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ELECTRODEPOSITION OF NICKEL

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This invention relates to the electrodeposition of fine-grained lustrous nickel plate from aqueous acidic nickel plating baths. More particularly it relates to the use of certain unsaturated sulfonic acids, particularly aliphatic sulfonic acid (or their sulfonates), in aqueous acidic nickel baths of the Watts type or its modifications, to obtain fine-grained, bright nickel plate.

We have found that certain alkyne and alkynoxy sulfonic acids of three to fourteen carbon atoms inclusive, carrying the unsaturated triple bonded carbon to carbon linkage (—C≡C—), as exemplified in Table I, when dissolved in the Watts type nickel bath or modifications thereof, make possible fine-grained plate of good luster. Depending on the position of the unsaturated linkage with respect to the sulfonic group, and depending also on the position, amount and nature of other groups present, various degrees of luster, brightness and ductility can be obtained. For example, propargyl sulfonic acid (2-propyne-1-sulfonic acid, $HC{\equiv}C{-}CH_2SO_3H$) makes possible the most brilliant and lustrous plate when used alone in the bath at a concentration of about 0.5 to 2 grams per liter, the optimum concentration depending on the temperature of the bath, the pH and on the degree of agitation of the solution or the article being plated (the more rapid the agitation, the smaller the concentration necessary for best results). On the other hand the symmetrical disulfonic acid, 2-butyne-1,4-disulfonic acid

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

requires about 10 to 15 grams per liter to cause good brightness, though the brightness does not equal that obtained with the propargyl sulfonic acid either from the standpoint of leveling or brilliance. However, the plate is more ductile with the disulfonic compound.

The 2-propyne-1-sulfonic acid ($HC{\equiv}C{-}CH_2SO_3H$) differs from 2-propene-1-sulfonic acid (i. e., allyl sulfonic acid, $CH_2{=}CH{-}CH_2SO_3H$), in that the former makes possible more brilliant plate, but plate that is less ductile than that obtained with 2-propene-1-sulfonic acid. In this respect, the plate obtained with 2-butyne-1,4-disulfonic acid is more similar in brightness and ductility to that obtained with 2-propene-1-sulfonic acid, though the latter is more effective. For example, 2 to 4 grams per liter of the latter gives similar plate in brightness and ductility to plate obtained when 10 grams per liter of 2-butyne-1,4-disulfonic acid is used in the Watts type bath, and 20 grams per liter in the high chloride type nickel baths. Also, if 0.01 to 0.03 gram per liter of N-allyl quinaldinium bromide or N-ethyl isoquinolinium bromide and similar compounds are added to the baths, then the bright plate obtained with the butyne disulfonic acid is of improved brilliance similar to the improved brilliance obtained with the allyl sulfonic acid, the comparisons being made in similar baths at similar temperatures and pH values (for example, pH=2.5 to 4.5).

The propargyl sulfonic acid ($HC{\equiv}C{-}CH_2SO_3H$) acts very differently in the nickel baths than does propargyl alcohol ($HC{\equiv}C{-}CH_2OH$). The latter does not produce fully bright plate alone in the bath and is far more sensitive to causing mis-plating (skipped areas free from plate), and it is very volatile and toxic to breathe, whereas, propargyl sulfonic acid, and its nickel salt are not appreciably volatile.

The propynoxy ethane sulfonic acid

$$(HC{\equiv}C{-}CH_2OC_2H_4SO_3H)$$

is different from propargyl alcohol to an exceptional degree in its effect in the bath in that it is very much less critical relative to causing mis-plating or skipped plate, poor adhesion, and brittleness when used with the compounds of Table II even with as low a concentration as 0.1 gram per liter of o-benzoyl sulfimide. Additionally it is non-volatile from the baths. The 2-butyne-1,4-disulfonic acid used alone gives a completely bright plate only at a concentration of 5 to 10 grams per liter in a Watts type bath (high nickel sulfate content) whereas 2-butyne 1,4 diol gives an exceedingly brittle darkish, easily stained and finger-marked, cloudy bright plate when used alone above a concentration of 1 to 3 grams per liter. In a high chloride nickel the 2-butyne-1,4-disulfonic acid alone gives a completely bright plate at a concentration of 10 to 20 grams per liter, where 2-butyne-1,4-diol gives darkish, easily stained and exceedingly brittle plate when used alone in any concentration above about 0.3 gram per liter.

The preferred alkyne sulfonic acids of this invention are the propynoxy ethane sulfonic acids, the propynoxy propane sulfonic acids, and their methyl substituted derivatives such as $HC{\equiv}C{-}C(CH_3)_2OC_2H_4SO_3H$ and $HC{\equiv}C{-}CH(CH_3)OC_2H_4SO_3H$.

If the sulfonic group is more than two carbon atoms away from the unsaturated triple bonded carbon to carbon linkage (—C≡C—), there is less effect from the sulfonic group in that less sulfur is added to the nickel plate and consequently the plates are more cloudy when these compounds are used alone, though there is still the decrease in criticalness with respect to the concentration that can be used in the baths without obtaining mis-plating, poor adhesion, and excessive brittleness. These unsaturated alkyne sulfonic compounds, especially those with the intermediate oxygen atom linkage (—O—) between the unsaturated group and the methane, ethane, propane, or butane sulfonic group (the alkynoxy sulfonic acids), can be used with increased effectiveness from the standpoint of cloud-free brightness, when used in conjunction with at least one organic sulfonic acid or organic sulfon-compound as exemplified in Table II, especially in combinations such as allyl sulfonic acid (2-propene-1-sulfonic acid) or a butene sulfonic acid together with at least one of the benzene sulfonic acids, sulfonamides and sulfonimides, such as benzene mono-, di-, and tri-sulfonic acids, and the fluoro-, chloro, bromo, iodo-, methyl and aldehydo (formyl) benzene sulfonic acids, and naphthalene sulfonic acids, benzene sulfonamide, toluene sulfonamides, di-benzene sulfonamides, di-toluene sulfonamides, o-benzoyl sulfimide, etc. These combinations of organic sulfon-compounds yield very bright ductile plate, and have a minimum of sensitivity to harmful effects (poor adhesion, excessive brittleness, cloudiness and mis-plating) from excess quantities of these compounds being accidentally added to the baths. Of the compounds set forth in Table II a preferred group consists of the benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and di-benzene sulfonamides and sulfonimides and the halogen, methyl, aldehydo (formyl) derivatives thereof and beta unsaturated alkene sulfonic acids having 4–2 carbon atoms.

To prevent pitting from the adhesion of hydrogen gas bubbles to the cathode during plating, certain 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 1.5 grams per liter of allyl sulfonic acid for prevention of hydrogen gas pitting of the cathode, without the use of a surface-active agent, is very advantageous, not only from the standpoint of its de-polarizing action but also because it greatly improves the brilliance of the plate, with 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.

In Table I and Table II below there are listed various examples to illustrate preferred combinations of addition agents (all organic sulfon-compounds) to give bright ductile nickel plate over a wide cathode current density range. The lower concentrations of addition agents are suitable to be used with the more rapid solution agitation and the higher bath temperatures.

TABLE I

	Alkyne and Alkynoxy Sulfonic Acids	Useful Conc. grams/liter
1	$HC\equiv C-CH_2-SO_3H$	0.01-2
2	$CH_3-C\equiv C-CH_2-SO_3H$	0.01-10
3	$Cl-C\equiv C-CH_2-SO_3H$	0.01-2
4	$HC\equiv C-C(CH_3)_2-SO_3H$	0.01-2
5	$H-C\equiv C-CH(C_2H_5)-SO_3H$	0.01-2
6	$HO-CH_2-C\equiv C-CH_2-SO_3H$	0.04-3
7	$HO_3S-CH_2-C\equiv C-CH_2-SO_3H$	3.5-20
8	$Br-C\equiv C-CH_2-SO_3H$	0.01-2
9	$CH_3C(=O)-OCH_2-C\equiv C-CH_2SO_3H$	0.04-3
10	$HOC_2H_4OCH_2-C\equiv C-CH_2SO_3H$	0.04-3
11	$HOOC-CH_2OCH_2-C\equiv C-CH_2-SO_3H$	0.04-3
12	$HC\equiv C-CH_2OCH_2-SO_3H$	0.005-0.2
13	$HC\equiv C-CH_2OC_2H_4-SO_3H$	0.005-0.2
14	$HC\equiv C-CH_2OC_3H_6-SO_3H$	0.01-0.2
15	$(HC\equiv C-CH_2O)_2-C_3H_5-SO_3H$	0.005-0.18
16	$Cl-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.4
17	$CH_3-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.5
18	$HO-CH_2-C\equiv C-CH_2OCH_2-SO_3H$	0.01-0.6
19	$HO-CH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.6
20	$HO_3S-C_2H_4O-CH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-5
21	$HO_3S-CH_2C(=O)-O-CH_2-C\equiv C-CH_2-SO_3H$	0.05-4
22	$ClCH_2C(=O)-O-CH_2-C\equiv C-CH_2OCH_2-SO_3H$	0.01-0.5
23	$HC\equiv C-CH_2OC_2H_4OC_2H_4-SO_3H$	0.01-0.2
24	$HC\equiv C-C(CH_3)_2OC_2H_4-SO_3H$	0.005-0.2
25	$HC\equiv C-CH(CH_3)OCH_2-SO_3H$	0.005-0.2
26	$HC\equiv C-CH(C_2H_5)OC_2H_4-SO_3H$	0.01-0.2
27	$HC\equiv C-C(C_2H_5)(CH_3)OC_2H_4-SO_3H$	0.01-0.2
28	$HO_3S-CH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.04-4
29	$HC\equiv C-CH_2OC_4H_8-SO_3H$	0.01-2
30	$CH_3C(=O)-OCH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.6
31	$HO-CH_2-C\equiv C-CH_2OC_3H_6-SO_3H$	0.01-0.6
32	$HO-CH_2-C\equiv C-CH_2OCH_2-C\equiv C-CH_2-SO_3H$	0.03-3.5
33	$HO-CH_2-C\equiv C-CH_2OCH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.8
34	$HO_3S-C_2H_4OCH_2-C\equiv C-CH_2OCH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-4
35	$HO-CH_2-C\equiv C-C\equiv C-CH_2-SO_3H$	0.03-3.5
36	$HO_3S-CH_2-C\equiv C-C\equiv C-CH_2-SO_3H$	1-10
37	$HO-CH_2-C\equiv C-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.6
38	$HO_3S-C_2H_4OCH_2-C\equiv C-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-4
39	$HO_3S-C_3H_6OCH_2-C\equiv C-CH_2OCH_2-C\equiv C-CH_2OC_3H_6-SO_3H$	0.01-5
40	$HO_3S-C_2H_4OCH_2-C\equiv C-CH_2OC_2H_4OCH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-5
41	$HO-CH_2-C\equiv C-CH_2OC_2H_4OCH_2-C\equiv C-CH_2OC_2H_4-SO_3H$	0.01-0.5
42	$HC\equiv C-CH_2O-C_6H_4-SO_3H$	0.01-0.15
43	$HO_3S-C_6H_4-OCH_2-C\equiv C-CH_2O-C_6H_4-SO_3H$	0.01-1.5
44	$HO-CH_2-C\equiv C-CH_2O-C_6H_4-SO_3H$	0.01-0.7
45	$HC\equiv C-C(CH_3)_2O-C_6H_4-SO_3H$	0.01-0.15
46	$C_6H_5-C\equiv C-CH_2SO_3H$	0.3-4
47	$C_6H_5-C\equiv C-CH_2OC_2H_4SO_3H$	0.03-1.2

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
27-a	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

The examples given below illustrate typical bath compositions and conditions of operation to accomplish the objectives of this invention, but are not intended to limit the invention to the specific materials, the quantities thereof or the conditions set forth therein.

The cathode current densities to be used 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 temperature and higher agitation permits higher current densities to be used satisfactorily.

Example 1

	Grams/liter
$NiSO_4.6H_2O$	150–300
$NiCl_2.6H_2O$	30–60
H_3BO_3	30–40
Chloro-propargyl sulfonic acid ($ClC{\equiv}C{-}CH_2SO_3H$)	0.05–1.5

pH—2.5 to 4.5.
Temperature, 45° C. to 75° C.

Example 2

	Grams/liter
$NiSO_4.6H_2O$	0–300
$NiCl_2.6H_2O$	200–30
H_3BO_3	30–40
2-butyne-1,4-disulfonic acid ($HO_3S{-}CH_2{-}C{\equiv}C{-}CH_2{-}SO_3H$)	10–20
N-Allyl quinaldinium bromide	0.01–0.03

pH—2.5 to 4.5.
Temperature, 45° C. to 80° C. (113° F.–176° F.).

Example 3

	Grams/liter
$NiSo_4.6H_2O$	50–300
$NiCl_2.6H_2O$	250–30
H_3BO_3	30–50
$NaBF_4$	0–3
Propynoxy ethane sulfonic acid ($HC{\equiv}C{-}CH_2OC_2H_4{-}SO_3H$)	0.005–0.15
Allyl sulfonic acid ($CH_2{=}CH{-}CH_2SO_3H$)	0.3–1
o-Benzoyl sulfimide	0.1–2
Benzene sulfonic acid	2–8

pH—2.5 to 4.8.
Temperature, 45° C. to 75° C.

Example 4

	Grams/liter
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45
Propynoxy ethane sulfonic acid ($HC{\equiv}C{-}CH_2OC_2H_4{-}SO_3H$)	0.005–0.08
2 - butynoxy - 1,4 - di-(ethane sulfonic) acid ($HO_3S{-}C_2H_4OCH_2{-}C{\equiv}C{-}CH_2OC_2H_4{-}SO_3H$)	0.3–3.5
Allyl sulfonic acid	0.3–1
o-Benzoyl sulfimide	0.1–2

pH—2.5 to 4.8.
Temperature, 45° C. to 75° C.

Example 5

	Grams/liter
$NiSO_4.6H_2O$	150–300
$NiCl_2.6H_2O$	30–60
H_3BO_3	30–40
2-butyne-1,4-disulfonic acid	5
Propynoxy ethane sulfonic acid	0.01–0.12
Allyl sulfonic acid	0.1–1
Benzene sulfonic acid	4–6
o-Benzoyl sulfimide	0.05–0.3

pH—2.5 to 4.5.
Temperature, 45° C. to 80° C.

Example 6

	Grams/liter
$NiSO_4.6H_2O$	150–300
$NiCl_2.6H_2O$	30–80
H_3BO_3	30–40
2-butynoxy-1,4-di-(ethane sulfonic acid)	0.3–3
4-hydroxy butynoxy-1-sulfonic acid	0.1–1.5
Allyl sulfonic acid	0.4–1.5
o-Benzoyl sulfimide	0.1–0.5

pH—2.5 to 4.8.
Temperature, 45° C. to 80° C.

Example 7

	Grams/liter
$NiCl_2.6H_2O$	150
H_3BO_3	40–50
Dimethyl propynoxy ethane sulfonic acid ($HC{\equiv}C{-}C(CH_3)_2{-}OC_2H_4{-}SO_3H$)	0.01–0.12
Allyl sulfonic acid	0.3–1.5
o-Benzoyl sulfimide	0.5–2
Benzene sulfonic acid	2–8

pH—2.5 to 4.8.
Temperature, 45° C. to 80° C.

Example 8

	Grams/liter
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45
Propynoxy ethane sulfonic acid ($HC{\equiv}C{-}CH_2OC_2H_4{-}SO_3H$)	0.005–0.2
Allyl sulfonic acid	0.1–1
o-Sulfobenzaldehyde (Formyl benzene sulfonic acid)	0.05–5
o-Benzoyl sulfimide	0.05–3

pH—2.5 to 4.8.
Temperature, 45° C. to 80° C.

Example 9

	Grams/liter
$NiSO_4.6H_2O$	25–300
$NiCl_2.6H_2O$	225–30
H_3BO_3	30–45
Dimethyl propynoxy ethane sulfonic acid ($HC{\equiv}C{-}C(CH_3)_2OC_2H_4SO_3H$)	0.01–0.2
Allyl sulfonic acid	0.1–1.5
Sulfobenzaldehydes (benzaldehyde sulfonic acids)	0.3–5
o-Benzoyl sulfimide	0.5–3

pH—2.5 to 4.8.
Temperature, 45° C. to 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 or 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.

The sulfonic acid compounds may be added to the nickel baths as such or as the sulfonate salts, such as the nickel, cobalt, sodium, potassium, magnesium, ferrous, etc., salts. In the baths they are present predominantly as ionized nickel salts and acids.

The preferred alkyne and alkynoxy sulfonic acids of this invention are those with small alkane sulfonic groups such as $—CH_2SO_3H$, $—C_2H_4SO_3H$, $—C_3H_6SO_3H$, both from the standpoint of economy in preparation and efficacy in the nickel baths. If the alkane radical of the alkane sulfonic group is larger than $—C_4H_8—$, then weak surface-active properties (anionic surface-active agent) start to manifest themselves, and the compounds are not as effective as brightening agents as with the smaller chain members.

With the use of propynoxy ethane sulfonic acid, 0.05 to 0.1 gram/liter (sodium or nickel salt) together with allyl sulfonic acid (sodium or nickel salt) 0.5 to 1 gram/liter and 0.1 to 1 gram/liter of o-benzoyl sulfimide and 4 to 5 grams/liter of benzene sulfonic acid in the Watts type nickel bath, a minimum of pitting is encountered without the use of surface-active agents and without the use of strong stirring or agitation of the solution. In these baths all the organic addition agents are strongly anionic and the tendency for pitting is, therefore, minimized, the tendency for brittleness is minimized, and the tendency for cloudy plate from break-down products is minimized.

What is claimed is:

1. A bath for electrodepositing lustrous fine-grained 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 an alkyne sulfonic acid having 3–14 carbon atoms inclusive, the alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said alkyne radical being selected from the group of radicals consisting of unsubstituted alkynes, alkanoxy alkynes, hydroxy alkynes, ester substituted alkynes, chlorine substituted alkynes, bromine substituted alkynes and alkanoxy carboxylic alkynes, said acid being present in a concentration of about 0.01 gram/liter to 20 grams/liter.

2. A bath for electrodepositing lustrous fine-grained 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 an alkyne sulfonic acid having 3–14 carbon atoms inclusive, the alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said alkyne radical being selected from the group of radicals consisting of unsubstituted alkynes, alkanoxy alkynes, hydroxy alkynes, ester substituted alkynes, chlorine substituted alkynes, bromine substituted alkynes and alkanoxy carboxylic alkynes, said acid being present in a concentration of about 0.005 gram/liter to 5 grams/liter, and about 0.1 gram/liter to saturation of at least one organic sulfon-compound selected from the class consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and dibenzene sulfonamides and sulfonimides and the halogen, methyl, aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carton atoms.

3. A bath in accordance with claim 1 wherein said alkyne sulfonic acid is 2-butyne-1,4-disulfonic acid and is present in said bath in a concentration of about 3–20 grams/liter.

4. A bath in accordance with claim 1 wherein said sulfonic acid is 2-butynoxy-1,4-di-(ethane sulfonic) acid and said acid is present in a concentration of about 0.05 to 5 grams/liter.

5. A bath in accordance with claim 1 wherein said sulfonic acid is propargyl sulfonic acid and said acid is present in said bath in a concentration of about 0.01 to 2 grams/liter.

6. A bath in accordance with claim 2 wherein said unsaturated aliphatic sulfonic acid is 2-propynoxy-1-ethane sulfonic acid and said acid is present in an amount of about 0.005 to 0.2 gram/liter.

7. A bath in accordance with claim 2 wherein said unsaturated aliphatic sulfonic acid is 1,1-dimethyl-2-propynoxy-1-ethane sulfonic acid and said acid is present in an amount of about 0.005 to 0.2 gram/liter.

8. A method for electrodepositing lustrous fine-grained nickel 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 also containing dissolved therein an alkyne sulfonic acid having 3–14 carbon atoms inclusive, the alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said alkyne radical being selected from the group of radicals consisting of unsubstituted alkynes, alkanoxy alkynes, hydroxy alkynes, ester substituted alkynes, chlorine substituted alkynes, bromine substituted alkynes and alkanoxy carboxylic alkynes, said acid being present in a concentration of about 0.01 gram/liter to 20 grams/liter.

9. A method for electrodepositing fine-grained nickel 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 also containing dissolved therein an alkyne sulfonic acid having 3–14 carbon atoms inclusive, the alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said alkyne radical being selected from the group of radicals consisting of unsubstituted alkynes, alkanoxy alkynes, hydroxy alkynes, ester substituted alkynes, chlorine substituted alkynes, bromine substituted alkynes and alkanoxy carboxylic alkynes, said acid being present in a concentration of about 0.005 gram/liter to 5 gram/liter, and about 0.1 gram/liter to saturation of at least one organic sulfon-compound selected from the class consisting of benzene, diphenyl and naphthalene sulfonic acids, benzene sulfonamides and sulfonimides and dibenzene sulfonamides and sulfonimides and the halogen, methyl, aldehydo derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

10. A method in accordance with claim 8 wherein said alkyne sulfonic acid is 2-butyne-1,4-di-sulfonic acid and

said acid is present in a concentration of about 0.05 to 5 grams/liter.

11. A method in accordance with claim 8 wherein said sulfonic acid is 2-butynoxy-1,4-di-(ethane sulfonic) acid and said acid is present in a concentration of about 0.05 to 5 grams/liter.

12. A method in accordance with claim 8 wherein said sulfonic acid is propargyl-sulfonic acid and said acid is present in said bath in a concentration of about 0.01 to 2 grams/liter.

13. A method in accordance with claim 9 wherein said unsaturated aliphatic sulfonic acid is 2-propynoxy-1-ethane sulfonic acid and said acid is present in a concentration of 0.005 to 0.2 gram/liter.

14. A method in accordance with claim 9 wherein said unsaturated aliphatic sulfonic acid is 1-1-dimethyl-2-propynoxy-1-ethane sulfonic acid and said acid is present in an amount of about 0.005 to 0.2 gram/liter.

15. A bath in accordance with claim 1 wherein said sulfonic acid is a disulfonic acid.

16. A method in accordance with claim 8 wherein said sulfonic acid is a disulfonic acid.

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