United States Patent Office 2,800,441 Patented July 23, 1957

2,800,441

ELECTRODEPOSITION OF NICKEL

Henry Brown, Huntington Woods, and Richard J. Clauss, Grosse Pointe Park, Mich., assignors to The Udylite Research Corporation, Detroit, Mich., a corporation of Michigan

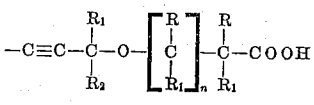
No Drawing. Application October 4, 1955, Serial No. 538,528

14 Claims. (Cl. 204—49)

This invention relates to the electrodeposition of ductile, fine-grained, bright nickel from aqueous acidic nickel baths.

This object can be accomplished by the use in Watts type nickel baths or modifications thereof, of certain soluble unsaturated organic compounds exemplified in Table I, together with one or more of the organic sulfon-compounds exemplified in Table II.

The unsaturated compounds of Table I consist of alkynoxy alkane carboxylic acids especially alkynoxy acetic, propionic, succinic, and propane tricarboxylic acids containing a total of from five to fifteen carbon atoms. The unsaturation of these compounds is due to the triple bonded carbon to carbon linkage (—C≡C—), and the unsaturated linkage is separated from the carboxyl group by two to four inclusive carbon atoms and one intervening or intermediate oxygen atom linkage. The compounds of Table I can be characterized by the following grouping (A):



(A)

where

R=H, CH_3, COOH, or CH_2COOH
R_1=H, or CH_3
R_2=H, CH_3, or C_2H_5
n=0 or 1

If the carboxylic group is in alpha position to the triple bond, that is, directly connected to the triple bonded carbon to carbon linkage, as in propiolic acid

HC≡C—COOH

or in acetylene dicarboxylic acid

HOOC≡C—C—COOH

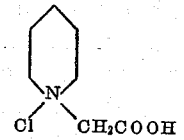
brightening only over a narrow current density range is obtained, and the low current density plate is dull and dark, and of poor ductility, when used in conjunction with the organic sulfon-compounds of Table II. This is similar to a certain extent to the results with acrylic acid, CH_2=CH—COOH, and maleic acid

HOOC—C=C—COOH

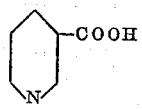
However, if the carboxyl group is separated from the triple bonded carbon atom by two to four carbon atoms and one intervening or intermediate oxygen atom linkage (—O—), as shown in Formula (A) above, then very bright ductile plate is obtained with a very good rate of brightening, over a very wide current density range. If, on the other hand, an intermediate sulfur atom linkage (—S—) is present instead of the intermediate oxygen atom in the above carboxylic compounds, a very pronounced dulling effect occurs, obscuring almost completely the brightness given by the most effective organic sulfon-compounds of Table II. If an

—NH—, —N(CH_3)—, —N(C_2H_5)—, or —N(C_6H_5)—

linkage is present instead of oxygen, the brightening produced by these unsaturated compounds is poor, offering little improvement over the brightness given by the sulfon-compounds of Table II. Thus, in certain respects and within certain compounds, the unsaturated —C≡C— bond acts not only like the —C=C— bond, but also like the unsaturated —C=N— bond. For example, with pyridine, when the carboxylic group is attached in quaternary form, the compound



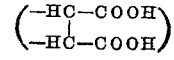
is an excellent brightener, whereas, the compound



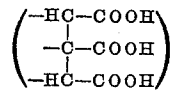
is a poor brightener, when used in conjunction with the organic sulfon-compounds of Table II.

The unsaturated compounds of Table I carrying the —C≡C— bond with a carboxyl group separated from the triple bond by two to four carbon atoms and an intermediate or intervening oxygen atom, when used in conjunction with the compounds of Table II, not only make possible very bright ductile plate over a very wide current density range, but also are not very critical to causing misplating or dark plate in the low current density areas (recesses of articles).

The preferred alkane carboxylic acid groupings in the alkynoxy alkane carboxylic compounds of this invention are those with —CH_2— or —CH_3 radical per carboxylic group such as in acetic acid (—CH_2COOH), succinic acid



and propane tricarboxylic



From the standpoint of low price and efficacy in the baths the preferred compounds are the alkynoxy acetic acids such as 2-butynoxy-1, 4-diacetic acid, and 2-propynoxy-1-acetic acid. Alkynoxy alkane carboxylic acids in which the alkane group is greater than propane, as for example in butyric, valeric, and caprylic, etc. acids, are of limited solubility in the baths and also are of an oily or fatty nature and are not as desirable to use.

The unsaturated compounds of Table I give especially high brilliance and ductility when used in conjunction with about 0.1 to 1 gram per liter of allyl sulfonic acid, and a second organic sulfon-compound selected from benzene sulfonic acids, benzene sulfonamides and benzene sulfonimides or mixtures, the latter organic sulfon-compounds in a concentration of about 0.1 to 6 grams per liter.

The compounds of Table I can be used as the free acids

or their nickel, sodium, potassium, magnesium, cobalt, ferrous, etc. salts. When dissolved in the nickel baths they are present predominantly as the free acids and their nickel salts.

TABLE I

Alkynoxy Alkane Carboxylic Acids	Useful Concentration, Grams per Liter (g/l.)
1. Propynoxy acetic acid $HC\equiv C-CH_2OCH_2-COOH$	0.005-0.15
2. Propynoxy propionic acid $HC\equiv C-CH_2OC_2H_4-COOH$	0.005-0.15
3. Chloropropynoxy-1-acetic acid $ClC\equiv C-CH_2OCH_2-COOH$	0.01-0.2
4. Butynoxy-1-acetic acid $CH_3-C\equiv C-CH_2OCH_2-COOH$	0.03-0.5
5. Hydroxy-2-butynoxy-1-acetic acid $HO-CH_2-C\equiv C-CH_2OCH_2COOH$	0.03-0.6
6. 4-Hydroxy-2-butynoxy-1-propionic acid $HO-CH_2-C\equiv C-CH_2OC_2H_4-COOH$	0.03-0.6
7. Dipropynoxy acetic acid $(HC\equiv C-CH_2O)_2CH-COOH$	0.01-0.12
8. Butynoxy-1,4-diacetic acid $HOOC-CH_2OCH_2-C\equiv C-CH_2OCH_2-COOH$	0.04-1.5
9. Butynoxy-1,4-dipropionic acid $HOOC-C_2H_4OCH_2-C\equiv C-CH_2OC_2H_4-COOH$	0.03-2.0
10. Methyl propynoxy acetic acid $HC\equiv CH(CH_3)-OCH_2-COOH$	0.01-0.12
11. Dimethyl propynoxy acetic acid $HC\equiv C-C(CH_3)_2-OCH_2-COOH$	0.01-0.12
12. Methyl ethyl propynoxy acetic acid $HC\equiv C-C(C_2H_5)(CH_3)-OCH_2-COOH$	0.01-0.14
13. Methyl propynoxy propionic acid $HC\equiv C-CH(CH_3)-OC_2H_4-COOH$	0.01-0.14
14. Propynoxy malonic acid $HC\equiv C-CH_2OC(COOH)(COOH)$	0.01-0.15
15. Dimethyl butynoxy 1,4 diacetic acid $HOOC-CH_2O-CH(CH_3)-C\equiv C-CH(CH_3)-OCH_2-COOH$	0.03-0.5
16. Di-(hydroxy butynoxy) succinic acid $HO-CH_2-C\equiv C-CH_2O-CH-COOH$ $HO-CH_2-C\equiv C-CH_2O-CH-COOH$	0.03-0.15
17. Di-propynoxy acetic acid $(HC\equiv C-CH_2O)_2CH-COOH$	0.005-0.12
18. Di-propynox succinic acid $HC\equiv C-CH_2O-CH-COOH$ $HC\equiv C-CH_2O-CH-COOH$	0.01-0.15

Table I—Continued

Alkynoxy Alkane Carboxylic Acids	Useful Concentration, Grams per Liter (g/l.)
19. Di-propynoxy propane tricarboxylic acid CH_2-COOH $HC\equiv C-CH_2O-C-COOH$ $HC\equiv C-CH_2O-C-COOH$	0.01-0.2
20. Di-(hydroxy butynoxy) propane tricarboxylic acid CH_2-COOH $HO-CH_2-C\equiv C-CH_2O-C-COOH$ $HO-CH_2-C\equiv C-CH_2O-CH-COOH$	0.03-0.6
21. 6-Hydroxy-2,4-hexadiyne-1-acetic acid $HO-CH_2-C\equiv C-C\equiv C-CH_2OCH_2-COOH$	0.02-0.5
22. 2,4-Hexadiyne-1,6-diacetic acid $HOOC-CH_2OCH_2-C\equiv C-C\equiv C-CH_2OCH_2COOH$	0.03-0.6
23. 3-Methyl-2-butynoxy-1,4, diacetic acid $HOOC-CH_2O-CH(CH_3)-C\equiv C-CH_2OCH_2COOH$	0.03-1.6
24. Di-propynoxy methyl succinic acid $HC\equiv C-CH_2O-CH_2$ $HC\equiv C-CH_2O-C-COOH$ $H_2C-COOH$	0.005-0.12

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-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
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-sulfobenzaldehyde	1-5
26	m-Benzene disulfonamide	0.5-1
27	Allyl sulfonic acid	0.4-12
27a	Dichlorobenzene sulfonic acids	0.5-8
28	Di-benzene sulfonimide	0.1-3
29	Di-toluene sulfonimide	0.1-3
30	2-Butyne-1, 4-disulfonic acid	5-20
31	4-Hydroxy-2-butyne-1-sulfonic acid	0.2-2
32	2-Butyne-1-sulfonic acid	0.05-1.5
33	3-Chloro-2-propyne-1-sulfonic acid	0.05-1.5
34	2-butene-1, 4-disulfonic acid	0.3-5
35	2-chloro butene-4-sulfonic acid	0.3-5
36	2-chloro-propene sulfonic acid	0.1-1.5
37	Cinnamyl sulfonic acid	0.1-3.0
38	3-Phenyl-2-propyne-1-sulfonic acid	0.3-3.0

Below are listed examples which illustrate various preferred combinations of addition agents to give bright ductile plate over a wide cathode current density range. To prevent hydrogen gas pitting, suitable surface active agents such as sodium lauryl glycol ether sulfate or sodium lauryl sulfate can be used, or air or mechanical solution agitation. When air agitation is employed, the use of about 0.3 to 1 gram per liter of allyl sulfonic acid in the baths is very advantageous in preventing hydrogen

gas pitting of the cathode without the use of surface active agents, and besides it greatly improves the brilliance of the plate, with and without air agitation. The faster the agitation of the solution or of the cathode, the less the concentration of the compounds of Table I that need to be employed to obtain high brilliance, also the brighter the plate at a given ductility. At the higher temperatures of the bath, the less the concentration of the compounds of Table I that need to be used to obtain bright plate at rapid rates of solution agitation. It is to be understood that the compounds of Tables I and II may be used in various combinations in baths of the general type illustrated below by employing the concentrations indicated in Tables I and II.

The cathode current densities to be used in the following examples average from about 10 to 200 amps./sq. ft. depending mainly on the temperature, degree of solution agitation, and the composition of the bath. Higher temperatures and higher degrees of agitation permit higher current densities to be employed satisfactorily.

Example 1

	g./l.
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45

Propynoxy propionic acid

$(HC{\equiv}C{-}CH_2O{-}C_2H_4COOH)$

at 0.01 to 0.12 g./l.
Allyl sulfonic acid at 0.3 to 1.5 g./l.
o-Benzoyl sulfimide at 0.1 to 2 g./l.
pH=2.5 to 4.8, temp.=45° C. to 70° C.

Example 2

	g./l.
$NiSO_4.6H_2O$	150–300
$NiCl_2.6H_2O$	30–60
H_3BO_3	30–40

Butynoxy-1,4-diacetic acid

$(HOOC{-}CH_2OCH_2{-}C{\equiv}C{-}CH_2{-}OCH_2COOH)$

at 0.05 to 0.6 g./l.
Allyl sulfonic acid at 0.5 to 1.5 g./l.
o-Benzoyl sulfimide at 0.1 to 0.3 g./l.
pH=2.5 to 4.5, temp.=45° C. to 80° C. (113° F.–176° F.)

Example 3

	g./l.
$NiCl_2.6H_2O$	150
H_3BO_3	40–50
$NaBF_4$	0–3

Propynoxy acetic acid ($HC{\equiv}C{-}CH_2{-}O{-}CH_2COOH$) at 0.005 to 0.08 g./l.
Butynoxy-1,4-diacetic acid

$(HOOC{-}CH_2{-}O{-}CH_2{-}C{\equiv}C{-}CH_2{-}O{-}CH_2COOH)$

at 0.05 to 0.5 g./l.

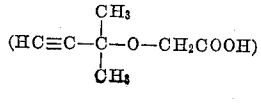
	g./l.
Allyl sulfonic acid	0.5 to 1.5
o-Benzoyl sulfimide	0.5 to 3

pH=2.5 to 4.5, temp.=45° C. to 75° C.

Example 4

	g./l.
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45

Dimethyl propynoxy acetic acid

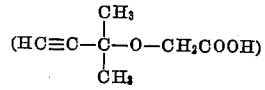


at 0.01 to 0.12 gram per liter
Allyl sulfonic acid at 0.3 to 1 g./l.
o-Benzoyl sulfimide at 0.1 to 2 g./l.
Benzene disulfonic acid at 2 to 6 g./l.
pH=2.5 to 4.8, temp.=45° C. to 80° C.

Example 5

	g./l.
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45

Dimethyl propynoxy acetic acid



at 0.005 to 0.08 gram per liter
Butynoxy-1,4-diacetic acid

$(HOOC{-}CH_2OCH_2{-}C{\equiv}C{-}CH_2OCH_2COOH)$

at 0.03 to 0.3 g./l.
Butyne-1,4-disulfonic acid

$(HO_3S{-}CH_2{-}C{\equiv}C{-}CH_2{-}SO_3H)$

at 3–10 g./l.
o-Benzoyl sulfimide at 0.1 to 2 g./l.
Benzene sulfonic acid at 2 to 6 g./l.
pH=2.5 to 4.8, temp.=45° C. to 80° C.

Example 6

	g./l.
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45

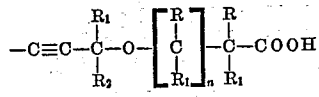
Propynoxy acetic acid ($HC{\equiv}C{-}CH_2O{-}CH_2COOH$) at 0.005 to 0.12 g./l.
Allyl sulfonic acid at 0.1 to 1.5 g./l.
o-Sulfobenzaldehyde (formyl benzene sulfonic acid) at 0.5 to 4 g./l.
o-Benzoyl sulfimide at 0.05 to 3 g./l.
pH=2.5 to 5.2, temp.=45° C.–80° C.

Instead of nickel baths made up predominantly of nickel sulfate and nickel chloride, or mixtures of these salts, nickel fluoborate and nickel sulfamate may be used in whole or in part. Instead of boric acid, other buffers such as nickel formate, succinate, citrate, etc., may be used, though in general boric acid is the preferred buffer as it allows the best leveling action. The best pH values for the baths are about 2.5 to 5.0, though pH values from 2 to 6 at least, may be used. The bath temperatures may be from room to boiling, though in general the most convenient temperatures of operation are from about 120° F. to 170° F. Ammonium ions make the plate less ductile, but sodium, lithium, potassium or magnesium ions are not nearly as critical. The bromide ion may be present in high concentrations, but not the iodide ion as the latter in excessive concentration may cause a loss of cathode efficiency (from the free iodine formed by anodic oxidation of the iodide ion). Ferrous salts or cobalt salts or mixtures up to at least a concentration of forty grams per liter as sulphates, chlorides of fluoborates may be present in the nickel bath, and yield nickel alloy plates containing as low as about sixty percent nickel and still the plate obtained is bright and ductile.

What is claimed:

1. A bath for electrodepositing bright nickel comprising 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 also containing dissolved therein about 0.005 to about 2 grams/liter of at least one alkynoxy alkane carboxylic acid having a total of 5 to 15 carbon atoms in which the unsaturated triple bonded carbon to carbon linkage is separated from the carboxyl group by 2 to 4 inclusive

carbon atoms and 1 intermediate oxygen atom, and containing the grouping,

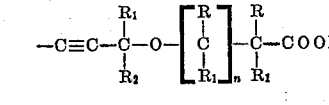


in which R is selected from the group consisting of hydrogen, methyl, carboxyl and carboxymethyl radicals, R_1 is selected from the group consisting of hydrogen and methyl radicals, R_2 is selected from the group consisting of hydrogen, methyl and ethyl radicals, and n is not greater than 1 and in conjunction therewith about 0.1 gram/liter to saturation of at least one brightener selected from the group consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and di-benzene sulfonamides and sulfonimides and the halogenic, methyl, aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

2. A bath for electrodepositing bright nickel comprising 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 also containing dissolved therein 2-butynoxy-1,-4-diacetic acid (HOOC—CH_2—O—CH_2—C≡C—CH_2—O—CH_2—COOH) in a concentration of 0.01 to 0.6 grams/liter, and in conjunction therewith about 0.1 gram/liter to saturation of at least one brightener selected from the group consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and di-benzene sulfonamides and sulfonimides and the halogenic, methyl, aldehydo (formyl) derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

3. A bath for electrodepositing bright nickel comprising 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 also containing dissolved therein 2-propynoxy-1-acetic acid (HC≡C—CH_2OCH_2COOH) in a concentration of 0.005 to 0.15 grams/liter, and in conjunction therewith about 0.1 gram/liter to saturation of at least one brightener selected from the group consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and dibenzene sulfonamides and sulfonimides and the halogenic, methyl, aldehydo (formyl) derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

4. A method for electrodepositing bright nickel which comprises the steps of electrolyzing 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 also containing dissolved therein about 0.005 to about 2 grams/liter of at least one alkynoxy alkane carboxylic acid having a total of 5 to 15 carbon atoms in which the unsaturated triple bonded carbon to carbon linkage is separated from the carboxyl group by 2 to 4 inclusive carbon atoms and 1 intermediate oxygen atom, and containing the grouping,



in which R is selected from the group consisting of hydrogen, methyl, carboxyl and carboxymethyl radicals, R_1 is selected from the group consisting of hydrogen and methyl radicals, R_2 is selected from the group consisting of hydrogen, methyl and ethyl radicals, and n is not greater than 1 and in conjunction therewith about 0.1 gram/liter to saturation of at least one brightener selected from the group consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and di-benzene sulfonamides and sulfonimides and the halogenic, methyl, aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

5. A method in accordance with claim 4 wherein said carboxylic acid is 2-butynoxy-1,4-diacetic acid (HOOC—CH_2OCH_2—C≡C—CH_2OCH_2—COOH) and is present in a concentration of 0.04–1.5 gram/liter.

6. A method in accordance with claim 4 wherein said carboxylic acid is 2-propynoxy-1-acetic acid (HC≡C—CH_2OCH_2COOH) and is present in a concentration of 0.005 to 0.15 gram/liter.

7. A method in accordance with claim 4 wherein said carboxylic acid is propynoxy propionic acid (HC≡C—$CH_2OC_2H_4$—COOH) and is present in a concentration of 0.005–0.15 gram/liter.

8. A method in accordance with claim 4 wherein said carboxylic acid is 1,1-dimethyl-2-propynoxy-1-acetic acid (HC≡C—$C(CH_3)_2$—OCH_2COOH) and is present in a concentration of 0.01 to 0.2 gram/liter.

9. A method in accordance with claim 4 wherein said carboxylic acid is butynoxy-1,4-dipropionic acid (HOOC—$C_2H_4OCH_2$—C≡C—$CH_2OC_2H_4$—COOH) and is present in a concentration of 0.03 to 2.0 grams/liter.

10. A bath for electrodepositing bright nickel in accordance with claim 1 and having dissolved therein propynoxy acetic acid (HC≡C—CH_2OCH_2—COOH) in a concentration of 0.005 to 0.15 gram/liter.

11. A bath for electrodepositing bright nickel in accordance with claim 1 and having dissolved therein 1,1-dimethyl-2-propynoxy-1-acetic acid (HC≡C—$C(CH_3)_2$—OCH_2COOH) in a concentration of 0.01 to 0.2 gram/liter.

12. A bath for electrodepositing bright nickel in accordance with claim 1 and having dissolved therein propynoxy propionic acid (HC≡C—$CH_2OC_2H_4$—COOH) in a concentration of 0.005 to 0.15 gram/liter.

13. A bath for electrodepositiong bright nickel in accordance with claim 1 and having dissolved therein 2-butynoxy-1,4-diacetic acid (HOOC—CH_2OCH_2—C≡C—CH_2OCH_2—COOH) in a concentration of 0.04 to 1.5 gram/liter.

14. A bath for electrodepositing bright nickel in accordance with claim 1 and having dissolved therein butynoxy-1,4-dipropionic acid in a concentration of 0.03 to 2.0 gram/liter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,712,522 Kardos et al. ---------- July 5, 1955