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2,800,442

ELECTRODEPOSITION OF NICKEL

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16 Claims. (Cl. 204-49)

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 or their sulfonates in aqueous acidic nickel baths of the Watts type or its modifications, to obtain fine-grained, lustrous, bright nickel plate.

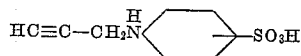
We have found that certain unsaturated sulfonic acids of the class of aryl alkyne and aryl alkynoxy sulfonic acids (or their sulfonates) as exemplified in Table I, when dissolved in the Watts type nickel bath or modifications thereof, make possible fine-grained plate of very good luster. These aryl alkyne and aryl alkynoxy sulfonic compounds can be used with increased effectiveness from the standpoint of cloud-free brightness, when used in conjunction with certain other organic sulfon-compounds 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 effect (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 sulfonic acids, benzene sulfonamides and sulfonimides (o-benzoyl sulfimide), 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 gram per liter of

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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. As an added safe-guard when air agitation is used for the prevention of hydrogen gas pitting of the cathode or gas pitting resulting from dissolved air depositing or sticking to the cathode in fine bubbles, a shorter chain (about 6-8 carbon atoms) anionic surface-active agent may be used such as sodium 2-ethyl hexyl sulfate ("Tergitol 08") or sodium n-heptyl or n-octyl sulfonic acid (or mixtures). These shorter chain anionic surface-active agents do not cause over-foaming with air agitation. The concentrations may be from 0.1 to 3 grams per liter. 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.

With the use of the aryl alkyne and aryl alkynoxy sulfonic acids of this invention in concentrations of about 0.005 to about 0.6 gram per liter with or without allyl sulfonic acid (sodium or nickel salt) 0.5 to 1 gram/liter and 0.1 to 1 gram/liter of o-benzoyl sulfimide 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, which is very unlike the acetylenic alcohols and glycols, such as 1,4 butyne diol which causes pitting without the use of surface-active agents or strong air agitation. In these baths all the organic addition agents being sulfonic acids are strongly anionic, also they are not of an oily nature and the tendency for pitting is, therefore, minimized, the tendency for poor adhesion is minimized, the tendency for brittleness is minimized, and the tendency for cloudy plate from break-down products is minimized. The aryl alkyne and aryl alkynoxy sulfonic acids of this invention can be removed from the baths with activated carbon. If the aryl group is linked to the aliphatic carbon chain by a nitrogen linkage, for example,



then the compound has little value as a brightener in the nickel baths.

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

TABLE I

		Useful Conc., grams/liter
(1)---	$\text{HC}\equiv\text{C}-\text{CH}_2\text{O}-\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01-0.15
(2)---	$\text{HO}_3\text{S}-\text{C}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{C}-\text{CH}_2\text{O}-\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01-1
(3)---	$\text{HO}-\text{CH}_2\text{C}\equiv\text{C}-\text{CH}_2\text{O}-\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01-0.7
(4)---	$\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{O}-\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01-0.15

TABLE I—Continued

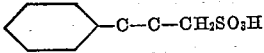
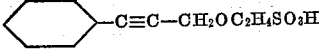
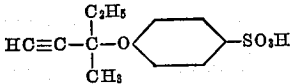
		Useful Conc., grams/liter
(5)---		0.1-4.0
(6)---		0.03-1.2
(7)---		0.01-0.2
(8)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OCH}_2\text{SO}_3\text{H}$	
(9)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	
(10)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	
(11)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_3\text{H}_7\text{SO}_3\text{H}$	
(12)---		0.005-0.2
	$(\text{HC}\equiv\text{C}-\text{CH}-\text{O})_2-\text{C}_3\text{H}_7\text{SO}_3\text{H}$	
(13)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_4\text{H}_9\text{SO}_3\text{H}$	
(14)---		0.005-0.3
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_8\text{H}_{17}\text{SO}_3\text{H}$	
(15)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	
(16)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	
(17)---		0.005-0.2
	$\text{HC}\equiv\text{C}-\text{CH}-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	

TABLE I—Continued

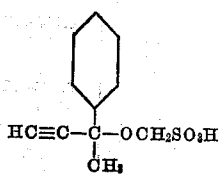
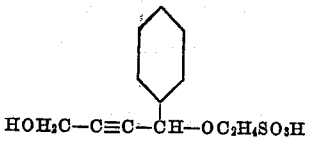
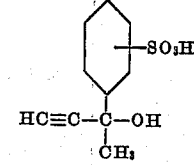
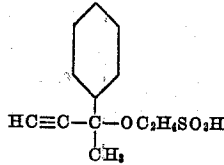
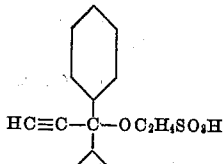
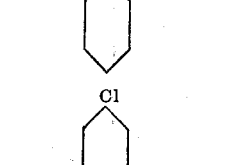
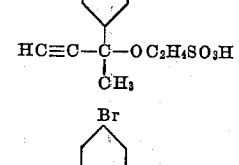
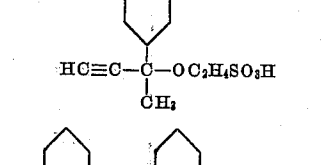
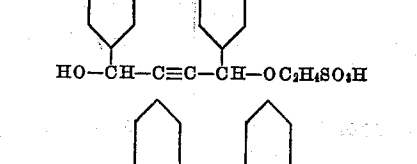
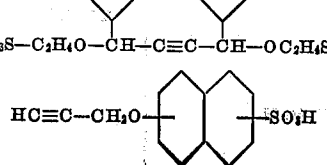
		Useful Conc., grams/liter
(18)---	 <chem>CC(C#CC1=CC=CC=C1)OS(=O)(=O)O</chem>	0.005-0.2
(19)---	 <chem>OS(=O)(=O)OCC1=CC=CC=C1C#CCO</chem>	0.005-0.2
(20)---	 <chem>CC(C#CC1=CC=C(S(=O)(=O)O)C=C1)OS(=O)(=O)O</chem>	0.01-0.8
(21)---	 <chem>CC(C#CC1=CC=CC=C1)OC2=CC=C(S(=O)(=O)O)C=C2</chem>	0.005-0.2
(22)---	 <chem>CC(C#CC1=CC=CC=C1)OC2=CC=C(S(=O)(=O)O)C=C2</chem>	0.005-0.2
(23)---	 <chem>CC(C#CC1=CC=C(Cl)C=C1)OS(=O)(=O)O</chem>	0.005-0.2
(24)---	 <chem>CC(C#CC1=CC=C(Br)C=C1)OS(=O)(=O)O</chem>	0.005-0.2
(25)---	 <chem>OS(=O)(=O)OCC1=CC=CC=C1C#CC(O)C1=CC=CC=C1</chem>	0.01-0.4
(26)---	 <chem>OS(=O)(=O)OCC1=CC=CC=C1C#CC(O)C1=CC=CC=C1</chem>	0.01-0.6
(27)---	 <chem>CC(C#CC1=CC2=C(C=C1)C=CC=C2)OS(=O)(=O)O</chem>	0.005-0.2

TABLE I—Continued

		Useful Conc., grams/liter
(28)---	$\text{HC}\equiv\text{C}-\text{CH}_2\text{O}-\text{C}_6\text{H}_{10}-\text{SO}_3\text{H}$	0.005-0.2
(29)---	$\text{HC}\equiv\text{C}-\text{CH}(\text{C}_6\text{H}_9)-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.005-0.2
(30)---	$\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.005-0.2
(31)---	$\text{HO}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.01-0.4
(32)---	$\text{HO}_2\text{S}-\text{C}_2\text{H}_4\text{O}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.01-0.8
(33)---	$\text{HO}-\text{C}(\text{C}_6\text{H}_9)_2-\text{C}\equiv\text{C}-\text{C}(\text{C}_6\text{H}_9)_2-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.01-0.4
(34)---	$\text{HO}_2\text{S}-\text{C}_2\text{H}_4\text{O}-\text{C}(\text{C}_6\text{H}_9)_2-\text{C}\equiv\text{C}-\text{C}(\text{C}_6\text{H}_9)_2-\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.01-0.6
(35)---	$\text{HC}\equiv\text{C}-\text{CH}_2\text{OCH}_2-\text{C}_6\text{H}_{10}-\text{SO}_3\text{H}$	0.005-0.15
(36)---	$\text{HC}\equiv\text{C}-\text{CH}_2\text{OC}_2\text{H}_4-\text{C}_6\text{H}_{10}-\text{SO}_3\text{H}$	0.005-0.15
(37)---	$\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OCH}_2-\text{C}_6\text{H}_{10}-\text{SO}_3\text{H}$	0.005-0.2
(38)---	$\text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{OCH}_2-\text{C}_6\text{H}_{10}-\text{SO}_3\text{H}$	0.005-0.4
(39)---	$\text{HO}_2\text{S}-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{O}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_9)-\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SO}_3\text{H}$	0.01-0.8

TABLE I—Continued

		Useful Conc., grams/liter
(40)		0.01-0.4
(41)		0.01-2
(42)		0.01-2
(43)		0.01-0.8

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-Aldehyde benzene sulfonamide	0.1-1
9	Sulfomethyl benzene sulfonamide	0.1-6
10	Benzene sulfonamide m-carboxylic amide	0.1-3
11	7-Aldehyde 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-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-Chloro butene-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-sulfo phenyl) 2-propyn 1-ol	0.1-3.0

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

35 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
40	
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----
	H_3BO_3 -----
	Phenyl propyloxy ethane sulfonic acid (Example 9, Table I)-----
45	Allyl sulfonic acid-----
	o-Benzoyl sulfimide-----
	pH—2.5 to 4.5.
	Temperature, 45° C. to 75° C.

Example 2

	Grams/liter
40	
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----
	H_3BO_3 -----
55	3-phenyl-2-propyne-1-sulfonic acid
	()-----
60	N-Allyl quinaldinium bromide-----
	pH—2.5 to 4.5.
	Temperature, 45° C. to 80° C. (113°–176° F.)

Example 3

	Grams/liter
65	
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----
	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----
	H_3BO_3 -----
	NaBF_4 -----
	Phenyl butyloxy ethane sulfonic acid (Example 21, Table I)-----
70	Allyl sulfonic acid ($\text{CH}_2=\text{CH}-\text{CH}_2\text{SO}_3\text{H}$)-----
	o-Benzoyl sulfimide-----
	Benzene sulfonic acid-----
	pH—2.5 to 4.8.
75	Temperature, 45° C. to 75° C.

Example 4

	Grams/liter
NiSO ₄ ·6H ₂ O	25-300
NiCl ₂ ·6H ₂ O	225-30
H ₃ BO ₃	30-45
2-butyloxy-1,4-di(phenyl sulfonic) acid (Example 2, Table I)	0.03-0.3
Allyl sulfonic acid	0.3-1
o-Benzoyl sulfimide	0.7-3
pH—2.5 to 4.8.	
Temperature, 45° C. to 75° C.	

Example 5

	Grams/liter
NiSO ₄ ·6H ₂ O	150-300
NiCl ₂ ·6H ₂ O	30-60
H ₃ BO ₃	30-40
Propyloxy phenyl sulfonic acid (Example 1, Table I)	0.005-0.15
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 ₂ O	150-300
NiCl ₂ ·6H ₂ O	30-80
H ₃ BO ₃	30-40
3,6-di-phenyl hexyn-1,6-di-oxyethane sulfonic acid (Example 32, Table I)	0.01-0.6
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
NiSO ₄ ·6H ₂ O	25-300
NiCl ₂ ·6H ₂ O	225-30
H ₃ BO ₃	30-45
Propyloxy methyl phenyl sulfonic acid (Example 35, Table I)	0.005-0.15
Allyl sulfonic acid	0.1-1
o-Sulfobenzaldehyde (Formyl benzene sulfonic acid)	0.05-5
o-Benzoyl sulfimide	0.8-3
pH—2.5 to 4.8.	
Temperature, 45° C. to 80° C.	

Example 8

	Grams/liter
NiSO ₄ ·6H ₂ O	200-300
NiCl ₂ ·6H ₂ O	30-80
H ₃ BO ₃	30-45
2-sulfophenyl propynol (Example 42, Table I)	0.1-2
Allyl sulfonic acid	0-1
o-Benzoyl sulfimide	0-2
pH—2.5 to 4.8.	
Temperature, 45° C. to 80° C.	

Example 9

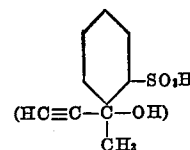
	Grams/liter
NiSO ₄ ·6H ₂ O	150-300
NiCl ₂ ·6H ₂ O	30-60
H ₃ BO ₃	30-40
Propyloxy phenyl sulfonic acid (Example 1, Table I)	0.005-0.15
or	
Propyloxy phenyl disulfonic acid (Example 2, Table I)	0.01-0.4
Allyl quinaldinium bromide	0.005-0.02
Allyl sulfonic acid	0.1-1
o-Benzoyl sulfimide	0.3-3
Benzene sulfonamide	0.3-3

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 2-6 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 aryl alkyne and aryl alkynoxy sulfonic acids of this invention are those with one or two phenyl groups from the standpoint of efficacy in the nickel baths. In the case of the compounds with alkane sulfonic groups, if the alkane radical of the alkane sulfonic group is larger than —C₆H₁₂—, then weak surface-active properties (anionic surface-active agent) start to manifest themselves, and the compounds are not quite as effective as brightening agents as with the smaller chain members. Thus, the preferred number of aliphatic carbon atoms are from 3 to 14 carbon atoms inclusive.

Certain of the aryl alkyne sulfonic acids of this invention can be used alone as illustrated in Example 2, in the acidic nickel plating baths such as the Watts type to give full bright nickel plate. This is not only true for 3-phenyl-2-propyne-1-sulfonic acid (or its sodium, nickel, etc. salt), but also true of 1-(2-sulfohenyl)-2-propyn-1-ol, and 2-(6-sulfohenyl) butyn-2-ol



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Additionally the aryl alkyne and aryl alkynoxy sulfonic acids of this invention can be used satisfactorily in conjunction with small concentrations of not only allyl quinaldinium bromide but other examples of auxiliary brighteners disclosed in my Patents Numbers 2,647,866 and 2,648,628.

This is a continuation-in-part of application Serial No. 538,527, filed October 4, 1955.

What is claimed is:

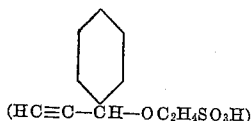
1. A bath for electrodepositing lustrous fine-grained nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said bath also containing dissolved therein an unsaturated sulfonic acid having 3-14 aliphatic carbon atoms inclusive selected from the class consisting of aryl alkyne sulfonic acids and alkyne aryl sulfonic acids containing one to two aryl groups selected from the class consisting of phenyl, biphenyl, and naphthyl groups, the aryl alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said aryl alkyne radical being

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selected from the group of radicals consisting of unsubstituted aryl alkynes, alkanoxy-aryl alkynes, chlorine substituted aryl alkanoxy alkynes, bromine substituted aryl alkanoxy alkynes, methoxy substituted aryl alkanoxy alkynes, and alkanoxy aryl hydroxy substituted alkynes, said sulfonic acid compounds being dissolved in the baths in a concentration of about .005 to about 4 grams/liter.

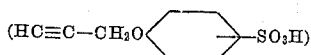
2. A bath for electrodepositing lustrous fine-grained nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said bath also containing dissolved therein an unsaturated sulfonic acid having 3-14 aliphatic carbon atoms inclusive selected from the class consisting of aryl alkyne sulfonic acids and alkyne aryl sulfonic acids containing one to two aryl groups selected from the class consisting of phenyl, biphenyl, and naphthyl groups, the aryl alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said aryl alkyne radical being selected from the group of radicals consisting of unsubstituted aryl alkynes, alkanoxy aryl alkynes, chlorine substituted aryl alkanoxy alkynes, bromine substituted aryl alkanoxy alkynes, methoxy substituted aryl alkanoxy alkynes, and alkanoxy aryl hydroxy substituted alkynes, said sulfonic acid compounds being dissolved in the baths in a concentration of about 0.005 gram/liter to 0.8 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, aldehyde derivatives of said sulfonic acids, sulfonamides and sulfonimides, and beta unsaturated alkene sulfonic acids having 4 to 2 carbon atoms.

3. A bath in accordance with claim 1 wherein said unsaturated sulfonic acid is phenyl propynoxy ethane sulfonic acid



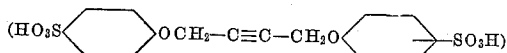
and is present in said bath in a concentration of about 0.005 to 0.2 gram/liter.

4. A bath in accordance with claim 1 wherein said unsaturated sulfonic acid is propynoxy phenyl sulfonic acid



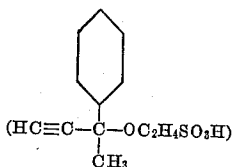
and said acid is present in a concentration of about 0.005 to 0.3 gram/liter.

5. A bath in accordance with claim 1 wherein said unsaturated sulfonic acid is 2-butyne-1,4-di(oxyphenyl sulfonic) acid



and said acid is present in said bath in a concentration of about 0.005 to 0.4 gram/liter.

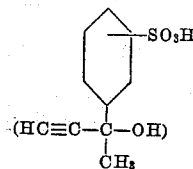
6. A bath in accordance with claim 2 wherein said unsaturated sulfonic acid is phenyl butynoxy sulfonic acid



and said acid is present in an amount of about 0.005 to 0.2 gram/liter.

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7. A bath in accordance with claim 2 wherein said unsaturated sulfonic acid is 2-sulphophenyl butynol

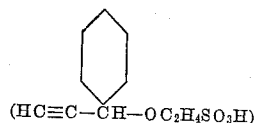


and said acid is present in an amount of about 0.01 to 0.8 gram/liter.

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 unsaturated sulfonic acid having 3-14 aliphatic carbon atoms inclusive selected from the class consisting of aryl alkyne sulfonic acids and alkyne aryl sulfonic acids containing 1 to 2 aryl groups selected from the class consisting of phenyl, biphenyl and naphthyl groups, the aryl alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said aryl alkyne radical being selected from the group of radicals consisting of unsubstituted aryl alkynes, alkanoxy aryl alkynes, chlorine substituted aryl alkanoxy alkynes, bromine substituted aryl alkanoxy alkynes, methoxy substituted aryl alkanoxy alkynes, and alkanoxy aryl hydroxy substituted alkynes, said sulfonic acid compounds being dissolved in the baths in a concentration of about 0.005 gram/liter to about 4 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 unsaturated sulfonic acid having 3-14 aliphatic carbon atoms inclusive selected from the class consisting of aryl alkyne sulfonic acids and alkyne aryl sulfonic acids containing 1 to 2 aryl groups selected from the class consisting of phenyl, biphenyl and naphthyl groups, the aryl alkyne radical of said sulfonic acid consisting of atoms selected from the group consisting of carbon, hydrogen, oxygen, chlorine and bromine and said aryl alkyne radical being selected from the group of radicals consisting of unsubstituted aryl alkynes, alkanoxy aryl alkynes, chlorine substituted aryl alkanoxy alkynes, bromine substituted aryl alkanoxy alkynes, methoxy substituted aryl alkanoxy alkynes, and alkanoxy aryl hydroxy substituted alkynes, said sulfonic acid compounds being dissolved in the baths in a concentration of about 0.005 gram/liter to 0.8 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, aldehyde 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 unsaturated sulfonic acid is phenyl propynoxy ethane sulfonic acid

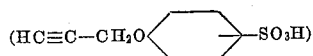


and said acid is present in a concentration of about 0.005 to 0.2 gram/liter.

11. A method in accordance with claim 8 wherein

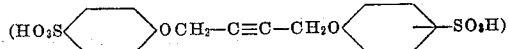
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said unsaturated sulfonic acid is propynoxy phenyl sulfonic acid



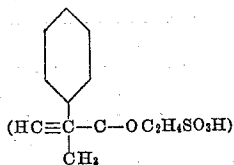
and said acid is present in a concentration of about 0.005–0.3 gram/liter.

12. A method in accordance with claim 8 wherein said unsaturated sulfonic acid is 2-butyn-1,4, di(oxyphenyl sulfonic) acid



and said acid is present in said bath in a concentration of about 0.005 to 0.4 gram/liter.

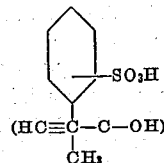
13. A method in accordance with claim 9 wherein said unsaturated sulfonic acid is phenyl butynoxy sulfonic acid.



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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 sulfonic acid is 2-sulfophenyl butynol



and said acid is present in an amount of about 0.01 to 0.8 gram/liter.

15. A bath in accordance with claim 1 containing dissolved therein an anionic surface-active agent having 6–8 saturated aliphatic carbon atoms and selected from the group consisting of sulfates and sulfonates.

16. A method in accordance with claim 8 wherein air agitation is employed during the electrodeposition.

References Cited in the file of this patent

UNITED STATES PATENTS

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