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ELECTRODEPOSITION OF NICKEL FROM AN ACID BATH

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2 Claims. (Cl. 204—49)

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 alifatic sulfonic acids such as the alpha and/or beta unsaturated alifatic acids as exemplified by vinyl sulfonic acid ($CH_2{=}CHSO_3H$) and allyl sulfonic acid ($CH_2{=}CH{-}CH_2SO_3H$). In Table I are listed a number of alpha and beta unsaturated alifatic sulfonic acids 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 brightness 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 sulfonic acids present in the acidic baths is very fine-grained, of good color and ductile, and remarkably free from pitting. On buffed surfaces the plate obtained is as good in reflectivity and brightness as the base.

It is a surprising and remarkable fact, for example, that in a warm nickel chloride bath (Bath No. 2—300 g./l.$NiCl_2.6H_2O$ 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 8 g./l. of vinyl sulfonic or allyl sulfonic acid (added as the Ni salt) will produce very ductile fine-grained plate of good luster or brightness and color under otherwise the same conditions, i. e., temperatures, pH values, and current densities whereas 1,5 naphthalene disulfonic acid will not accomplish this, and the plate is still very brittle and of poor color (it is, however, 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 sulfate and 150 g./l. of nickel chloride. It is also interesting to note that formaldehyde alone at about 1 g./l. also gives brittle, darkish, fine-grained, frosty plate in the high nickel chloride baths.

If other nickel brightners 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 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 appreciable 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, the vinyl and allyl sulfonic acids are extremely good. That is, they are very effective for the very low current density values while at the same time being very effective for the middle and high current density values.

While the beta unsaturated alifatic sulfonic acids (i. e., allyl sulfonic acid) are similar in their effects in the nickel baths to the alpha unsaturated sulfonic acids (e. g., vinyl sulfonic acid), they differ to a certain degree. The vinyl sulfonic acid, for example, makes possible a toleration of 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 sulfonic acid does exert an epect on, or transmits an effect to, the sulfonic group and increases its reactivity, but not as strongly as does an alpha unsaturated bond. Apparently, conversely the sulfonic group affects the active unsaturation 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 sulfonic acid 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., Bath No. 2), the addition of sodium or nickel acrylate from 1 g./l. to saturation only produces finer grain but the plate is still dark and very brittle.

It is also interesting to note that saturated alifatic sulfonic acids (when pure), unlike the alpha or beta unsaturated alifatic sulfonic acids, do not produce brightness or such desirable effects as an increase in tolerance to materials which plate out preferentially to nickel and cause deposits of poor color in the low current density areas. Often impure saturated alifatic sulfonic acids tend to produce some transient brightening effects, and this I have found to be due to traces of mercaptans or sulfites left over from some of the starting materials used in the synthesis. For example, pure ethane sulfonic acid or pure 2-bromo ethane sulfonic acid do not produce any appreciable brightening effect, nor do pure saturated alifatic sulfones such as "Sulfonal."

The alpha and beta unsaturated sulfonic acids 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 sulfonic acid with vinyl sulfonic. 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, 0.1–.2 g./l. of o-benzoyl sulfimide with 0.1–3 g./l. of vinyl and allyl sulfonic acids. In general the nickel salts of the alpha or beta unsaturated alifatic sulfonic acids are preferred for additions instead of the free acids in order not to alter the pH of the baths very much.

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 alpha and beta unsaturated sulfonic acids such as the vinyl (ethylene) sulfonic acids and the allyl sulfonic acids 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. $NiCl_2.6H_2O$.

TABLE I

Alpha and beta unsaturated aliphatic sulfonic acids

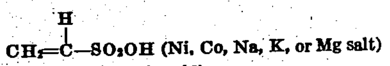
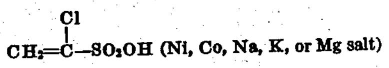
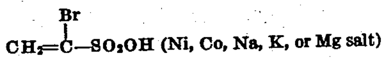
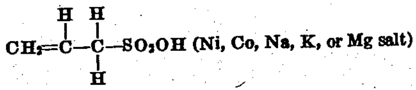
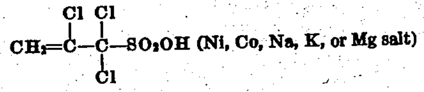
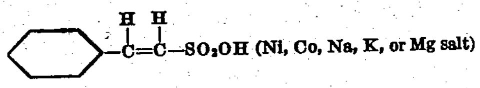
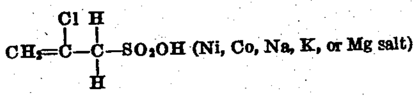
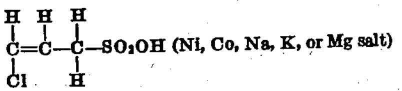
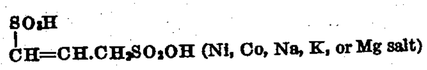
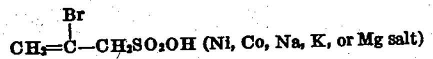
		Opt. Conc. (g./l.)
1.	 $CH_2{=}\overset{H}{C}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt) (vinyl sulfonic acid)	1-8
2.	 $CH_2{=}\overset{Cl}{C}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt)	1-8
3.	 $CH_2{=}\overset{Br}{C}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt)	1-8
4.	 $CH_2{=}\overset{H}{C}{-}\overset{H}{\underset{H}{C}}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt) (allyl sulfonic acid)	1-8
5.	 $CH_2{=}\overset{Cl}{C}{-}\overset{Cl}{\underset{Cl}{C}}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt)	1-6
6.	 (Ni, Co, Na, K, or Mg salt)	1-8
7.	 $CH_2{=}\overset{Cl}{C}{-}\overset{H}{\underset{H}{C}}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt) (2 chloro allyl sulfonate)	1-8
8.	 $\overset{H}{\underset{Cl}{C}}{=}\overset{H}{C}{-}\overset{H}{\underset{H}{C}}{-}SO_2OH$ (Ni, Co, Na, K, or Mg salt) (3-chloro allyl sulfonate)	1-8
9.	 $\overset{SO_3H}{CH}{=}CH.CH_2SO_2OH$ (Ni, Co, Na, K, or Mg salt)	1-8
10.	 $CH_2{=}\overset{Br}{C}{-}CH_2SO_2OH$ (Ni, Co, Na, K, or Mg salt) (2-bromo allyl sulfonic acid)	1-8

TABLE II

Bath No.	NiSO₄ 7H₂O, g./l.	NiCl₂ 6H₂O, g./l.	Buffer		Other Salts		Temp., °F.	pH	Current Debsity amps./sq. ft.
			Formula	g./l.	Formula	g./l.			
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	do	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 Ni-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		do	15	NH_4Cl		75	5.3	5–20

The allyl sulfonate suppresses hydrogen evolution and for this reason tends to prevent pitting. In nickel baths that employ naphthalene sulfonic acids or benzene sulfonamides or sulfonimides with wetting agents, it is of rather common occurrence that concentrated pitting will start on the underside of work when the baths are contaminated with small amounts of oily material. If to such baths is added about 1 gram per liter of sodium or nickel allyl sulfonate, the "grease pitting" or foam pitting is usually eliminated because of the suppression of hydrogen evolution.

This application is a continuation-in-part of my copending application Serial No. 603,753, filed July 7, 1945.

I claim:

1. A bath for electrodepositing fine-grained, lustrous nickel consisting essentially of 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, a mixture of nickel fluorborate and nickel chloride, a mixture of nickel fluoborate and nickel sulfate, a mixture of nickel sulfate, nickel chloride and nickel fluoborate, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of allyl sulfonic acid

$$(CH_2{=}CH{-}CH_2SO_3H)$$

chlor allyl sulfonic acid and brom allyl sulfonic acid, said unsaturated organic compound having a concentration in the bath falling within a range of from about 1 gram per liter to saturation.

2. A method for electrodepositing fine-grained, lustrous nickel comprising the step of electrodepositing fine-grained, lustrous nickel from an aqueous acid solution consisting essentially of a material selected from the group consisting of nickel chloride, nickel sulfate, a mixture of nickel sulfate and nickel chloride, 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, said solution also having dissolved therein an unsaturated organic compound selected from the group consisting of allyl sulfonic acid ($CH_2{=}CH{-}CH_2SO_3H$), chlor allyl sulfonic acid and brom allyl sulfonic acid, said unsaturated organic compound having a concentration in the bath falling within a range of from about 1 gram per liter to saturation.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,818,229	Lutz	Aug. 11, 1931
2,029,387	Pine	Feb. 4, 1936
2,112,818	Waite	Mar. 29, 1938
2,125,229	Harshaw et al.	July 26, 1938
2,171,842	Barrett et al.	Sept. 5, 1939
2,198,267	Lind et al.	Apr. 23, 1940