United States Patent Office 3,075,898
Patented Jan. 29, 1963

3,075,898

ELECTRODEPOSITION OF NICKEL

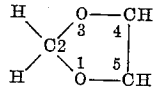
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No Drawing. Filed May 29, 1961, Ser. No. 113,061
10 Claims. (Cl. 204—49)

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

More particularly it relates to improvements in the electrodeposition of semi-bright sulfur-free nickel by the use of new unsaturated organic compounds added to Watts type nickel baths, and to the electrodeposition of improved bright nickel by the use of these new unsaturated compounds in conjunction with the organic sulfon-compounds of the type illustrated in Table I.

It has now been found that by reacting unsaturated alifatic alcohols and carboxylic acids of 6 carbons or less with 1,3-dioxolane shown in the formula designated (A),



(A)

or the hydroxymethyl or methyl derivatives of 1,3-dioxolane in the presence of acidic catalysts preferably under essentially anhydrous conditions, adduct compounds are formed which give greatly improved results in obtaining semi-bright sulfur-free nickel from acidic nickel baths and fully bright high leveling nickel plate when used in conjunction with the organic sulfon-compounds of Table I.

The unsaturated alifatic alcohols and carboxylic acids of 6 carbons and less which react with the 1,3-dioxolanes in the presence of acidic catalysts to give improved addition agents in the nickel baths include allyl alcohols, butenediol, propargyl alcohol, methyl butynol, butynediol, methyl pentynol, and acrylic, maleic, fumaric, itaconic, aconitic, propiolic and acetylene dicarboxylic acids.

The reacted ratio of 1 mole to 2 moles of 1,3-dioxolane with 1 mole of unsaturated alcohol in the presence of an acidic catalyst gives the following improved results. With allyl alcohol, the adduct compound is far less volatile and also the strong tendency for allyl alcohol to produce skipped plate in the low current density areas is greatly decreased. The same holds true for the improvements obtained with the 1,3-dioxolane adducts of propargyl alcohol, methyl butynol and methyl pentynol. With butynediol, the tendency to form harmful electrolytic breakdown products with continuous plating is greatly decreased, and far better plating results are obtained at the higher bath temperatures of, for example, 60° to 70° C. from the standpoint of far less tendency to form dullish areas of plate. This is also true of the 1,3-dioxolane adduct of butenediol compared to butenediol. In the case of the unsaturated acids, acrylic, maleic, fumaric, itaconic, aconitic, propiolic and acetylene dicarboxylic acids used alone in the nickel baths, only darkish plate is produced, and when used together with the organic sulfon-compounds practically no enhanced brightness results. In comparison, however, the use of the adduct compounds of these unsaturated acids formed with the 1,3-dioxolane in the ratio of 1 mole of the dioxolane to each dicarboxylic acid group products astoundingly different results. These adducts used alone in the Watts type nickel bath produce semi-bright, ductile, leveling nickel plate and when used in conjunction with the organic sulfon-compounds produce ductile, high leveling, fully bright nickel plate.

Instead of the 1,3-dioxolane adducts, the hydroxymethyl-1,3-dioxolane and methyl dioxolane adducts may be used with about equally excellent results.

The exact structure of the 1,3-dioxolane adducts is not definitely known in these cases, but the adduct reaction only goes with acidic catalysts and not alkaline catalysts.

With the unsaturated alcohols, the adduct reaction with the 1,3-dioxolanes goes very well under moderate acid catalysts, but with the unsaturated acids, it is best to react the acids with the 1,3-dioxolanes formed in situ from formaldehyde or acetaldehyde and ethylene glycol as illustrated with organic acids in U.S. Patent 2,366,738, issued January 9, 1945, to D. J. Loder and W. F. Gresham.

For semi-bright sulfur-free nickel plating the adducts can be used with other well known addition agents such as formaldehyde, bromal hydrate, chloral hydrate, coumarin, etc. Also for fully bright plate, the adducts can be used in conjunction with amino, polyamino, and heterocyclic amino compounds such as those disclosed in U.S. Patents 2,647,866 and 2,648,628, together with organic sulfon-compounds.

For the semi-bright sulfur-free nickel, the Watts type bath is preferred, though good results are obtained with other bath compositions such as a dilute all chloride nickel bath, or in the fluoborate nickel baths. For fully bright nickel plate, excellent results can also be obtained in the chloride, fluoborate and sulfamate baths as well as the Watts. Boric acid is the best buffer, but other buffers such as formic, acetic, citric, succinic acids may be used, with or without the boric aid. The baths may be operated at pH values of 2 to 6, with best results at pH values of about 3.5 to 5. The bath temperatures may be from room to at least about 90° C., but the preferred temperatures are from 50 to 70° C.

The preferred concentrations of the adducts may range from about 0.01 to about 1 gram per liter, with the adducts of the unsaturated alcohols used in somewhat lower concentration ranges than those of the glycols, and the adducts of the unsaturated carboxylic acids at somewhat higher concentrations, that is, for the latter, concentrations of even 1.5 grams per liter can be used, although in general, the optimum concentrations range from about 0.01 to 1 gram per liter. Mixtures of adducts may also be used in a total concentration in the above stated range, and are preferred for some applications. Besides the organic sulfon-compounds, the sulfinic acids, especially benzene sulfinic acid or p-toluene sulfinic acid preferably used as the sodium, potassium, zinc or nickel salts, can also be used, alone or in conjunction with the organic sulfon-compounds and together with the adducts.

TABLE I

Organic Sulfon-Compounds

	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-Aldehydo benzene sulfonamide	0.1–1
(9) Sulfomethyl benzene sulfonamide	0.1–6
(10) Benzene sulfonamide m-carboxylic amide	0.1–3
(11) 7-aldehydo 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

Organic Sulfon-Compounds—Continued

	Optimum conc., grams/liter
(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	0.3–5
(36) 2-chlorobutene-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) 1-(2-sulfophenyl) 2-propyn 1-ol	0.1–3.0

The following examples of preferred bath compositions are given to illustrate the use of 1,3-dioxolane adducts for both semi-bright sulfur-free nickel plating (Examples I, II, III) and for fully bright nickel plating (Examples IV, V, VI).

EXAMPLE I

	Grams/liter
$NiSO_4.6H_2O$	200–400
$NiCl_2.6H_2O$	30–50
H_3BO_3	30–40
Adduct of 1 mole, 1,3-dioxolane with 1 mole acrylic acid	0.2–0.5

pH, 3.5–5.0.
Temp., 50–65° C.

EXAMPLE II

$NiSO_4.6H_2O$	200–400
$NiCl_2.6H_2O$	30–50
H_3BO_3	30–40
Adduct of 2 moles 1,3-dioxolane with 1 mole maleic acid or fumaric acid, or acetylene dicarboxylic acid, in a concentration of 0.2–0.5 g./l., together with 0.1–0.2 g./l. bromal hydrate.	

EXAMPLE III

$NiSO_4.6H_2O$	200–400
$NiCl_2.6H_2O$	30–50
H_3BO_3	30–40
Adduct of 1 mole 1,3-dioxolane with 1 mole of butynediol, in a concentration of 0.01 to 0.1 g./l., alone or together with chloral hydrate at 0.02–0.2 g./l., and formaldehyde at 0.02 to 0.1 g./l.	

EXAMPLE IV

$NiSO_4.6H_2O$	50–300
$NiCl_2.6H_2O$	200–50
H_3BO_3	30–40
$Ni(BF_4)_2$	1–6
Adduct of 1 mole of 2-hydroxymethyl-1,3-dioxolane with 1 mole of allyl alcohol, in a concentration of 0.1 to 0.3 g./l. together with the adduct of 2 moles of 5-methyl-1,3-dioxolane with 1 mole butynediol in a concentration of 0.05–0.3 g./l., and in conjunction with 2 to 3 g./l. o-benzoyl sulfimide.	

EXAMPLE V

$NiSO_4.6H_2O$	50–300
$NiCl_2.6H_2O$	200–500
H_3BO_3	30–40
$Ni(BF_4)_2$	1–6
Adduct of 1 mole of 1,3-dioxolane with 1 mole butynediol in a concentration of 0.01 to 0.5 g./l. and N-carboxymethyl quinaldinium chloride in a concentration of 0.003 to 0.02 g./l., and in conjunction with 0.1 to 2 g./l. allyl sulfonic acid and 1 to 3 g./l. o-benzoyl sulfimide and 1 to 2 g./l. of benzene sulfonamide.	

EXAMPLE VII

$NiSO_4.6H_2O$	50–300
$NiCl_2.6H_2O$	200–50
H_3BO_3	30–40
$Ni(BF_4)_2$	1–6
Adduct of 1 mole of 2-hydroxymethyl-1,3-dioxolane with 1 mole methyl butynol in a concentration of 0.01 to 0.02 g./l. and the adduct of 1 mole 1,3-dioxolane and 1 mole butynediol at 0.1 to 0.5 g./l. together with 0.1 to 2 g./l. allyl sulfonate and 2 to 3 g./l. of o-benzoyl sulfimide.	

The following example illustrates a general method useful in the preparation of a 1,3-dioxolane adduct for the nickel electrodeposition process of this invention.

One mole of anhydrous allyl alcohol or anhydrous propargyl alcohol is heated to about 90° C., and 3 ml. of borontrifluoride-etherate catalyst dissolved in 10 ml. of toluene is added gradually, while separately and at the same time about 1.2 moles of the 1,3-dioxolane is also added gradually in the ratio of 1 ml. of the borontrifluoride-etherate toluene mixture with each 8 ml. of dioxolane. After all the catalyst and dioxolane has been added, the mixture is heated for 2 to 3 hours or longer at 95° C. The catalyst is then destroyed by the addition of 8 ml. of aqueous ammonia. The flask is then put under about 15 mm. vacuum and the toluene and any excess dioxolane are distilled over. The temperature should be kept below about 90° C. The adduct compounds should not be distilled because at the high temperatures that would be required they would be subject to alteration such as further polymerization and some decomposition.

What is claimed is:

1. A bath for the electrodeposition of lustrous nickel plate comprising essentially an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said bath having dissolved therein, in a concentration of 0.01 to about 1 gram per liter, an adduct formed by the acid catalyzed reaction of a 1,3-dioxolane selected from the group consisting of 1,3-dioxolane and the hydroxymethyl and methyl substituted 1,3-dioxolanes and an unsaturated compound containing a multiple bond carbon to carbon linkage selected from the group consisting of allyl alcohol, butenediol, propargyl alcohol, methyl butynol, methyl pentynol, butynediol and acrylic, maleic, fumaric, itaconic, aconitic, propiolic and acetylene dicarboxylic acids, said adduct formed in the ratio of 1 to 2 moles of the 1,3-dioxolane to 1 mole of the unsaturated compound.

2. A bath in accordance with claim 1 wherein the adduct is formed by the acid actalyzed reaction of 1 mole of 1,3-dioxolane and 1 mole of acrylic acid and is present in the bath in a concentration of 0.1 to 1 gram per liter.

3. A bath in accordance with claim 1 wherein the adduct is the one formed by the acid catalyzed reaction of 1 mole of 1,3-dioxolane and 1 mole of butynediol and

is present in the bath in a concentration of 0.01 to about 0.2 gram per liter together with an aldehyde in a concentration of 0.01 to 0.2 gram per liter selected from the group consisting of formaldehyde, chloral hydrate and bromal hydrate.

4. A bath in accordance with claim 1 wherein the adduct is the one formed by the acid catalyzed reaction of 2 moles of 1,3-dioxolane and 1 mole of acetylene dicarboxylic acid and is present in the bath in a concentration of 0.05 to 0.5 gram per liter.

5. A bath in accordance with claim 1 wherein the bath also contains dissolved therein an organic sulfon-compound in a concentration of 0.1 gram per liter to saturation to give a fully bright nickel plate.

6. A method for the electrodeposition of lustrous nickel comprising the step of electrodepositing lustrous nickel from an aqueous acidic nickel plating bath comprising essentially a nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said solution containing dissolved therein in a concentration of 0.01 to about 1 gram per liter an adduct formed by the acid catalyzed reaction of a 1,3-dioxolane selected from the group consisting of 1,3-dioxolane and the hydroxymethyl and methyl substituted 1,3-dioxolanes and an unsaturated compound containing a multiple bond carbon to carbon linkage selected from the group consisting of allyl alcohol, butenediol, propargyl alcohol, methyl butynol, methyl pentynol, butynediol, and acrylic, maleic, fumaric, itaconic, aconitic propiolic and acetylene dicarboxylic acids, said adduct formed in the ratio of 1 to 2 moles of the 1,3-dioxolane to 1 mole of the unsaturated compound.

7. A method for the electrodeposition of lustrous nickel in accordance with claim 6 wherein the adduct is the one formed by the acid catalyzed reaction of 1 mole of 1,3-dioxolane and 1 mole of acrylic acid and is present in the bath in a concentration of 0.1 to 1 gram per liter.

8. A method for the electrodeposition of lustrous nickel in accordance with claim 6 wherein the adduct is one formed by the acid caatlyzed reaction of 1 mole of 1,3-dioxolane and 1 mole of butyne diol and is present in the bath in a concetnration of 0.01 to about 0.2 gram per liter together with an aldehyde in a concentration of 0.01 to 0.2 gram per liter selected from the group consisting of formaldehyde, chloral hydrate and bromal hydrate.

9. A method for the electrodeposition of lustrous nickel in accordance with claim 6 wherein the adduct is the one formed by the acid catalyzed reaction of 2 moles of 1,3-dioxolane and 1 mole of acetylene dicarboxylic acid and is present in the bath in a concentration of 0.05 to 0.5 grams per liter.

10. A method for the electrodeposition of lustrous nickel in accordance with claim 6 wherein the bath also contains dissolved therein an organic sulfon-compound in a concentration of 0.1 gram per liter to saturation to give a fully bright nickel plate.

References Cited in the file of this patent

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