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ELECTRODEPOSITION OF BRIGHT NICKEL

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No Drawing. Filed July 17, 1963, Ser. No. 295,818
9 Claims. (Cl. 204-49)

This invention relates to electroplating nickel and more particularly to the electrodeposition of bright nickel.

Nickel electrodeposits as plated from Watts, high chloride, fluoborate, etc. type baths are not bright when plated in thickness substantially greater than those of very thin "strike" or "flash" coatings. Such deposits do not increase in luster with increasing thickness but rather decrease in brightness until dull matte deposits are obtained. To obtain thick bright deposits from such baths, it is necessary to add certain additives, commonly of organic nature, which assist in producing highly lustrous deposits with good rate of brightening. It is a common characteristic of such so-called "bright nickel" plating baths that the deposits tend to increase in luster with increasing thickness. A particular advantage of these "bright nickel" baths is that bright deposits can be obtained on basis metals which have not been polished or which do not have a high starting luster, within reasonable specification thickness of nickel. Other concomitant advantages such as "leveling" or the ability of the deposits to fill in pores, scratches, or other superficial defects of the basis metal, may also be obtained.

Addition agent useful as brighteners in nickel plating baths are generally divided into two classes on the basis of their predominant function. Primary brighteners are materials used in very low or relatively low concentration, typically 0.002-0.2 g./l., which by themselves may or may not produce visible brightening action. Those primary brighteners which may exhibit some brightening effects generally also produce deleterious side effects such as reduced cathode efficiency, poor deposit color, deposit brittleness and exfoliation, very narrow bright plate range, or failure to plate at all on the low current density areas. Secondary brighteners are materials which are ordinarily used in combination with primary brighteners but in appreciably higher concentration than that of the primary brighteners—typically 1 g./l. to 30 g./l. These materials, by themselves, may produce some brightening or grain refining effects, but the deposits are not usually mirror bright and the rate of brightening is usually inadequate.

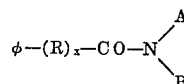
Ideally, when primary and secondary brighteners of properly chosen and compatible nature are combined it is possible to obtain, over a wide current density range, ductile, leveled deposits which exhibit a good rate of brightening. The rate of brightening and leveling may vary in degree depending on the particular cooperating additives chosen and their actual and relative concentrations. A high degree of rate of brightening and leveling is generally desirable, particularly where maximum luster is desired with minimum nickel thicknesses. The concentrations of the secondary brighteners may usually vary within fairly wide limits. The concentrations of the primary brighteners must usually be maintained within fairly narrow limits in order to maintain desirable properties including good ductility, adequate coverage over low current density areas, etc. Any bright nickel system which can be rendered more tolerant to fluctuations in primary brightener concentrations will have obvious advantages, particularly since the low concentration of primary brighteners and the intrinsic chemical nature of some make strict control by chemical analysis difficult. A primary brightener which can be used over a wide range of concentration is of great value in bright nickel plating.

It is an object of this invention to provide improved nickel plate by use of a new class of superior primary

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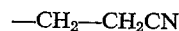
brighteners. It is a further object of this invention to provide an efficient process for electrodepositing bright and smooth nickel deposits. Another object of this invention is to provide bath compositions for nickel plating from which bright nickel electrodeposits are obtained. Other objects of this invention may be apparent to those skilled in the art on inspection of the following description.

In accordance with certain of its aspects, the process of this invention comprises electrodepositing nickel from nickel-containing baths containing a secondary brightener; and a primary brightener having the following structure:



wherein R is a hydrocarbon radical, typically on aliphatic radical, preferably selected from the group consisting of $-CH_2-CH_2-$, $-CH=CH-$, and $-C\equiv C-$, wherein ϕ is the phenyl group, C_6H_5 , wherein x is 0 or 1, wherein A is a cyano-hydrocarbon radical, typically an omega-cyano aliphatic radical, preferably having less than about 20 carbon atoms, and more preferably a cyano-hydrocarbon radical of the formula $-CN$ or $(CH_2)_aCN$ wherein a is an integer from 1 to 10, and wherein B is selected from the group consisting of hydrogen, $(CH_2)_aCN$ wherein a is an integer 1-10, and saturated or unsaturated hydrocarbon radicals having less than 6 carbon atoms.

A may be, for example, $-CN$, or $-CH_2CN$,



$-C_3H_6CN$, $-C_4H_8CN$, $-C_5H_{10}CN$, etc. depending upon the value of a in the range 1-10. Typically B may be methyl, ethyl, vinyl, ethynyl, n-propyl, isopropyl, allyl, 2-propyn-1-yl, propyn-2-yl, n-butyl, isobutyl, t-butyl, sec-butyl, etc. The preferred compounds may be those wherein R may be $-CH=CH-$ or $-C\equiv C-$, wherein A may be $-CH_2CN$ or $-CH_2CH_2CN$; and B may be hydrogen or saturated or unsaturated hydrocarbon radicals having less than 6 carbon atoms.

Typical compounds of this class which may be effective as primary brighteners are the following:

TABLE I

- A. N,N-bis-β-cyanoethyl phenylpropiolamide
- B. N,N-bis-cyanomethyl phenylpropiolamide
- C. N-β-cyanoethyl phenylpropiolamide
- D. N-methyl-N-β-cyanoethyl phenylpropiolamide
- E. N,N-bis-β-cyanoethyl cinnamide
- F. N,N-bis-cyanomethyl cinnamide
- G. N-β-cyanoethyl cinnamide
- H. N-β-cyanoethyl 3-phenylpropionamide
- I. N,N-bis-β-cyanoethyl 3-phenylpropionamide
- J. N-allyl-N-β-cyanoethyl phenylpropiolamide
- K. N-β-cyanoethyl benzamide
- L. N-cyano phenylpropiolamide
- M. N-w-cyanopentamethylene phenylpropiolamide
- N. N-cyanomethyl phenylpropiolamide

The novel class of primary brighteners of this invention when used in combination with (a) suitable secondary brighteners or (b) secondary and secondary auxiliary brighteners, may give brilliant nickel deposits which have excellent ductility, good low current density coverage and luster, good rate of brightening, and good leveling characteristics. It is a particular feature of this invention that the preferred novel primary brighteners may be used over a wide range of concentration with attainment of good low current density coverage and ductility of the deposits.

Another outstanding advantage is that these novel primary brighteners can withstand long electrolysis with-

out build-up in the nickel plating bath of harmful decomposition products. Prior art nickel plating techniques include the use of a number of aliphatic saturated and unsaturated cyano compounds as primary brighteners; but they produce rapid accumulation of harmful decomposition products on electrolysis; they give deposits of poor ductility; they give inferior low current density coverage; they have impractically narrow usable concentration limits; they create objectionable sensitivity to momentary current interruptions, resulting in deposits in which one layer peels from another; and they have limited compatibilities with other commonly used additives. The compounds of this invention, cyano derivatives of aromatic amides, do not have these defects and, in addition, exhibit economically low rates of consumption.

The primary brighteners of this invention may be used in concentrations of 0.002 g./l. to 0.1 g./l., the particular concentration chosen depending on the particular types and concentration of secondary and secondary auxiliary brighteners used, and also on such factors as the concentrations of nickel sulfate, nickel chloride, and boric acid; operating conditions with respect to temperature and degree of agitation; degree of luster, rate of brightening and leveling desired; and the finish of the basis metal. It is preferred to use between 0.005 g./l. and 0.06 g./l.

Secondary brighteners (typically present in amount of 1 g./l. to 75 g./l., and preferably 1 g./l. to 20 g./l.) which are useful in combination with the primary brighteners, are generally aromatic sulfonates, sulfonamides or sulfimides which may include such substituted aromatic compounds as 1,3,6-naphthalene trisulfonate, sodium or potassium salts of saccharin, sodium or potassium salts of ortho-sulfo-benzaldehyde, benzene sulfonamide, benzene monosulfonate, etc. For use in high chloride type nickel plating baths, a preferred secondary brightener may be a sodium or potassium salt of sulfonated dibenzothiophene dioxide, prepared by sulfonating diphenyl with fuming sulfuric acid (20% oleum) for about 2 hours, isolating the reaction product, and neutralizing. The predominant reaction product is believed to be the compound containing three sulfonic acid groups, together with some mono- and di-substituted components. The secondary brighteners are generally characterized by having at least one sulfone or sulfonic acid group attached to a nuclear carbon of a homocyclic aromatic ring.

Auxiliary secondary brighteners such as sodium-2-propene-1-sulfonate, sodium-3-chloro-2-butene-1-sulfonate, mixed isomer of sodium-3-butene-2-hydroxy-1-sulfonate and sodium-3-butene-1-hydroxy-2-sulfonate, prepared by reacting butadiene monoxide with sodium sulfite; or phenyl propiolamide may be used in conjunction with the secondary brightener or brighteners.

Conventional baths and processes for electroplating bright nickel are described in "Principles of Electroplating and Electroforming," Blum and Hogaboom, pp. 362-381, revised third edition, 1949, McGraw-Hill Book Co., Inc., New York; and in "Modern Electroplating," edited by A. G. Gray, The Electrochemical Society, 1953, pp. 299-

355. The control and operating conditions, including the concentration of the bath ingredients, pH, temperature, cathode current density, etc., of these conventional baths are generally applicable to the present invention. Practically all baths for electroplating bright nickel contain nickel sulfate; a chloride, usually nickel chloride; a buffering agent, usually boric acid; and a wetting agent, e.g. sodium lauryl sulfate, sodium lauryl ether sulfate, or sodium 7-ethyl-2-methyl-4-undecanol sulfate. Such baths include the well-known Watts bath and the high chloride bath. Other baths may contain, as the source of the nickel, a combination of nickel fluoborate with nickel sulfate and nickel chloride, or a combination of nickel fluoborate with nickel chloride. Typical Watts-type baths and high chloride baths are noted in Tables II and III.

TABLE II.—WATTS-TYPE BATHS

Nickel sulfate	g./l.	200 to 400
Nickel chloride	g./l.	30 to 75
Boric acid	g./l.	30 to 50
Temperature	° C.	38 to 65
Agitation.		
pH	electrometric	2.5 to 4.5

TABLE III.—HIGH CHLORIDE BATHS

Nickel chloride	g./l.	150 to 300
Nickel sulfate	g./l.	40 to 150
Boric acid	g./l.	30 to 50
Temperature	° C.	38 to 65
Agitation.		
pH	electrometric	2.5 to 4.5

Best plating results are usually achieved in the electrodeposition process when there is used a method of preventing the thin film immediately adjacent to the cathode from becoming depleted in cation content. This is desirably accomplished by agitation, such as by air agitation, solution pumping, moving cathode rod, etc.

For the purpose of giving those skilled in the art a better understanding of the invention, illustrative examples are given. In each of the examples, an aqueous acidic nickel-containing bath was made up with the specified components. Electrodeposition of nickel was carried out by passing electric current through an electric circuit comprising a nickel anode and a sheet metal or rod cathode, both immersed in the bath. The baths were agitated, usually by a moving cathode. Bright electrodeposits were obtained in all the tests included herein as examples.

In Example 1 through 22 inclusive, the following standard bath was used as a base solution:

	G./l.
Nickel sulfate	300
Nickel chloride	60
Boric acid	45
Sodium lauryl sulfate	0.25

The primary brightener is identified from Table I, supra. In the following examples "asd" signifies amperes per square decimeter. The pH figures are electrometric values.

TABLE IV

Ex. No.	Additives	Amt. (g./l.)	CD, (asd)	pH	Temp. (° C.)
1	Saccharin (as K salt)	4	4.0	4.0	55
	Primary Brightener A	0.008			
2	Saccharin (as K salt)	2	4.0	4.0	55
	Benzene sulfonamide	2			
	Primary Brightener A	0.008			
3	Sulfonated dibenzothiophene dioxide (as Na salt)	4	4.0	4.0	58
	Primary Brightener A	0.020			
4	Sodium-1,3,6-naphthalene trisulfonate	15	4.0	3.8	58
	Primary Brightener A	0.016			
5	Saccharin (as K salt)	4	4.0	4.0	55
	Primary Brightener B	0.012			
6	Saccharin (as K salt)	4	4.0	4.0	55
	Mixed isomer of sodium 3-butene-2-hydroxy-1-sulfonate and sodium 3-butene-1-hydroxy-2-sulfonate	2			
	Primary Brightener B	0.012			

TABLE IV—Continued

Ex. No.	Additives	Amt. (g./l.)	CD, (asd)	pH	Temp. (° C.)
7	Saccharin (as K salt).....	4	4.0	3.8	60
	Phenyl propiolamide.....	0.16			
	Primary Brightener B.....	0.006			
8	Saccharin (as K salt).....	2	4.5	4.2	60
	Sodium-3-chloro-2-butene-1-sulfonate.....	4			
	Primary Brightener C.....	0.016			
9	Saccharin (as K salt).....	2	4.5	4.0	55
	Phenyl propiolamide.....	0.2			
	Primary Brightener C.....	0.060			
10	Saccharin (as K salt).....	4	4.0	4.0	55
	Sodium 2-propene-1-sulfonate.....	2			
	Primary Brightener C.....	0.032			
11	Saccharin (as K salt).....	4	4.0	4.0	58
	Mixed isomer of sodium 3-butene-2-hydroxy-1-sulfonate and sodium 3-butene-1-hydroxy-2-sulfonate.....	2			
	Primary Brightener C.....	0.032			
12	Saccharin (as K salt).....	4	4.0	4.0	55
	Primary Brightener D.....	0.012			
13	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	3.5	55
	Primary Brightener E.....	0.016			
14	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	3.8	58
	Primary Brightener F.....	0.016			
15	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	3.5	55
	Phenyl propiolamide.....	0.16			
	Primary Brightener F.....	0.008			
16	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	3.5	3.5	55
	Primary Brightener G.....	0.040			
17	Saccharin (as K salt).....	4	4.0	4.0	55
	Mixed isomer of sodium 3-butene-2-hydroxy-1-sulfonate and sodium 3-butene-1-hydroxy-2-sulfonate.....	2			
	Primary Brightener H.....	0.050			
18	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	4.0	55
	Primary Brightener I.....	0.010			
19	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	4.0	55
	Phenyl propiolamide.....	0.16			
	Primary Brightener I.....	0.010			
20	Saccharin (as K salt).....	4	4.0	4.0	55
	Sodium-3-chloro-2-butene-1-sulfonate.....	4			
	Primary Brightener J.....	0.015			
21	Saccharin (as K salt).....	4	4.0	3.5	55
	Mixed isomer of sodium 3-butene-2-hydroxy-1-sulfonate and sodium 3-butene-1-hydroxy-2-sulfonate.....	2			
	Primary Brightener K.....	0.060			
22	Saccharin (as K salt).....	4	4.0	3.8	60
	Phenyl propiolamide.....	0.16			
	Primary Brightener K.....	0.040			

The compounds designated L, M, and N supra, were also used in similar baths and similar bright electrodeposits were obtained.

In Example 23 to 26 inclusive, the following standard bath was used as a base solution:

	G./l.
Nickel chloride	250
Nickel sulfate	45
Boric acid	45
Sodium lauryl sulfate	0.25

The foregoing examples illustrate specific baths and processes. It is understood that the compositions and conditions may be varied. Although the potassium and sodium salts were most often used and are preferred, they may be partially or completely replaced by such other salts as nickel, magnesium, etc. salts.

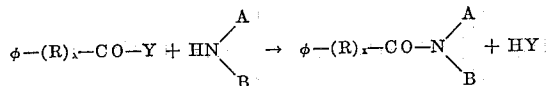
The nickel electrodeposits obtained from baths utilizing the novel brightener combination are advantageous in that mirror-bright lustrous electrodeposits having a high degree of ductility are obtained over a wide range

TABLE V

Ex. No.	Additives	Amt. (g./l.)	CD, (asd)	pH	Temp. (° C.)
23	Saccharin (as K salt).....	2	4.0	4.5	55
	Sodium-3-chloro-2-butene-1-sulfonate.....	2			
	Primary Brightener C.....	0.016			
24	Saccharin (as K salt).....	2	4.0	4.0	55
	Sodium-3-chloro-2-butene-1-sulfonate.....	2			
	Primary Brightener J.....	0.020			
25	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	4.0	55
	Primary Brightener C.....	0.015			
26	Sulfonated dibenzothiophene dioxide (as Na salt).....	4	4.0	4.0	58
	Primary Brightener J.....	0.015			

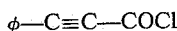
of cathode current densities. The bright nickel electrodeposits are preferably plated on a copper or copper alloy basis metal. However, they may be electrodeposited directly on such metals as iron, steel, etc.

The novel primary brighteners of this invention may advantageously be prepared by the following reaction:



wherein Y may be selected from the group consisting of chloride and bromide and ϕ , R, A, B and x are as defined supra. Thus, for example, when B is hydrogen the product may be a monocyano substituted compound; when B is cyano-substituted group, the product may be a dicyano substituted product.

Typical $\phi-(R)_x-CO-Y$ reactants which may be employed in the novel preparative process of this invention may include phenylpropioloyl chloride



phenyl cinnamoyl bromide $\phi-CH=CH-COBr$; 3-phenylpropanoyl bromide $\phi-CH_2CH_2COBr$; benzoyl chloride; benzoyl bromide; etc.

Typical

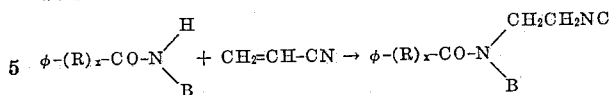


reactants which may find use in the process of this invention may include β -cyanoethyl amine; N,N-di- β -cyanoethyl amine; N-allyl-N- β -cyanoethylamine; cyanomethylamine; N-ethyl-N-cyanomethylamine; N,N-dicyanomethylamine; N-N-butyl-N- β -cyanoethylamine; hydrogen cyanamide; ω -cyanopentamethyleneamine; etc. It will be apparent to one skilled in the art that reactive derivatives of the noted amines, e.g., the amine sulfates, may be substituted for the amine in this preparation.

The reaction of the acid chloride or bromide reactant with the amine reactant may typically be effected under mild conditions, preferably in the presence of a solvent or solvents. The reaction may occur readily and in high yield, typically at temperatures as low as 0° C. or lower. The by-product HY may be removed from the reaction system by reaction with a suitable base, such as sodium hydroxide, sodium carbonate, ammonia, etc. If desired, the use of an additional base may be avoided by employing an excess of the amine reactant which may react with HY to form, e.g., the amine hydrochloride, amine hydrobromide, etc.

A typical preparation may be as follows. The amine reactant in 100% excess may be dissolved in water and the resulting solution may be added to an inert hydrocarbon solvent, say benzene. This mixture may be cooled to a low temperature, say 0° C. The acid chloride or bromide reactant may be dissolved in an inert hydrocarbon solvent, say benzene, preferably a hydrocarbon solvent which has previously been dried. The acid chloride solution may then be added dropwise to the amine solution with moderate stirring, and the reaction mixture may be maintained at a low temperature, say 0° C., throughout the addition. When the addition is complete, the mixture may be allowed to reach room temperature, say 20-30° C., and may be stirred at this temperature for a short period of time, typically about one hour. The two layers may be physically separated and the product may be isolated from the benzene layer by evaporation or distillation after all the residual amine or amine hydrochloride or hydrobromide has been removed, typically by washing with water, and drying. If desired, the product may be further purified by recrystallization or distillation.

Certain of the products of this invention may also be prepared by the reaction:



wherein ϕ , R, B and x are as defined supra. It will be understood that when B is hydrogen, a second equivalent of acrylonitrile may be reacted to form the corresponding N,N-dicyanoethyl product.

This reaction may typically be carried out with or without the use of a suitable insert solvent, typically water. Moderate temperatures, typically 30-100° C. may be employed. Basic catalysts such as sodium hydroxide, triethylamine, etc., may be used in small amounts to accelerate the reaction. Excess acrylonitrile may be stripped off after the reaction is complete.

Preparation of the novel compounds of this invention may be further illustrated by the following specific examples.

Example 27.—N-cyanoethylphenylpropiolamide

Thirty grams of 3-aminopropionitrile (β -cyanoethylamine) was dissolved in 100 cc. of water and chilled in an ice bath. Phenylpropioloyl chloride (22 grams) was added dropwise to the chilled solution and stirring and cooling were maintained throughout the addition. The reaction mixture was allowed to come to room temperature. When the reaction was complete, the product, a soft white solid, was filtered off, washed and recrystallized. N-cyanoethylphenylpropiolamide was obtained in 90% yield as large, plate-like crystals having a melting point of 103-105° C.

Example 28.—N,N-bis- β -cyanoethylphenylpropiolamide

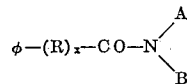
Five grams of phenylpropiolamide was mixed with 25 grams of acrylonitrile and 2 drops of a 40% by weight solution of sodium hydroxide in water. The mixture was warmed for several minutes, after which the excess acrylonitrile was stripped off. The remaining brown gum was leached out with 200 cc. of ethanol, and the resulting solution was then carbon-treated, filtered and cooled. The oil which separated on chilling was separated and treated with petroleum ether to give 2.7 grams of soft solid. After recrystallization the product had a melting point of 97-98° C.

Analysis.—Theory: C, 71.7%; H, 5.2%; N, 16.7%. Found: C, 71.9%; H, 5.2%; N, 16.3%.

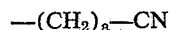
Although this invention has been illustrated by reference to certain specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

I claim:

1. A process for electrodepositing nickel which comprises electrodepositing nickel from a Watts type electroplating bath containing a secondary brightener and, as a primary brightener, an effective amount of a compound having the structure



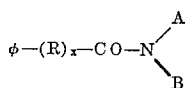
wherein R is selected from the group consisting of $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}=\text{CH}-$, and $-\text{C}\equiv\text{C}-$; x is 0 or 1; A is selected from the group consisting of $-\text{CN}$ and $-(\text{CH}_2)_a-\text{CN}$ wherein a is an integer 1-10; B is selected from the group consisting of hydrogen,



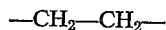
wherein a is an integer 1-10, and hydrocarbon radicals having less than 6 carbon atoms.

2. A process as claimed in claim 1 wherein said primary brightener is present in amount of 0.002 g./l. to 0.100 g./l.

3. An aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of nickel and containing as a primary brightener an effective amount of a compound having the structure



wherein R is selected from the group consisting of



$-CH=CH-$, and $-C\equiv C-$; x is 0 or 1; A is selected from the group consisting of $-CN$ and $-(CH_2)_a-CN$ wherein a is an integer 1-10; and B is selected from the group consisting of hydrogen, $-(CH_2)_a-CN$ wherein a is an integer 1-10, and hydrocarbon radicals having less than 6 carbon atoms.

4. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is present in amount of 0.002 g./l. to 0.100 g./l.

5. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is N,N-bis β -cyanoethyl phenylpropiolamide.

6. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is N,N-bis cyanomethyl phenylpropiolamide.

7. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is N- β -cyanoethyl phenylpropiolamide.

8. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is N-methyl-N- β -cyanoethyl phenylpropiolamide.

9. An aqueous acid electrolytic bath as claimed in claim 3 wherein said primary brightener is N,N-bis β -cyanoethyl cinnamide.

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