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3,677,912

NICKEL ELECTROPLATING AND ELECTROLYTES THEREFOR

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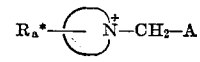
No Drawing. Continuation-in-part of application Ser. No. 587,393, Oct. 18, 1966. This application Sept. 30, 1970, Ser. No. 76,987

Int. Cl. C23b 5/08, 5/46

U.S. Cl. 204—49 13 Claims

ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, the novel process of this invention for electroplating nickel may comprise electrodepositing nickel from an aqueous nickel electroplating bath containing (a) as a first primary brightener an effective amount of a water-soluble acetylenic compound, and (b) as a second primary brightener, an effective amount of a compound having as cation:



(I)

wherein

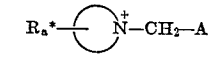
is a pyridine, quinoline, or isoquinoline nucleus; *a* is 0–5; A is —CX=CHX or —C≡CH; X is an active halide; and R* is a substituent selected from the group consisting of alkyl, preferably having 1–4 carbon atoms, hydroxy-alkyl preferably having 1–4 carbon atoms, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano.

This application is a continuation-in-part application of U.S. patent application Ser. No. 587,393, filed Oct. 18, 1966, now abandoned.

The present invention relates to a process for nickel plating. More particularly it relates to a process for bright nickel plating characterized by outstanding coverage in low current density areas.

It is an object of this invention to provide a process for nickel plating and in particular one which is characterized by outstanding coverage in low current density areas. Other objects will be apparent to those skilled in the art on inspection of the following description.

In accordance with certain of its aspects, the novel process of this invention for electroplating nickel may comprise electrodepositing nickel from an aqueous nickel electroplating bath containing (a) as a first primary brightener an effective amount of a water-soluble acetylenic compound, and (b) as a second primary brightener, an effective amount of a compound having as cation:



(I)

wherein

is a pyridine, quinoline, or isoquinoline nucleus; *a* is 0–5; A is —CX=CHX or —C≡CH; X is an active halide; and R* is a substituent selected from the group consisting of alkyl, preferably, having 1–4 carbon atoms, hydroxy-alkyl preferably having 1–4 carbon atoms, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano.

The basis metals which may be electroplated in accordance with the process of this invention may include copper or copper alloys; ferrous metals including steel, iron, etc.; zinc and its alloys including zinc-base die castings; nickel; etc. Preferably the basis metal may bear a plate of copper and of semi-bright nickel before being subjected to the process of this invention.

The primary brighteners of the present invention may be useful with e.g. Watts type baths, High Chloride type baths, and Sulfamate type baths, including those typified by the illustrative baths of Tables I, II; and III.

TABLE I

Watts-type baths

Nickel sulfate	200–400 g./l.
Nickel chloride	30–75 g./l.
Boric acid	30–50 g./l.
Temperature	30° C.–65° C.
pH	3.5–5.0 electrometric.

With agitation (either mechanical, air, or solution circulation by pumping).

TABLE II

High chloride baths

Nickel chloride	150–300 g./l.
Nickel sulfate	40–225 g./l.
Boric acid	30–50 g./l.
Temperature	30° C.–65° C.
pH	3.5–5.0 electrometric.

With agitation (either mechanical, air, or solution circulation by pumping).

TABLE III

Sulfamate-type baths

Nickel sulfamate	330–600 g./l.
Nickel chloride	15–60 g./l.
Boric acid	35–55 g./l.
Temperature	30–55° C.
pH	3.5–5.0 electrometric.

With agitation (either mechanical, air, or solution circulation by pumping).

Other nickel plating baths include those containing, as a source of nickel, nickel fluoborate with nickel chloride, nickel sulfamate with nickel chloride, etc. In the above tables, the nickel chloride is metered as the hexahydrate $NiCl_2 \cdot 6H_2O$, and the nickel sulfate as the heptahydrate $NiSO_4 \cdot 7H_2O$. Other compounds e.g. boric acid are metered on an anhydrous basis.

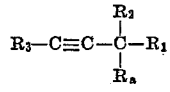
The plating conditions for electrodeposition from the aforementioned baths may for example include temperature of 30° C.–65° C., pH of 3.5–5 electrometric, and preferably 3.8–4.5, cathode current density of 1–10 amps. per sq. dm. Typical preferred current density of the baths of Table I may be 4–6 amps. per sq. dm. Agitation may be preferred while plating.

It is a particular feature of the process of this invention that it permits outstanding results when a Watts-type bath is employed.

The first primary brightener which may be employed in practice of this invention may include water-soluble acetylenic compounds.

Water-soluble acetylenic compounds which may be employed in this invention may be particularly characterized by a highly nucleophilic triple bond which is free from steric hinderance and thus has a clear and unimpeded path in approaching the cathode.

The preferred water-soluble acetylenic compounds which may be employed in the process of this invention to produce nickel deposits may include α-substituted acetylenic compounds having the formula



in which each of R_1 and R_2 may be substituents selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and R_1 and R_2 may together be a carbonyl oxygen; R_3 may be a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkynyl groups, and substituted-alkyl groups having the formula

in which each of R_4 and R_5 may be substituents selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and when R_1 and R_2 together are carbonyl oxygen, R_2 may be an aryl group, including hydroxy and alkoxy and alkyl-substituted aryl; each of R_a and R_a' may be substituents selected from the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy, halogen and polyoxy groups and R_a may also be an amino group including alkyl and aryl substituted amino group wnen R_1 and R_2 together form a carbonyl oxygen and R_3 is an aryl group. Where R_3 is a substituted-alkyl group having the above-illustrated formula, the acetylenic compound may be termed an α,α'-disubstituted acetylenic compounds, since both carbon atoms vicinal to the same acetylenic bond contain either the same or a different functional group.

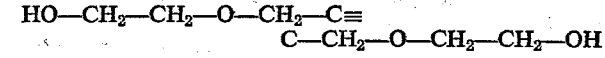
The compounds listed in Table IV are illustrative of the water-soluble acetylenic compounds which may be used in practice of the process of this invention.

TABLE IV

2-butyne-1,4-diol
1,4-di-(3-hydroxyethoxy)-2-butyne
1-(β-hydroxyethoxy)-2-butyne-4-ol
1,4-diacetoxy-2-butyne
3-butyne-1,2-diol
3-methyl-1-butyne-3-ol
3-methyl-1-pentyn-3-ol
2-propyn-1-ol
2,5-dimethyl-1-octen-3-yn-5-ol
3-methyl-1-nonyn-3-ol
2,4-hexadiyne-1,6-diol
1-methoxy-2-propyne
3-methoxy-3-methyl-4,6-heptadiyne
3-ethoxy-3,5,7-trimethyl-1-octyne
1-formoxy-2-propyne
1-acetoxy-2-propyne
3-methyl-1-nonyn-3-yl-acetate
phenyl-propiolamide
phenyl-propiol-N-phenylamide
phenyl-propiol-N,N'-dimethylamide
3-methyl-1-butyn-3-yl acetate

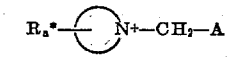
1-chlor-6-methoxy-2,4-hexadiyne
3-chloro-3-methyl-4-hexyne
1-bromo-2-propyne
1,2-di-(β-hydroxyethoxy)-3-butyne
3-(β-hydroxy-γ-chloropropoxy)-3-methyl-4-pentyne
3-(β-γ-epoxypropoxy)-3-methyl-4-pentyne

Those acetylenic compounds which may be employed in the instant invention include those containing at least one hydroxy moiety, and most preferably those which contain two hydroxy moieties, e.g. the β-hydroxy-ethyl ether of 2-butyne-1,4-diol, i.e. 1-(β-hydroxy-ethoxy)-4-hydroxy-2-butyne, and preferably the bis (β-hydroxy ethyl ether(of 2-butyne-1,4-diol, i.e. 1,4-bis (β-hydroxyethoxy)-2-butyne:



The first primary brightener may be present in the bath in effective amounts of 0.002 g./l.–0.5 g./l., preferably 0.005 g./l.–0.10 g./l., say 0.01 g./l.–0.05 g./l.

The second primary brightener which may be employed in practice of this invention may include nitrogen heterocyclic compounds having as cation

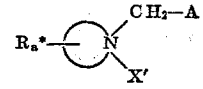


(I)

wherein

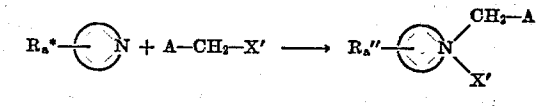
is a pyridine, quinoline, or isoquinoline nucleus (including such nuclei when substituted or unsubstituted); *a* is 0–5; A is —CX=CHX or —C=CH; X is an active halide; R* is a substituent selected from the group consisting of alkyl preferably having 1–4 carbon atoms, hydroxyalkyl preferably having 1–4 carbon atoms, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano.

More particularly, the second primary brightener may be a compound



(II)

wherein X' is a bath-soluble, bath-compatible anion, typically bromide, chloride, iodide, fluoride, acetate, sulfate, methosulfate, ethosulfate, citrate, chloroacetate, perchlorate, etc. Preferably X' may be halide including fluoride, chloride, bromide, and iodide. These compounds may be readily available or may be conveniently prepared by the reaction

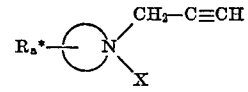


e.g. the reaction of 2,6-dimethyl pyridine and propargyl bromide to form 2,6-dimethyl, N-propargyl pyridinium bromide; or the reaction of pyridine and 1,2,3-trichloropropene to form 1,2-dichloropropene pyridinium chloride. When A is —CX=CHX and, when X is bromo, then compound (II) will preferably be prepared by the reaction of compound (III) infra with bromine e.g. reaction of 2,6-dimethyl, N-propargyl pyridinium bromide with bromine to form 2,6-dimethyl, N-2,3-dibromo propenyl pyridinium bromide.

It will be apparent to those skilled-in-the-art that Formula II may include, in addition to simple pyridine, quinoline, and isoquinoline derivatives, other compounds including those formed from e.g. 4,4'-dipyridine: such as N,N' bis-2-propynyl-4,4'-dipyridinium dibromide formed by the reaction 4,4'-dipyridine and propynyl bromide; or N,N' bis-2,3-dichloropropynyl, 4,4'-dipyridinium dichlo-

ride formed by the reaction of 4,4'-dipyridine and 2,3-dichloropropenyl chloride.

In the above Formula II when A is —C=CH, the compound may be



(III)

In this embodiment, it is preferred that R* be alkyl or hydroxyalkyl, and *a* be an integer 0–5. When *a* is 2–5, there may be both alkyl and hydroxyalkyl groups on the molecule. R* may typically be methyl, ethyl, propyl, i-propyl, n-butyl, i-butyl, t-butyl, n-amyl, n-hexyl, n-octyl, 2-ethylhexyl, etc., hydroxymethyl, β-hydroxyethyl, gamma-hydroxypropyl, β-dihydroxypropyl, etc.

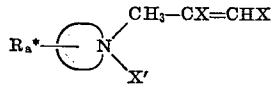
Typical compounds which may fall within the scope of Formula III may be:

TABLE V

2,6-dimethyl, N-propargyl pyridinium bromide
3,5-dimethyl, N-propargyl pyridinium bromide
2,4-dimethyl, N-propargyl pyridinium bromide
3,4-dimethyl, N-propargyl pyridinium bromide
2,5-dimethyl, N-propargyl pyridinium bromide
3-ethyl, 4-methyl, N-propargyl pyridinium bromide
2,4,6-trimethyl, N-propargyl pyridinium bromide
2-β-hydroxyethyl, N-propargyl pyridinium bromide
2-gamma-hydroxypropyl, N-propargyl pyridinium bromide
3-hydroxymethyl, N-propargyl pyridinium bromide
2-methyl, 6-gamma-hydroxypropyl, N-propargyl pyridinium bromide
2-ethyl, 4,6-di-β-hydroxyethyl, N-propargyl pyridinium bromide
2,4,6-tri-hydroxymethyl, N-propargyl pyridinium bromide

The preferred compounds may include 2,4,6-trimethyl, N-propargyl pyridinium bromide and 2,4-dimethyl, N-propargyl pyridinium bromide.

In the above Formula II when A is —CX=CHX, the compound may be



(IV)

In this embodiment, it is preferred that R be alkyl or halogen including bromine or chlorine, and that *a* be 0–3. These compounds may include N-2,3-dihalopropenyl pyridinium halide.

Typical compounds which may fall within the scope of Formula IV may include:

TABLE VI

N-2,3-dibromopropenyl 2,4,6-trimethylpyridinium bromide
N-2,3-dibromopropenyl 3,5-dimethylpyridinium bromide
N-2,3-dibromopropenyl 4-isopropylpyridinium bromide
N-2,3-dibromopropenyl 2,6-dimethylpyridinium bromide
N-2,3-dibromopropenyl 2-aminopyridinium bromide
N-2,3-dibromopropenyl 3-methylpyridinium bromide
N-2,3-dibromopropenyl 3-cyanopyridinium bromide
N-2,3-dibromopropenyl 4-ethylpyridinium bromide
N-2,3-dibromopropenyl 4-methylpyridinium bromide
N-2,3-dibromopropenyl 2,4-dimethylpyridinium bromide
N-2,3-dibromopropenyl 2-chloropyridinium bromide
N-2,3-dibromopropenyl 2-ethylpyridinium bromide
N-2,3-dibromopropenyl 2-β-hydroxyethylpyridinium bromide
N-2,3-dibromopropenyl 2-γ-hydroxypropylpyridinium bromide
N-2,3-dibromopropenyl 2-methylquinolinium bromide
N-2,3-dibromopropenyl 2p-methoxybenzylaminopyridinium bromide
N-2,3-dibromopropenyl isoquinolinium bromide

N-2,3-dibromopropenyl 3-sulfopyridinium bromide (Na salt)
N-2,3-dibromopropenyl 3-hydroxymethylpyridinium bromide
N-2,3-dibromopropenyl 2-methylpyridinium bromide
N-2,3-dibromopropenyl 3,4-dimethylpyridinium bromide
N-2,3-dibromopropenyl 2,5-dimethylpyridinium bromide
N-2,3-dibromopropenyl 3-ethyl-4-methylpyridinium bromide
N-2,3-dibromopropenyl 4-methylquinolinium bromide
N-2,3-dibromopropenyl 2-aldoximopyridinium bromide
N-2,3-dibromopropenyl 2,6-diaminopyridinium bromide
1,2-dichloropropenyl pyridinium chloride
1,2-dichloropropenyl pyridinium iodide
1,2-dichloropropenyl 3,4-dimethylpyridinium iodide
1,2-dichloropropenyl 4-methylpyridinium iodide
1,2-dichloropropenyl 2-methylpyridinium iodide
1,2-dichloropropenyl 3,5-dimethylpyridinium iodide

The second primary brightener may be present in the bath in effective amount of 0.002 g./l.–0.01 g./l., preferably 0.002 g./l.–0.05 g./l., say 0.01 g./l. Preferably the total amount of primary brightener, including the first and second primary brightener, may be 0.004 g./l.–0.6 g./l., more preferably 0.007 g./l.–0.15 g./l., say 0.02 g./l.

The preferred nickel electroplating baths of this invention may include secondary brighteners, present in typical amounts of 1 g./l.–75 g./l., preferably 1 g./l.–20 g./l., such as the sulfo-oxygen compounds typical of which may be saccharin and sodium benzene monosulfonate. The latter secondary brightener may be preferred because of its higher degree of zinc-tolerance, i.e. its ability to tolerate higher concentrations of zinc as contaminant without giving striations in the low current density areas. In high chloride baths, it may be preferred to use saccharin or the sodium salt of sulfonated dibenzothiophene dioxide. Naphthalene sulfonates may be found to be of little or no effectivity in the process of this invention.

Secondary auxiliary brighteners, typically present in amount of 2 g./l.–30 g./l., preferably 2 g./l.–10 g./l., say 4 g./l., may include unsaturated hydrocarbon sulfonates such as sodium 3-chloro-2-butene sulfonate; sodium 2-propen-1-sulfonate; sodium 1-phenylether-2-sulfonate; sodium 3-methyl-1-buten-3-ol-1-sulfonate; sodium 3-hydroxy-1-propen-1-sulfonate; etc.

Plating of nickel by the novel process of this invention permits attainment of a brilliant ductile, highly leveled deposit of bright nickel over a wide range of current density. In particular cases, such as when saccharin is used as the secondary brightener, coverage in the low current density region is substantially increased. Generally there may be an improvement in the rate of brightening and the elimination of build-up of satiny-to-dull micronodular deposits in low current density areas.

For purpose of providing those skilled-in-the-art with a better understanding of this invention, the following examples are set forth wherein all parts are parts by weight unless otherwise specified.

In these examples, the Watts Bath contained:

	G./l.
$NiSO_4 \cdot 7H_2O$	300
$NiCl_2 \cdot 6H_2O$	60
Boric acid	45

The High Chloride Bath contained:

	G./l.
$NiSO_4 \cdot 7H_2O$	225
$NiCl_2 \cdot 6H_2O$	225
Boric acid	45

The Sulfamate Bath contained:

	G./l.
Nickel Sulfamate	375
$NiCl_2 \cdot 6H_2O$	45
Boric acid	45

The Acetylenic Primary Brighteners used were:

TABLE VII

(A) 2-butyne 1,4-diol
(B) 1,4-di-(β-hydroxyethoxy)-2-butyne
(C) 3-methyl-1-butyne-3-ol
(D) 3-methyl-1-pentyne-3-ol
(E) 3-methyl-1-butyne-3-(β-hydroxyethoxy)

The N-heterocyclic Primary Brighteners used were:

TABLE VIII

(A') N-2,3-dichloropropenyl pyridinium chloride
(B') N-2,3-dibromopropenyl-2,4,6-trimethyl pyridinium bromide
(C') N-2-propynyl-2,4,6-trimethyl pyridinium bromide
(D') N,N'bis-2-propynyl-4,4'-dipyridinium dibromide
(E') N,N'bis-2,3-dichloropropenyl-4,4'-dipyridinium dichloride

The secondary Brighteners used were:

(A'') Saccharin (Na salt)
(B'') Sodium benzene monosulfonate
(C'') Disodium m-benzene disulfonate
(D'') Sodium p-toluene sulfonate
(E'') Sulfonated dibenzothiophene dioxide (Na salt)

The Secondary Auxiliary Brighteners used were:

(A''') Sodium 3-chloro-2-butene sulfonate
(B''') Sodium 2-propene-1-sulfonate
(C''') Sodium 1-phenylethene-2-sulfonate

The Anti-pitting Agents used were:

(A'''') Sodium lauryl sulfate
(B'''') Sodium di-n-hexyl sulfosuccinate

In the examples, the baths used were Watts Baths for Examples 1–19; High Chloride Baths for Examples 20–26; and Sulfamate Baths for Examples 27–34. The additives were present in the amount indicated. All runs were made using highly polished brass cathodes with the cathode current densities averaging 5 a.s.d. at a temperature of 60° C. for the Watts and Sulfamate Baths and 6 a.s.d. at a temperature of 65° C. for the High Chloride Bath. In Examples 1–19 and 27–34 air agitation was used and the baths contained 0.2 g./l. of B''''. In Examples 20–26 moving cathode rod type of agitation was used and the baths contained 0.5 g./l. of A''''. The plating time was 30 minutes. To evaluate the degree of leveling the brass cathodes were scratched before plating with a single pass of 4-Zero grit emery.

Example	Additives	Amt., g./l.
1	A	0.10
	A'	0.010
	A''	4.0
	A'''	4.0
2	B	0.05
	A'	0.01
	A''	4.0
	A'''	4.0
3	C	0.01
	A'	0.01
	A''	4.0
	A'''	4.0
4	D	0.01
	A'	0.01
	A''	4.0
	A'''	4.0
5	E	0.01
	A'	0.01
	A''	4.0
	A'''	4.0
6	C	0.01
	A'	0.01
	B''	7.5
	A'''	4.0
7	B	0.05
	A'	0.01
	A''	4.0
	B'''	3.0

Example	Additives	Amt., g./l.
8	C	0.01
	A'	0.01
	A''	4.0
	B'''	3.0
9	C	0.01
	A'	0.01
	A''	4.0
	C'''	2.0
10	C	0.01
	A'	0.01
	C''	7.5
	A'''	3.0
11	B	0.05
	B'	0.01
	A''	4.0
	A'''	4.0
12	B	0.05
	C'	0.01
	A''	4.0
	A'''	4.0
13	B	0.05
	D'	0.002
	A''	4.0
	A'''	4.0
14	B	0.05
	E'	0.005
	A''	4.0
	A'''	4.0
15	C	0.01
	C'	0.005
	B''	15
	B'''	3
16	C	0.01
	D'	0.002
	C''	15
	B'''	3
17	C	0.01
	A'	0.01
	D''	7.5
	A'''	4.0
18	D	0.01
	A'	0.01
	D''	7.5
	B'''	3
19	B	0.05
	A'	0.01
	E''	4.0
	A'''	3.2
20	B	0.05
	A'	0.01
	A''	4.0
	A'''	4.0
21	B	0.05
	A'	0.01
	A''	4.0
	B'''	3.0
22	C	0.01
	A'	0.01
	A''	4.0
	A'''	4.0
23	C	0.01
	A'	0.01
	A''	4.0
	B'''	3.0
24	C	0.01
	C'	0.005
	A''	4.0
	C'''	2.0
25	C	0.01
	A'	0.01
	E''	4.0
	A'''	4.0
26	B	0.05
	A'	0.01
	E''	4.0
	A'''	4.0
27	B	0.05
	A'	0.01
	A''	4.0
	A'''	4.0
28	C	0.01
	A'	0.01
	B''	7.5
	A'''	4.0

TABLE—Continued

Example	Additives	Amt., g./l.
29	C	0.01
	A'	0.01
	C''	7.5
	A'''	4.0
30	D	0.01
	A'	0.01
	B''	7.5
	A'''	4.0
31	D	0.01
	A'	0.01
	C''	7.5
	A'''	4.0
32	B	0.05
	A'	0.01
	A''	4.0
	B'''	3.0
33	C	0.01
	A'	0.01
	D''	7.5
	A'''	4.0
34	C	0.01
	C'	0.005
	D''	7.5
	B'''	3.0

In all of the above examples which fall within the scope of this invention, it was observed that the nickel plate was characterized by a high degree of leveling, ductility, and rate of brightening. In the case of Example 2, the preferred embodiment, the combination of primary brighteners gave extremely high leveling, ductility, rate of brightening, and substantial improvement in coverage in the low current density area. Improved coverage in low current density areas may be particularly outstanding when saccharin is used as the secondary brightener.

EXAMPLE 35

In a Watts nickel system the following additive system was tested on a four-liter laboratory scale over a relatively long period of electrolysis time:

(B'')—sodium benzene monosulfonate
(A''')—sodium 3-chloro-2-butyne sulfonate
(C)—3-methyl-1-butyne-3-ol
(B'''')—sodium di-n-hexyl sulfosuccinate

The above system gave deposits of high luster and good rates of brightening and leveling; ductility was acceptable and the system was very tolerant to zinc as a contaminant. Despite these good characteristics, it was found that on unpolished surfaces of basis metals this system had a very strong tendency to lose luster instead of gaining luster with increasing thickness of deposit. On examination under magnification, the loss of luster was found to be due to the very unusual and unexpected formation of closely spaced "micromounds" instead of a smooth highly lustrous deposit without discontinuities. To this bath there was then added another primary brightener [i.e. N-2,3-dichloropropenyl pyridinium chloride (A')] without any prior knowledge as to what the effects might be. The defect was immediately eliminated with all of the other good properties of the system being retained. If, instead of using the combinations of primary brighteners, only nitrogen heterocyclic were used, the system would produce an inadequate deposit luster, and rates of brightening and leveling would be lower. The combined system turned out to be highly successful in all respects while preserving all of the previous advantages and without introducing any new defects.

EXAMPLE 36

In a Watts nickel system the following additive system was investigated:

saccharin
sodium-3-chlorobutene sulfonate
1,4-di-(β-hydroxyethoxy)-2-butyne
sodium di-n-hexyl sulfosuccinate

The above system had all the desired characteristics of a bright nickel system except that at concentrations of the acetylenic primary brightener necessary to obtain adequate luster and rates of brightening and leveling, the low current density coverage was considered inadequate. On adding N-2,3-dichloropropenyl pyridinium chloride to the ssytem this defect was eliminated and a highly successful process resulted. When using the N-heterocyclic without the cooperating acetylenic brightener, the system possessed inadequate rates of brightening and leveling from a commercial standpoint.

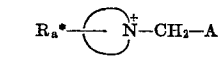
EXAMPLE 37

The system formulated under Example 36 (above) was found to be somewhat sensitive to zinc contamination when sodium allyl sulfonate was substituted for sodium 3-chlorobutene sulfonate. On adding 2-butyne-1,4-diol as an additional cooperating primary brightener, the sensitivity towards zinc contamination was remarkably reduced and a highly successful process resulted.

It will be apparent to those skilled in the art that various modifications may be made to the specific embodiments herein set forth by way of example.

I claim:

1. The process for electroplating nickel which comprises electroplating nickel from an aqueous acidic nickel electroplating bath containing (a) as a first primary brightener 0.002 gram per liter to 0.5 gram per liter of at least one compound selected from the group consisting of butynediol and hydroxyethoxylated butynediol and (b) as a second primary brightener, 0.002 gram per liter to 0.01 gram per liter of a compound having as cation



wherein

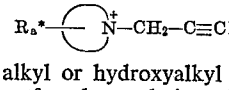
is a pyridine, quinoline, or isoquinoline nucleus; *a* is 0–5; A is —CX=CHX or —C≡CH; X is an active halide; and R* is a substituent selected from the group consisting of alkyl, hydroxyalkyl, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano.

2. The process for electroplating nickel as clamied in claim 1 wherein said water-soluble acetylenic compound is 2-butyne-1,4-diol.

3. The process for electroplating nickel as claimed in claim 1 wherein said water-solubel acetylenic compound is 1,4-di-(beta-hydroxyethoxy)-2-butyne.

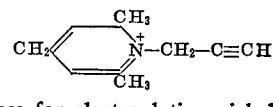
4. The process for electroplating nickel as claimed in claim 1 wherein said water-soluble acetylenic compound is 1-(beta-hydroxyethoxy)-4-hydroxy-2-butyne.

5. The process for electroplating nickel as claimed in claim 1 wherein said second primary brightener has as cation

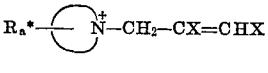


wherein R* is alkyl or hydroxyalkyl and *a* is 0–5.

6. The process for electroplating nickel as claimed in claim 1 wherein said second primary brightener has as cation

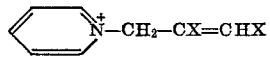


7. The process for electroplating nickel as claimed in claim 1 wherein said second primary brightener has as cation



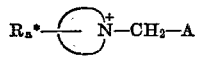
and *a* is 0–3.

8. The process for electroplating nickel as claimed in claim 1 wherein said second primary brightener has as cation



9. The process for electroplating nickel as claimed in claim 1 wherein second primary brightener is N-2,3-dichloropropenyl pyridinium chloride.

10. An aqueous acidic electrolytic bath containing soluble salts for the electrodeposition of nickel and containing 0.002 gram per liter to 0.5 gram per liter of at least one compound selected from the group consisting of butynediol and hydroxyethoxylated butynediol and 0.002 gram per liter to 0.01 gram per liter of a compound having as cation



wherein

is a pyridine, quinoline, or isoquinoline, nucleus; *a* is 0–5; A is —CX=CHX or —C≡CH; X is an actvie halide; and R* is a substituent selected from the group consisting of alkyl, hydroxyalkyl, halogen, alkoxy, carboxyl, carbalkoxy, acetyl, benzyl, sulfo, carboxamido, and cyano.

11. An aqueous electrolytic bath containing soluble salts for the electrodeposition of nickel as claimed in claim 10 wherein said water-soluble acetylenic compound is 2-butyne-1,4-diol.

12. An aqueous electrolytic bath containing soluble salts for the electrodeposition of nickel as claimed in claim 10 wherein said water-soluble acetylenic compound is 1,4-di(betahydroxyethoxy)-2-butyne.

13. An aqueous electrolytci bath containing soluble salts for the electrodeposition of nickel as claimed in clami 10 wherein said water-soluble acetylenic compound is 1-(betahydroxyethoxy)4-hydroxy-2-butyne.

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