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ELECTRODEPOSITION OF NICKEL

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ABSTRACT OF THE DISCLOSURE

The process of this invention comprises electrodepositing nickel from an aqueous nickel electroplating bath containing a secondary brightener and, as a primary brightener, an effective amount of a cyanoethyl compound selected from the group consisting of cyanoethyl thiohydantoin, cyanoethyl 2-imidazolidine thione, cyanoethyl thiobarbituric acid, and cyanoethyl 2-thiouracil.

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 thicknesses 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 agents 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 when used alone 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, levelled deposits which exhibit a good rate of brightening. The rate of brightening and levelling may vary in degree depending on the particular cooperative additives chosen and their actual and relative concentrations. A high degree of rate of brightening and levelling 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 pri-

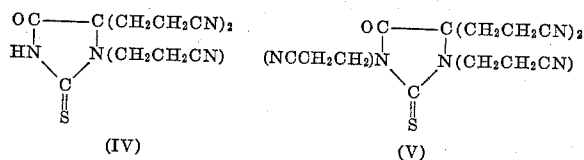
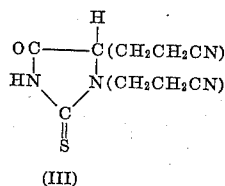
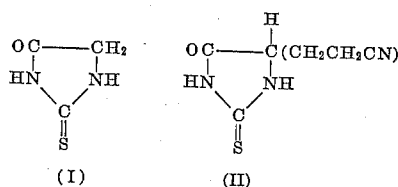
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mary brighteners must usually be maintained within fairly narrow limits in order to maintain desirable properties including good ductility, adequate coverage over low current density areas, etc. Any bright nickel system which can be rendered more tolerant 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.

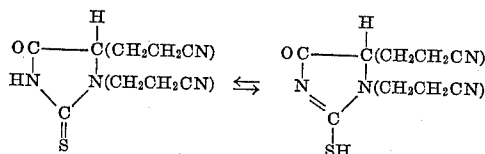
It is an object of this invention to provide improved nickel plate by use of a new class of superior primary brighteners. It is a further object of this invention to provide an efficient process for electrodepositing bright and smooth nickel deposits. Another object of this invention is to provide bath 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 an aqueous nickel electroplating bath containing a secondary brightener and, as a primary brightener an effective amount of a cyanoethyl compound selected from the group consisting of cyanoethyl thiohydantoin, cyanoethylated 2-imidazolidine thione, cyanoethyl thiobarbituric acid, and cyanoethyl 2-thiouracil.

The novel compounds which may be used in practice of this invention may include cyanoethyl thiohydantoin, cyanoethyl 2-imidazolidine thione, cyanoethyl thiobarbituric acid, and cyanoethyl 2-thiouracil. Thiohydantoin (I) may be cyanoethylated as herein disclosed to produce 4-mono- β -cyanoethyl thiohydantoin (II), 3,4,4-di- β -cyanoethyl thiohydantoin (III), 3,4-tri- β -cyanoethyl thiohydantoin (IV), and 1,3,4,4-tetra- β -cyanoethyl thiohydantoin (V):



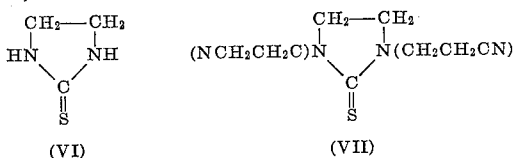
It will be apparent to those skilled in the art that each of these compounds I-IV may each exist in tautomeric equilibrium with its tautomer, e.g. for III:



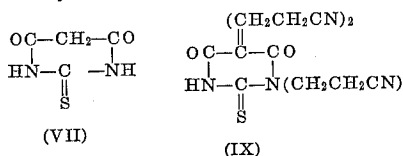
Other isomers may be formed depending upon the particular conditions of synthesis.

It will also be apparent that mixtures of compounds, e.g. isomers, or mixtures of compounds which have been cyanoethylated to a different degree may be simultaneously formed; and these mixtures need not be separated for utilization as hereinafter set forth, because it may be found that these mixtures perform as well as pure compounds or pure isomers. Inertly substituted thiohydantoin derivatives such as 1-acetyl-2-thiohydantoin may also be cyanoethylated to produce e.g. monocyanoethyl 1-acetyl-2-thiohydantoin. When the composition is such (as is the case with the compositions of Formulae II-IV) that the tautomerism permits formation of the thiol from the thione, then the compounds may be soluble in water or dilute alkali due to formation of the thiol salt.

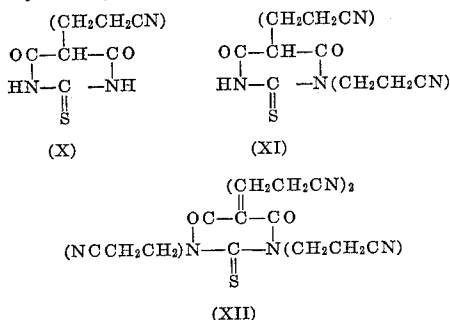
2-imidazolidine thione (VI) may be cyanoethylated, e.g. to produce 1,3-di-β-cyanoethyl-2-imidazolidine thione (VII).



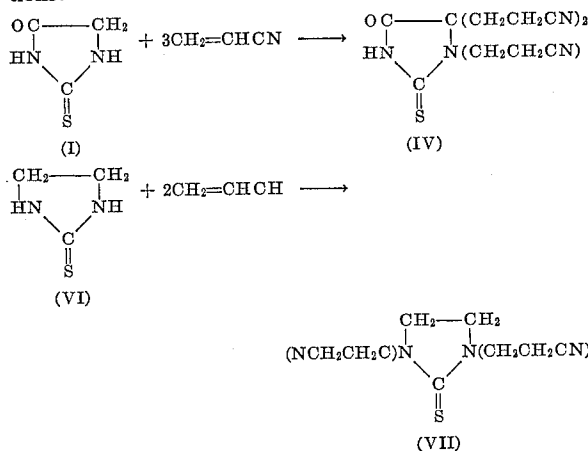
2-thiobarbituric acid (VIII) may be cyanoethylated to produce similarly designated compounds typified by 1,5,5-tri-β-cyanoethyl-2-thiobarbituric acid (IX):



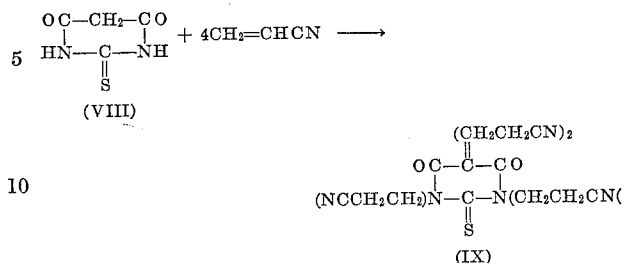
Other cyanoethyl thiobarbituric acid derivatives may include 5-β-cyanoethyl-2-thiobarbituric acid (X), 1,5-di-β-cyanoethyl-2-thiobarbituric acid (XI), and 1,3,5,5-tetra-β-cyanoethyl-2-thiobarbituric acid (XII):



Preparation of the novel compounds of this invention may be in accordance with the following illustrative reactions:

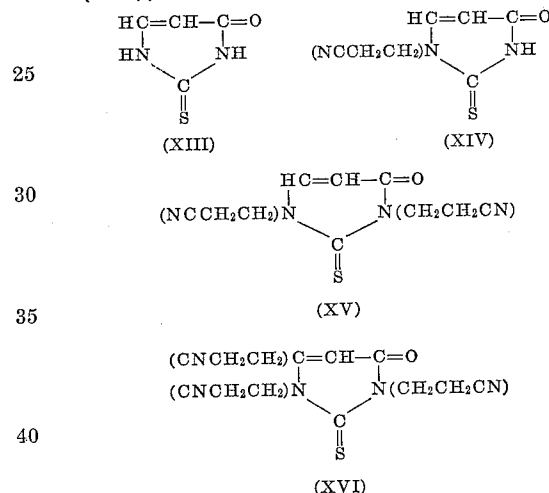


or



Similar to the cyanoethyl thiohydantoin, the cyanoethyl 2-imidazoline thiones and 2-thiobarbiturates, in which at least one imino group remains unsubstituted, may exist in the keto-enol tautomeric forms.

2-thiouracil (XIII) may be cyanoethylated to produce 3-mono-β-cyanoethyl 2-thiouracil (XIV); 1,3-di-β-cyanoethyl 2-thiouracil (XV); 1,3,4-tri-β-cyanoethyl 2-thiouracil (XVI); etc.



The reaction of the heterocyclic thiocarbonyl compound with acrylonitrile may be effected under relatively mild conditions. Preferably water may be used as a reaction medium. Preferably the reaction may be accelerated by use as catalyst of a proton acceptor such as a base such as sodium hydroxide, potassium hydroxide, or quaternary ammonium hydroxides such as benzyl trimethyl ammonium hydroxide or amines such as triethylamine.

Reaction may be effected by mixing the components preferably in the presence of a reaction medium and preferably accompanied by vigorous agitation. To effect lower degrees of cyanoethylation, e.g. to obtain products having up to about three cyanoethyl groups, the acrylonitrile may be present in the amount of 1-1.5 equivalent of acrylonitrile. To introduce four or more cyanoethyl groups, preferably the acrylonitrile may be used in amount of at least two or more equivalents. The position of the cyanoethyl groups may in all cases be readily confirmed by inspection of the infra-red spectrum of the compounds, by the Sodium Azide-Iodine test, elemental analysis, etc.

The temperature during the reaction may be controlled to fall in the range of 0° C. to about 70° C. Lower temperatures e.g. 0° C.-35° C. favor lower degrees of cyanoethylation, while higher temperatures, e.g. 35° C.-70° C. favor higher degrees of cyanoethylation. The time of reaction, depending on the specific compounds reacted, may be from a few minutes, e.g. 5 minutes, to several hours. Commonly it may be 30-60 minutes. At the end of the reaction time, the excess of the acrylonitrile may be removed by distillation (by heating to 80°

C. or higher) or by distillation under vacuum at lower temperatures.

Alkali-insoluble products, such as tetracyanoethyl 2-thiohydantoin, will precipitate on removal of the excess unreacted acrylonitrile. Alkali-soluble products may be recovered by acidification with e.g. dilute sulfuric acid. In either case, the product may then be removed by filtration or decantation depending on whether it is crystalline or liquid. Further purification of crystalline product may be recrystallization from aqueous solutions or organic solvents or mixtures thereof. Purification of liquid products may be effected by fractional distillation, solvent extraction, etc.

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

EXAMPLE 1

3,4-di- β -cyanoethyl-2-thiohydantoin

125 g. water, 18 g. C.P. sodium hydroxide pellets, and 50 g. 2-thiohydantoin were mixed together and stirred magnetically. To the solution, there was added 35 ml. of acrylonitrile, drop by drop, over 25 minutes (starting temperature 35° C., final temperature 58° C.). Stirring was continued for another 40 minutes. The pH after cooling to room temperature was adjusted to 5.5 with dilute sulfuric acid (1:1 by volume) and a heavy crystalline precipitate formed. The product was filtered off, washed with water, and air-dried (50.0 grams)—M.P. 192–194° C. (Fisher-Johns). The product gave a positive Sodium Azide-Iodine test indicating presence of the enol form of the thiocarbonyl group. The product on recrystallization from water gave M.P. 195–196° C. (capillary tube method).

Elemental analysis.—Found: C, 48.88%; H, 4.55%; N, 25.12%; S, 14.28%. Calculated: C, 48.63%; H, 4.54%; N, 25.21%; S, 14.42%.

EXAMPLE 2

3,4,4-tri- β -cyanoethyl-2-thiohydantoin

50 g. 2-thiohydantoin, 150 g. of a water solution containing 18 g. sodium hydroxide were mixed together and magnetically stirred. 175 ml. acrylonitrile was added, drop by drop, over a period of 1 hour. The starting temperature was 32° C. It rose to a maximum temperature of 58° C. after which it was cooled. Final temperature was 45° C. Stirring was continued for 2.5 hours. The reaction mixture was then diluted to 500 ml. with water and the pH adjusted to 7.0 with dilute sulfuric acid (1:1 by volume). A heavy oily layer settled out. The supernatant solution was decanted off and some of the oil recrystallized from methanol—M.P. 178–183° C. (Fisher-Johns). To the balance of the oil, 500 ml. of methanol were added and a crystalline precipitate formed which was filtered off, washed with methanol, and air-dried. Product recovered weighed 41.2 g. On recrystallization from water several times M.P. 190–192° C. (capillary tube method).

Elementary analysis.—Found: C, 52.56%; H, 4.83%; N, 25.64%; S, 11.43%. Calculated: C, 52.34%; H, 4.76%; N, 25.44%; S, 11.64%.

EXAMPLE 3

1,3,4,4-tetracyanoethyl-2-thiohydantoin

5 grams tricyanoethylated 2-thiohydantoin (M.P. of pure material 190–192° C.), 25 g. of water, 2 ml. Triton B (benzyl, trimethyl ammonium hydroxide) and 25 ml. acrylonitrile were mixed and magnetically stirred. Starting temperature was 25° C. The mixture was heated slowly. The temperature after 1 hour was 72° C. Heating was continued for 30 minutes to 80° C. The reaction mixture was then cooled in a refrigerator. An oil separated out which was separated from the upper aqueous layer. The aqueous layer was then extracted with chloroform

and the chloroform extract combined with the oil. The mixture was aspirated on steam bath under vacuum. The residue was a light-yellow oil, 7.30 grams in weight. On acidification in water, there was obtained a white crystalline precipitate which on recrystallization from water gave M.P. 105–107° C. (capillary tube method). A negative Sodium Azide-Iodine test indicated that both imino (NH) hydrogens were substituted by the β -cyanoethyl group.

Elemental analysis.—Found: C, 55.15%; H, 4.66%; N, 25.37%; S, 9.22%. Calculated: C, 55.03%; H, 4.62%; N, 25.67%; S, 9.79%.

EXAMPLE 4

10 g. of 2-imidazolidine thione, 25 g. water, 4 g. sodium hydroxide, and 25 ml. acrylonitrile were mixed and stirred at room temperature. The temperature rose within 2 minutes to 90° C. Stirring was interrupted and reaction mixture cooled to room temperature. The oil which was formed gave a crystalline precipitate on stirring at room temperature. The precipitate was filtered, water washed, ether washed, and dried in a vacuum desiccator. The product gave a negative test with sodium azide-iodine reagent indicating that the two hydrogen atoms attached to the nitrogen atoms had been cyanoethylated. The product on recrystallization from water had a M.P. of 125° C.–128° C. (Fisher-Johns). Yield was 5.3 grams (26.1%) of recrystallized product. The infra-red spectra showed presence of the thiocarbonyl group.

Elemental analysis.—Found: C, 52.33%; H, 5.84%; N, 26.73%; S, 15.45%. Calculated: C, 52.00%; H, 5.77%; N, 27.00%; S, 15.40%.

EXAMPLE 5

Cyanoethylation of 2-thiobarbituric acid

10 g. of 2-thiobarbituric acid, 40 ml. water, 5 g. sodium hydroxide, and 50 ml. acrylonitrile were mixed and stirred at room temperature. The heat of reaction rapidly raised the temperature to 50° C. and the reaction mixture was then slowly heated to 80° C. over 40 minutes. The reaction mixture was cooled to room temperature, acidified with sulfuric acid to a litmus end point, and then placed under vacuum to volatilize any unreacted acrylonitrile. The residue was extracted with two 20 ml. portions of chloroform, the extracts combined and evaporated under vacuum on a steam bath to obtain 8.70 g. of oily residue. This residue gave a positive test with sodium azide-iodine reagent. Boiling point 195–200° C.

EXAMPLE 6

Cyanoethylation of 2-thiouracil

To 75 ml. of water and 25 grams 2-thiouracil there were added, while stirring magnetically, 25 ml. of an aqueous solution of NaOH containing 15 grams of NaOH. The solution was cooled to 23° C. and while stirring there were added 50 ml. acrylonitrile, drop by drop, over a period of 15 minutes, at the end of which time the temperature was 24° C. The solution was then heated slowly over a period of 25 minutes to a final temperature of 50° C. The colorless reaction mixture was then placed under vacuum for 10 minutes to remove any residual unreacted acrylonitrile. To the solution there were then added 25 ml. of a 1:1 solution by volume of concentrated H₂SO₄ and water. The heavy, white crystalline precipitate which was formed was filtered off, washed with water and air dried. The weight of the product was 46.8 g. and the M.P. 225–230° C. A positive Sodium Azide-Iodine test indicated the presence of a thiol or thione group.

Typical compounds which may be effective as primary

brighteners in the novel nickel plating process of this invention, may include:

TABLE I

- (A) Dicyanoethyl 2-thiohydantoin (Example 1).
 (B) Tricyanoethyl 2-thiohydantoin (Example 2).
 (C) Tetracyanoethyl 2-thiohydantoin (Example 3).
 (D) Cyanoethyl 2-imidazolidine thione (Example 4).
 (E) Cyanoethyl 2-thiobarbituric acid (Example 5).
 (F) Cyanoethyl 2-thiouracil (Example 6).

The novel class of primary brighteners of this invention when used in combination with suitable secondary brighteners may give highly lustrous, brilliant deposits characterized by high rate of brightening and levelling, excellent receptivity for chromium plating, excellent low current density coverage, and relatively very low rates of consumption. It is possible to attain excellent ductility by control of concentration of the primary brightener as noted infra. The baths may be used with air agitation or mechanical agitation. The baths may be electrolyzed for relatively long periods without buildup of harmful decomposition products. The brighteners of this invention are also compatible with many secondary brighteners including those characterized by low cost e.g. benzene sulfonamide.

The primary brighteners of this invention may be used in concentrations of 0.002 g./l. to 0.050 g./l., the particular concentration chosen depending on: the particular types and concentrations 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 levelling desired; and the finish of the basis metal. It is preferred to use between 0.004 g./l. and 0.020 g./l.

Preferably baths containing the novel primary brighteners may operate at pH of 3-4.5 with 3.5-4.2 preferred. All pH values herein are electrometric.

Secondary brighteners (typically present in amount of 1-4 g./l. and preferably 2-3 g./l.) which are useful with the primary brighteners of this invention may include aromatic sulfonates, sulfonamides, and sulfimides, or derivatives thereof such as orthobenzoic sulfimide (saccharin), benzene sulfonamide, m-benzene disulfonamide, o-sulfobenzaldehyde, and N,N'-bis(phenylsulfonyl)-4,4'-diphenyl disulfonamide, and dibenzene sulfonamide.

It is a particular feature of the primary brighteners of this invention that it is not necessary to use, in cooperation with secondary brighteners, auxiliary secondary brighteners such as olefinic or acetylenic aliphatic sulfonates, which may be necessary for optimum results when using some prior art primary brighteners.

Typical baths and processes for electroplating bright nickel include those described in "Principles of Electroplating and Electroforming," Blum and Hogaboom, pages 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, pages 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, sodium 7-ethyl-2-methyl-4-undecanol sulfate, or sodium dihexyl sulfosuccinate. 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 BATH

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
pH, electrometric		3 to 4.5
Agitation—Mechanical and/or air, pumping, etc.		

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
pH, electrometric		3 to 4.5
Agitation—Mechanical and/or air, pumping, etc.		

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. With increasing agitation a lower concentration of primary brightener may advantageously be used.

For the purpose of giving those skilled in the art a better understanding of the invention, illustrative examples are hereinafter set forth. 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 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 Examples 7-21, the following standard bath was used as a standard solution:

	G./l.
Nickel sulfate	300
Nickel chloride	60
Boric acid	45
Sodium dihexyl sulfosuccinate	0.10

The primary brightener is identified from Table I supra. In Tables IV and V, the current density (CD) is expressed in ASD, amperes per square decimeter, and the pH is the electrometric pH.

TABLE IV

Ex. No.	Additives	Amount, g./l.	CD	pH	° C.
7	Saccharin	2	4	4	55
	Primary Brightener A	0.016			
8	Saccharin	2	4	4	55
	Primary Brightener B	0.016			
9	Saccharin	2	4	4	55
	Primary Brightener C	0.016			
10	Saccharin	2	4	4	55
	Primary Brightener D	0.016			
11	Saccharin	2	4	4	55
	Primary Brightener E	0.016			
12	Saccharin	0.3	4	4	55
	Benzene sulfonamide	2.0			
	Primary Brightener F	0.032			
13	Benzene sulfonamide	2	4	4	55
	Primary Brightener A	0.016			
14	Benzene sulfonamide	2	4	4	55
	Primary Brightener B	0.016			
15	Benzene sulfonamide	2	4	4	55
	Primary Brightener C	0.016			
16	Benzene sulfonamide	2	4	4	55
	Primary Brightener D	0.016			
17	Benzene sulfonamide	2	4	4	55
	Primary Brightener E	0.016			
18	Saccharin	0.3	5	3.5	55
	Benzene sulfonamide	2			
	Primary Brightener A	0.012			
19	N,N'-bis(phenylsulfonyl)-4,4'-diphenyl disulfonamide	2	4	3.5	50
	Primary Brightener C	0.008			
20	Dibenzene sulfonamide	3	5	3.7	55
	Primary Brightener C	0.008			
12	o-Sulfobenzaldehyde (Nasalt)	2	4	3.5	50
	Saccharin	0.3			
	Primary Brightener C	0.008			

In Examples 22-26 the following standard bath was used as a standard solution:

Nickel chloride -----	G./l.
Nickel sulfate -----	250
Boric acid -----	45
Sodium dihexyl sulfosuccinate -----	45
	0.10

TABLE V

Ex. No.	Additives	Amount, g./l.	CD	pH	° C.
22	Benzene sulfonamide	2	4	4	55
	Saccharin	0.3			
	Primary Brightener A	0.008			
23	Benzene sulfonamide	2	4	4	55
	Saccharin	0.3			
	Primary Brightener B	0.008			
24	Benzene sulfonamide	2	4	4	55
	Saccharin	0.3			
	Primary Brightener C	0.008			
25	Benzene sulfonamide	2	4	4	55
	Saccharin	0.3			
	Primary Brightener D	0.008			
26	Benzene sulfonamide	2	4	4	55
	Saccharin	0.3			
	Primary Brightener E	0.008			

Because of the exceptionally good low current density coverage obtained with the primary brighteners of this invention, they may be particularly useful in plating deeply recessed articles. They have a very high tolerance to metallic contaminants such as zinc and copper, and can therefore be used in plating zinc-base die-castings which are a problem to plate using many prior art nickel brighteners because of their sensitivity to these metals as contaminants particularly in low current density recessed areas.

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 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.

Although this invention has been illustrated by reference to specific examples, numerous changes and modifications thereof which clearly fall within the scope of the invention will be apparent to those skilled in the art. I claim:

1. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener an effective amount of a cyanoethyl compound selected from the group consisting of cyanoethyl thiohydantoin, cyanoethyl 2-imidazolidine thione, cyanoethyl thiobarbituric acid, and cyanoethyl 2-thiouracil.

2. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl thiohydantoin.

3. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl 2-imidazolidine thione.

4. The process for electrodepositing nickel from an

aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener cyanoethyl thiobarbituric acid.

5. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl 2-thiouracil.

6. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath containing a secondary brightener and as a primary brightener an effective amount of tricyanoethyl 2-thiohydantoin.

7. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath as claimed in a secondary brightener and as a primary brightener an effective amount of 3,4,4-tricyanoethyl 2-thiohydantoin.

8. The process for electrodepositing nickel from an aqueous acidic nickel electroplating bath as claimed in claim 1 wherein said primary brightener is present in amount of 0.002 g./l.-0.050 g./l.

9. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of a cyanoethylated compound selected from the group consisting of cyanoethyl thiohydantoin, cyanoethyl 2-imidazolidine thione, cyanoethyl thiobarbituric acid, and cyanoethyl 2-thiouracil.

10. An aqueous acid electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl thiohydantoin.

11. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl 2-imidazolidine thione.

12. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl thiobarbituric acid.

13. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of cyanoethyl 2-thiouracil.

14. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of tricyanoethyl 2-thiohydantoin.

15. An aqueous acidic electroplating bath for electroplating nickel containing a secondary brightener and as a primary brightener an effective amount of 3,4,4-tricyanoethyl 2-thiohydantoin.

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