to the nickel and tend at the slightest excess to discolor the very low current areas, vinyl and allyl sulfonamides are extremely good. That is, they are very effective for the very low current density values while at the same time being very effective in brightening for the middle to the very highest current density values.

While the beta unsaturated aliphatic sulfonamides (e. g., allyl sulfonamide) are similar in their effects in the nickel baths to the alpha unsaturated sulfonamide (e. g., vinyl sulfonamide), they differ to a certain degree. The vinyl sulfonamide, for example, makes possible a toleration of somewhat larger concentrations of materials (both inorganic and organic) which plate out preferentially to nickel and which when alone in the bath cause brittle and easily stained plate or poor color. Apparently, the beta olefinic double bond as present in allyl sulfonamide does exert an effect on, or transmits an effect to, the sulfonamide group and increases its reactivity, but not as strongly as does an alpha unsaturated bond. Apparently, conversely the sulfonamide group affects the active unsatura-

tion characteristics of the alpha carbon double bonds more strongly than the more distant beta, that is, the beta double bonds are more strongly olefinic in character, and thus allyl sulfonamide also exerts a brightening effect in a somewhat similar manner as does allyl alcohol, allyl amine, allyl urea, allyl arsonic acid, and acrylic acid. The latter, however, do not increase the toleration of impurities, in fact; they decrease the tolerance. For example, in the high nickel chloride bath (e. g., batn No. 2), the addition of allyl alcohol or allyl amine or sodium or nickel acrylate from 1 g./l. to saturation only produces finer grain but the plate is still dark and very brittle.

The alpha and beta unsaturated aliphatic sulfonamides can be used with beneficial effects in other acidic nickel baths, besides those listed in Table II, for example, in baths made up with nickel sulfamate in whole or in part.

The best buffer as far as the cathode film is concerned is boric acid and is preferred, though other buffers can be used, as, for example, formic, citric, or fluoboric acids.

Mixtures of compounds of Table I can be used with beneficial effects (improved brightness of plate) as, for example, allyl sulfonamide with vinyl sulfonamide. Also mixtures of the compounds of Table I with aryl sulfonates, aryl sulfonamides, aryl sulfimides, aryl sulfone sulfonic acids enhance or improve the brightness of the plate. For example, 1–2 g./l. of o-benzoyl sulfimide with 0.1–1 g./l. of allyl sulfonamide. Also mixtures of vinyl or allyl sulfonamides or sulfonimides with vinyl or allyl sulfonic acids give beneficial effects.

Even concentrations as low as 0.1 g./l. of compounds of Table I show beneficial effects over small ranges of current density, though in general at least 1 g./l. concentrations should be used. The

TABLE I

Alpha and beta unsaturated aliphatic sulfonamides and sulfonimides

		Opt. Conc.
		G./l.
1	$CH_2=C(H)-SO_2NH_2$ (Vinyl (ethylene) sulfonamide)	2-6
2	$CH_2=C(Cl)-SO_2NH_2$	2-6
3	$CH_2=C(Br)-SO_2NH_2$	2-6
4	$CH_2=C(H)-CH_2-SO_2NH_2$ (Allyl sulfonamide)	2.6
5	$CH_3-C(H)=C(H)-CH_2SO_2NH_2$ (Crotonyl sulfonamide)	2-6
6	$CH_2=C(Cl)-C(H)(H)-SO_2NH_2$	2-6
7	$CH_2=C(H)-CH_2-SO_2NHCH_3$	[1] 1
8	$CH_2=C(H)-SO_2NHC_6H_5$	[1] 0.5
9	$-C(H)=C(H)-SO_2NH_2$	2
10	$CH_3-C(SO_2NH_2)=CCl-CHO.H_2O$	0.5-4

[1] Sat.

TABLE II

Bath No.	$NiSO_4 7H_2O$, g./l.	$NiCl_2 6H_2O$, g./l.	Buffer Formula	Buffer g./l.	Other Salts Formula	Other Salts g./l.	Temp., °F.	pH	Current Density, amps./sq. ft.
1	300	45	H_3BO_3 (boric acid)	40			75-160	2-6	10-75
2		300	H_3BO_3	35			75-160	1-5	10-100
3	75	225	H_3BO_3	35			75-160	2-6	10-85
4	300	45	H.COOH (formic acid)	35			75-140	3-6	10-60
5	200 to 300	45	H_3BO_3 + NiF_2 or HF	40 + 4 to 8 + 2 to 4			75-140	2-6	10-60
6	300	45	Citric Acid (nickel salt)	30			75-140	3-6	10-60
7	300	45	H_3BO_3	40	$MgSO_4.7H_2O$	125	75-160	2-6	10-60
8	75		H_3BO_3 + N-citrate	15 + 8	NaCl	40	75	5.5	10-25
9	75		H_3BO_3	15	NH_4Cl + Na_2SO_4	15 + 75	75	5.3	10-25
10	100		H_3BO_3	15	NH_4Cl		75	5.3	5-20

alpha and beta unsaturated sulfonamides and sulfonimides such as the vinyl (ethylene) and allyl sulfonamides are very beneficial when added to acidic nickel baths containing from .1 g./l. to saturation of any one or more of the following: the naphthalene sulfonic acids, the benzene sulfonic acids, the benzene sulfonamides, the diphenyl sulfone sulfonic acids, in that the ductility of the plate and the brightness in the recesses (low current density areas) is improved. This is especially true if the chloride concentration of such nickel baths is above 75 g./l. $NiCl_2.6H_2O$.

I claim:

1. A bath for electrodepositing fine-grained, lustrous nickel comprising essentially an aqueous acid solution of a material selected from the group consisting of nickel chloride, nickel sulfate, a mixture of nickel sulfate and nickel chloride, nickel sulfamate, a mixture of nickel sulfamate and nickel chloride, nickel fluoborate, a mixture of nickel fluoborate and nickel chloride, a mixture of nickel fluoborate and nickel sulfate, a mixture of nickel sulfate, nickel chloride and nickel fluoborate, and a mixture of nickel fluobo-

rate and nickel sulfamate, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of alpha unsaturated aliphatic sulfonamides and sulfonimides and beta unsaturated aliphatic sulfonamides and sulfonimides in a concentration sufficient to increase the luster and brightness of the nickel deposit and falling within a range from .05 gram per liter to saturation.

2. A bath for electrodepositing fine-grained, lustrous nickel comprising essentially an aqueous acid solution of a material selected from the group consisting of nickel chloride, nickel sulfate, a mixture of nickel sulfate and nickel chloride, nickel sulfamate, a mixture of nickel sulfamate and nickel chloride, nickel fluoborate, a mixture of nickel fluoborate and nickel chloride, a mixture of nickel fluoborate and nickel sulfate, a mixture of nickel sulfate, nickel chloride and nickel fluoborate, and a mixture of nickel fluoborate and nickel sulfamate, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of vinyl (ethylene) sulfonamide and allyl sulfonamide in a concentration sufficient to increase the luster and brightness of the nickel deposit and falling within a range from 0.5 gram per liter to saturation.

3. A method for electrodepositing fine-grained, lustrous nickel comprising the step of electrodepositing fine-grained, lustrous nickel from an aqueous acid plating solution having dissolved therein and constituting the essential electrolyte thereof a material selected from the group consisting of nickel chloride, nickel sulfate, a mixture of nickel sulfate and nickel chloride, nickel sulfamate, a mixture of nickel sulfamate and nickel chloride, nickel fluoborate, a mixture of nickel fluoborate and nickel chloride, a mixture of nickel fluoborate and nickel sulfate, a mixture of nickel sulfate, nickel chloride and nickel fluoborate, and a mixture of nickel fluoborate and nickel sulfamate, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of alpha unsaturated aliphatic sulfonamides and sulfonimides and beta unsaturated aliphatic sulfonamides and sulfonimides in a concentration sufficient to increase the luster and brightness of the nickel deposit and falling within a range from .05 gram per liter to saturation.

4. A method for electrodepositing fine-grained, lustrous nickel comprising the step of electrodepositing fine-grained, lustrous nickel from an aqueous acid plating solution having dissolved therein and constituting the essential electrolyte thereof a material selected from the group consisting of nickel chloride, nickel sulfate, a mixture of nickel sulfate and nickel chloride, nickel sulfamate, a mixture of nickel sulfamate and nickel chloride, nickel fluoborate, a mixture of nickel fluoborate and nickel chloride, a mixture of nickel fluoborate and nickel sulfate, a mixture of nickel sulfate, nickel chloride and nickel fluoborate, and a mixture of nickel fluoborate and nickel sulfamate, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of vinyl (ethylene) sulfonamide and allyl sulfonamide in a concentration sufficient to increase the luster and brightness of the nickel deposit and falling within a range from .05 gram per liter to saturation.

HENRY BROWN.

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