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ELECTRODEPOSITION OF NICKEL

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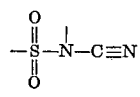
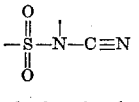
This invention relates to electroplating and, more particularly, to electrodepositing nickel from an aqueous acidic nickel plating bath. The invention is based on the discovery that N-cyanosulfonamides which contain the structural configuration



when incorporated in a nickel electroplating bath, either as the sole brightener or in conjunction with various Class I "carrier" brightness or Class II "leveling" brightening addition agents (or both), are remarkably effective for promoting the formation of nickel deposits which are bright over a very wide current density range and which also possess satisfactory mechanical properties, particularly low internal stress and fair ductility.

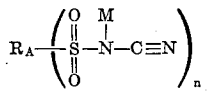
Only relatively small quantities of these N-cyanosulfonamides are required in the plating bath, for, in general, concentrations as low as 0.01 millimole per liter have been found to be effective. In many cases, however, at least 0.1 millimole per liter should be employed to secure the full benefit of its presence in the bath. There appears to be no sharp upper limit on the concentration of these N-cyanosulfonamides, but there is generally no advantage in employing more than 25 millimoles per liter, and in most plating baths substantially the full benefit of their presence is achieved with an amount in the range from about 0.1 to about 10 or even 5 millimoles per liter.

Any N-cyanosulfonamide which contains the structural configuration



may be selected for inclusion in the plating bath. Many of these N-cyanosulfonamides produce fully bright nickel deposits over the entire, or almost the entire, current density range of the Hull Cell panel, yielding bright nickel deposits with low internal stress. Moreover, I have also found that these N-cyanosulfonamide brighteners impart to the plating solution high tolerances to contamination with zinc and copper, which usually occurs upon plating zinc-base die castings.

A preferred process according to this invention for producing low-stress, ductile nickel deposits comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula



in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali

metals, magnesium, cobalt, and nickel, and n is an integer from 1 to 3.

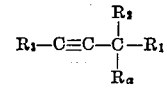
Particularly satisfactory results have been obtained by using in the plating bath such N-cyanosulfonamides as benzene-N-cyanosulfonamide, p-bromobenzene-N-cyanosulfonamide, 3,4-dichlorobenzene - N-cyanosulfonamide, p-toluene-N - cyanosulfonamide, benzyl-N - cyanosulfonamide, p-acetamidobenzene-N-cyanosulfonamide, m-benzenedi-(N-cyanosulfonamide), diphenylsulfone - 3,3'-di-(N-cyanosulfonamide), or their alkali metal, magnesium, cobalt, or nickel salts.

The N-cyanosulfonamides are much more effective brighteners than the related sulfonamides which do not contain the N-cyano group, such as benzene sulfonamide, p-toluenesulfonamide, N-chloro - p-toluenesulfonamide, m-benzenedisulfonamide. As a haze remover in bright nickel baths, e.g. in a Watts' nickel bath containing benzene sulfonic acid and 2-butyne-1,4-diol, o-sulfobenzoic imide (saccharin) is about equally effective as benzene-N-cyanosulfonamide but o-sulfobenzoic imide produces low-current discoloration in presence of 0.15 gram per liter of zinc, while the benzene-N-cyanosulfonamide does not.

Preparation of the N-cyanosulfonamides may be accomplished by reacting a sulfonyl halide, generally the chloride, with a stoichiometric amount of hydrogen cyanamide, and twice the stoichiometric amount of aqueous alkali metal hydroxide.

In contrast to sulfur free cyano compounds, such as ethylenecyanohydrin or hydrogen cyanamide, many N-cyanosulfonamides yield bright nickel deposits with low internal stress when used as the sole addition agents to a nickel bath, but do not exert any appreciable leveling effect. If in addition to brightness, leveling is desired, the N-cyanosulfonamides may be used in the plating bath in conjunction with leveling agents, e.g. water-soluble acetylenic compounds, such as propargyl alcohol, 2-butyne - 1,4-diol or 1,4-di-(β-hydroxyethoxy) - 2-butyne; olefinic glycols, such as 2-butene-1,4-diol; nitriles such as ethylenecyanohydrin; hydrogen cyanamide; coumarin; and quinolinimum compounds.

While any water-soluble acetylenic brightening compound may be employed in a nickel plating bath conjointly with an N-cyanosulfonamide, particularly satisfactory results have been obtained using α-substituted acetylenic compounds having a structure represented by the formula

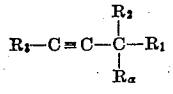


in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, R_3 is a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkynyl groups, and substituted-alkyl groups having the structural configuration

in which each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and each of R_a and R_a' are substituents of the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy, halogen, and polyoxy groups. Where R_3 is a substituted-alkyl group having the above-illustrated structural configura-

tion, then the acetylenic compound is termed an α,α'-disubstituted acetylenic compound, since both carbon atoms vicinal to the same acetylenic bond contain either the same or a different functional group. The compounds listed in Table I are examples of various α-substituted acetylenic compounds which may be used successfully in plating baths containing an N-cyanosulfonamide brightener. These acetylenic compounds are preferably used in concentrations from about 0.1 to about 25 millimoles per liter.

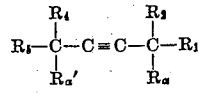
TABLE I.—α-SUBSTITUTED ACETYLENIC COMPOUNDS



Compound	R_1	R_2	R_3	R_α
3-butyne-1,2-diol	$-CH_2OH$	$-H$	$-H$	$-OH$
3-methyl-1-butyn-3-ol	$-CH_3$	$-CH_3$	$-H$	$-OH$
3-methyl-1-pentyn-3-ol	$-C_2H_5$	$-CH_3$	$-H$	$-OH$
2-propyn-1-ol	$-H$	$-H$	$-H$	$-OH$
2,4-hexadiyne-1,6-diol	$-H$	$-H$	$-C\equiv C-CH_2OH$	$-OH$
1-butyn-3-ol	$-CH_3$	$-H$	$-H$	$-OH$
1,2-di-(β-hydroxyethoxy)-3-butyne.	$-CH_2OCH_2CH_2OH$	$-H$	$-H$	$-OCH_2CH_2OH$
3-(β-hydroxy-γ-chloropropoxy)-3-methyl-4-pentyne.	$-C_2H_5$	$-CH_3$	$-H$	$-OCH_2\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}HOH$

Table II sets forth examples of α,α'-disubstituted acetylenic compounds which, when used in the plating bath in conjunction with an N-cyanosulfonamide brightener, yield bright nickel electroplates which possess good ductility, have low internal stress and have excellent leveling.

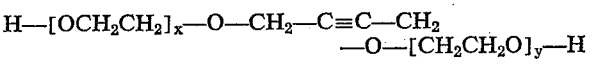
TABLE II.—α,α'-DISUBSTITUTED ACETYLENIC COMPOUNDS



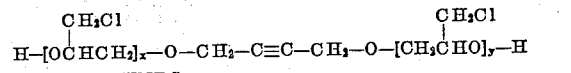
Compound	R_1	R_2	R_4	R_5	R_α	$R_{\alpha'}$
2-butyne-1,4-diol	$-H$	$-H$	$-H$	$-H$	$-OH$	$-OH$
2,5-dimethyl-3-hexyne-2,5-diol	$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$	$-OH$	$-OH$
2,5-Diphenyl-3-hexyne-2,5-diol	$-C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_5$	$-OH$	$-OH$
4-methoxy-2-butyn-1-ol	$-H$	$-H$	$-H$	$-H$	$-OH$	$-OCH_3$
1,4-di-(β-hydroxyethoxy)-2-butyne	$-H$	$-H$	$-H$	$-H$	$-OCH_2CH_2OH$	$-OCH_2CH_2OH$
4,7-di-(β-hydroxy-γ-chloropropoxy)-4,7-dimethyl-5-decyne.	$-C_3H_7$	$-CH_3$	$-CH_3$	$-C_3H_7$	$-OCH_2CH_2OH$	$-OCH_2CH_2OH$
1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne.	$-H$	$-H$	$-H$	$-H$	$-OCH_2\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}HOH$	$-OCH_2\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}HOH$
1-(β-hydroxyethoxy)-2-butyn-4-ol	$-H$	$-H$	$-H$	$-H$	$-OH$	$-OCH_2CH_2OH$
3,6-di-(β-hydroxy-γ-chloropropoxy)-1,4,7-octatriyne.	$-C\equiv CH$	$-H$	$-H$	$-C\equiv CH$	$-OCH_2\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}HOH$	$-OCH_2\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}HOH$
4-chloro-2-butyn-1-ol	$-H$	$-H$	$-H$	$-H$	$-Cl$	$-OH$

Among the most satisfactory acetylenic brightening agents are those prepared by reacting either an α-hydroxy or an α,α'-dihydroxy acetylenic compound, such as those listed in Tables I and II, with either ethylene oxide or epichlorohydrin. These adducts readily dissolve in acidic nickel plating baths, and are unusually effective in such baths both in promoting the formation of bright and ductile electrodeposits over wide current density ranges and in exerting a pronounced leveling effect on the bath during the plating operation. Two such adducts which are notably effective when used in conjunction with the N-cyanosulfonamide brightening additives are the α,α'-di(polyoxy)-2-butynes obtained upon the reaction of 2-butyne-1,4-diol with ethylene oxide and with epichlorohydrin.

2-butyne-1,4-diol reacts with ethylene oxide in the presence of a base to form a 1,4-di-(hydroxypolyethoxy)-2-butyne which is structurally characterized by the formula



and with epichlorohydrin to form a 1,4-di-[hydroxypoly-(β-chloromethyethoxy)]-2-butyene, the structure of which is represented by the formula



x and y in both formulas being integers from 1 to 8. The leveling effect of both of these reaction products in combination with N-cyanosulfonamides in nickel plating baths is especially pronounced.

In addition to the use of the acetylenic brighteners in the plating solution, the usual Class I "carrier" sulfo-oxygen brightening additives may also be employed in the bath together with the N-cyanosulfonamides. These sulfo-oxygen "carrier" brighteners, which are generally used in concentrations in the range from about ¼ to about 80 grams per liter (and preferably in the range from about 1 to about 20 grams per liter), are unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, mag-

nesium, cobalt and nickel salts of these acids, and mononuclear sulfonamides and sulfonimides.

The following examples are illustrative of the effectiveness with which N-cyanosulfonamides may be used in nickel plating baths in accordance with this invention. In each example, the electrodeposit was formed from a Watts' plating bath having the following basic composition:

	Grams/liter
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	300
Nickel chloride, $NiCl_2 \cdot 6H_2O$	60
Boric acid, H_3BO_3	42

Plating operations in each example were carried out in a Hull Cell on brass cathodes, using air agitation, a bath pH of 3.8, a bath temperature of 60° C., a total current of 2 amperes, and a plating time of 10 minutes.

Example I

Nickel was electrodeposited from the basic Watts' bath to which had been added 0.8 gram per liter (ca. 4 millimoles per liter) of sodium benzene-N-cyanosulfonamide, yielding a fully bright nickel deposit, with little or no leveling, over the entire current density range of the Hull Cell panel. The addition of 0.2 gram per liter of zinc (as zinc sulfate) had no deleterious effect.

When (i) 0.08 to 0.32 gram per liter of 2-butyne-1,4-diol, (ii) 0.08 to 0.12 gram per liter of 1,4-di-(α-hydroxyethoxy)2-butyne, (iii) 0.4 to 0.8 gram per liter of the reaction product of equimolar quantities of 2-butyne-1,4-diol and sodium bisulfite (cf. U.S. Patents 3,002,902 and 3,002,903), (iv) 0.06 gram per liter of 1,4-(diethylamino)-2-butyne dihydrochloride, (v) 1 to 1.6 grams per liter of 2-butene-1,4-diol, (vi) 0.04 to 0.06 gram per liter of hydrogen cyanamide, (vii) 0.08 gram per liter of acetylcyanamide, or (viii) 0.08 gram per liter of N-ethylquinolinium iodide were added to the bath containing sodium benzene-N-cyanosulfonamide, the resultant nickel deposits were bright over the entire current density range of the Hull Cell and were appreciably smoother than the basis metal to which the particular deposit was applied.

Example II

When nickel was electrodeposited from the standard Watts' solution described above, to which had been added 9 grams per liter of sodium benzenesulfonate, and 0.27 gram per liter of 2-butyne-1,4-diol, the resultant deposit was marred by a haze in the low current density areas. Upon the addition of 0.2 gram per liter of sodium benzene-N-cyanosulfonamide to this bath, this haze was completely eliminated. Addition of 0.15 gram per liter of zinc (as zinc sulfate) to the bath did not result in any deleterious effect to the appearance of the electroplate.

Example III

When 0.8 gram per liter (ca. 2.4 millimoles per liter) of disodium m-benzenedi-(N-cyanosulfonimide) was added to the basic Watts' solution, the resultant nickel deposit was bright over the entire current density range of the Hull Cell panel. Cooperation with 0.1 gram per liter of 2-butyne-1,4-diol, or with the acetylenic diol and 4 grams per liter of sodium benzenesulfonate, was excellent, with addition of 0.2 gram per liter of zinc (as the sulfate) having no harmful effect on the appearance of the electroplate.

Example IV

The addition of 0.8 gram per liter of sodium p-bromobenzene-N-cyanosulfonamide to the basic Watts' bath produced a fully bright nickel electrodeposit over the entire current density range of the Hull Cell panel. Cooperation with the leveling agent, 2-butyne-1,4-diol (0.16 gram per liter), was satisfactory.

Example V

The addition of 0.8 gram per liter of sodium 3,4-dichlorobenzene-N-cyanosulfonamide to a Watts' nickel bath produced a bright nickel deposit over the whole current density range of the Hull Cell with the exception of the very low current density areas (below 10 amp/sq. ft.), where the deposit was somewhat dark. At a pH of 3.2 this low current density darkness disappeared. Further addition of 0.24 gram per liter of 2-butyne-1,4-diol produced fully bright and strongly leveled deposits.

Example VI

The addition of 0.8 gram per liter of sodium p-toluene-N-cyanosulfonamide to a Watts' nickel bath gave a bright nickel deposit over almost the whole current density range of the Hull Cell panel at 60° C., and a pH of 3.8. Even better results were obtained at a pH of 3.2. Cooperation with 4 grams per liter of sodium benzenesulfonate and 0.16 gram per liter of 2-butyne-1,4-diol was, in a purified Watts' nickel bath, as satisfactory as with the corresponding sodium benzene-N-cyanosulfonamide; however, the benzene derivative tolerated 0.1 gram per liter (and more) of zinc ion (ph=3.8 and 3.2), while the toluene derivative gave a discolored low current density area in the presence of a like amount of zinc.

Example VII

When 0.4 gram per liter of sodium benzyl-N-cyanosulfonamide was added to a Watts' nickel bath (65° C., pH=3.8, air agitation), the resultant nickel deposit was fully bright, non-leveling with the exception of one hazy spot, 0.8 gram per liter of the additive producing a larger haze area. When 0.1 gram per liter to 0.2 gram per liter of this additive was added to a Watts' nickel bath (60° C., pH=3.8) containing 9 grams per liter of sodium benzenesulfonate and 0.24 gram per liter of 2-butyne-1,4-diol, the slight center haze was completely eliminated.

Example VIII

0.1 mole of 3,3'-diphenylsulfonedisulfonyl chloride was allowed to react with 0.2 mole of aqueous hydrogen cyanamide (50%) and 0.4 mole aqueous sodium hydroxide (25%). No separation of the solid disodium salt was attempted in this case, but the reaction mixture was used as an addition agent after appropriate dilution. Addition of this reaction product solution in an amount equivalent to 0.8 gram per liter (or 1.7 millimoles per liter) to a Watts' nickel bath (60° C., pH=3.8) produced a fully bright nickel deposit from 10 to 120 amperes per square foot.

Example IX

To a mixture of 0.1 mole (23.37 g.) N-acetylsulfanilyl chloride, 0.1 mole cyanamide (50% aqueous solution) and 8 ml. of water, was slowly added dropwise a solution of 0.2 mole (8 g.) of sodium hydroxide in 16 ml. of water. The temperature was maintained at 45° C. Since the reaction product did not separate out easily, it was diluted with water to 200 ml. and treated with 2 g. of activated carbon. Addition of 16 milliliters per liter of this product, equivalent to 8 millimoles per liter, produced a fully bright deposit over almost the whole current density range of the Hull Cell panel.

Example X

Addition of only 0.8 millimole per liter of N-acetylsulfanilylcyanamide removed the residual hazes from the nickel deposit obtained from a Watts' nickel bath (pH =3.8) containing 4.5 grams per liter of sodium benzenesulfonate and 0.24 gram per liter of 2-butyne-1,4-diol. The non-acetylated sulfanilylcyanamide had a much stronger embrittling effect and a much weaker brightening effect than the N-acetylated derivative.

Example XI

Recrystallized sodium β-naphthalene-N-cyanosulfonamide, when added to a Watts' nickel bath, acted differently from the N-cyanosulfonamide mentioned in the preceding examples. Addition of 0.1 to 0.8 gram per liter produced increasingly discolored and matte nickel deposits. However, addition of only 0.01 to 0.04 gram per liter (0.04 to 0.16 millimoles/liter) to a Watts' nickel bath containing 4 grams per liter sodium benzenesulfonate and 0.16 gram per liter of 2-butyne-1,4-diol was very effective in brightening local haze areas on the Hull Cell panel and thus promoting the production of a leveling nickel deposit which was fully bright over the whole current density range of the Hull Cell.

Example XII

To 0.5 mole hydrogen cyanamide (50% aqueous solution) and 1.0 mole sodium hydroxide (25% aqueous solution), 0.25 mole of sulfuryl chloride, SO_2Cl_2, were added dropwise and with stirring and cooling, the temperature being maintained at 45° C. The reaction mixture was then diluted to 400 ml. Addition of 1.6 milliliters per liter of this reaction product (equivalent to 1 millimole per liter of SO_2Cl_2) to a Watts' nickel bath containing 4.5 grams per liter of sodium benzenesulfonate gave bright nickel deposits over almost the entire current density range of the Hull Cell, instead of the essentially semibright deposit obtained with benzenesulfonate by itself.

Example XIII

To a mixture of 0.1 mole (21.8 grams) of trichloromethanesulfonyl chloride, 0.1 mole hydrogen cyanamide (50% aqueous solution) and 8 ml. of water was added 0.2 mole of sodium hydroxide (8 grams in 24 ml. of water), with stirring and cooling, the temperature being maintained at 40° C. The red-colored solution was filtered from some unreacted trichloromethanesulfonyl chloride and then diluted to a volume of 200 ml.

Eight milliliters per liter of this solution (equivalent to 4 millimoles per liter), when added to a Watts' nickel bath, brightened only the low current density area; twice this amount produced strong spontaneous cracking of the nickel deposit. But 4 milliliters per liter acted as a very effective haze remover in a Watts' nickel bath also containing 9 grams per liter of sodium benzenesulfonate and 0.16 gram per liter of 2-butyne-1,4-diol.

Example XIV

Addition of 0.2 to 0.4 gram per liter of sodium 2-thiophene-N-cyanosulfonamide to a Watts' nickel bath gave nickel deposits which were bright, but not leveled, up to 60 to 90 amperes per square foot. In presence of 8 grams per liter of sodium benzenesulfonate and 0.16 gram per liter of 2-butyne-1,4-diol, addition of only 0.1 gram per liter, or about 0.5 millimole per liter) of the thiophene derivative was sufficient to remove residual hazes and produce a fully bright, leveled nickel deposit over the whole current density range of the Hull Cell. The resultant bath had excellent tolerance to 0.1 gram per liter of zinc contamination.

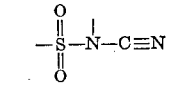
Example XV

0.1 mole of m-benzenedisulfonyl chloride and 0.1 mole of hydrogen cyanamide were allowed to react in presence of 0.4 mole of aqueous sodium hydroxide. The reaction product was diluted to a volume of 200 ml., treated with some activated carbon, and filtered. Addition of 8 milliliters per liter (corresponding to 4 millimoles per liter) of this reaction product to a Watts' nickel bath (60° C., pH=3.8) produced a bright nickel deposit over the entire current density range. Further addition of leveling agents, such as 2-butyne-1,4-diol (0.16 gram per liter) or hydrogen cyanamide (0.06 gram per liter) produced bright and leveled nickel deposits.

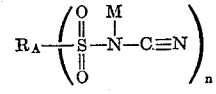
In the foregoing examples of the invention, the N-cyanosulfonamides were successfully employed alone and in combination with various acetylenic and Class I "carrier" brighteners in the standard Watts' nickel electroplating bath, which is prepared by dissolving nickel sulfate, nickel chloride, and boric acid in water. Similar advantages are also attained when the N-cyanosulfonamide is used in other types of aqueous acidic nickel electroplating baths. For example, these N-cyanosulfonamides are beneficial when used in high chloride nickel baths, and in various other nickel plating baths based on using nickel sulfamate or nickel fluoborate as the principal nickel salt which is dissolved in an aqueous acidic solvent.

I claim:

1. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide which contains the structural configuration



2. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.01 to about 10 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula



in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, and acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, magnesium, cobalt, and nickel, and *n* is an integer from 1 to 3.

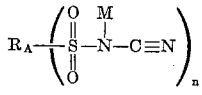
3. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, M-benzene-di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides and the alkali metal, magnesium, cobalt, and nickel salts thereof.

4. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, m-benzene-di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides, and the alkali metal, magnesium, cobalt, and nickel salts thereof; and (b) from about 0.1 to about 25 millimoles per liter of a water-soluble leveling agent.

5. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, m-benzene-di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides and the alkali metal, magnesium, cobalt, and nickel salts thereof; (b) from about ¼ to

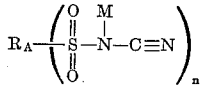
about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, cobalt, and nickel salts of said acids and mononuclear aromatic sulfonamides and sulfonimides; and (c) from about 0.1 to about 25 millimoles per liter of a water-soluble leveling agent.

6. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula



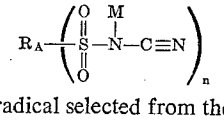
in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, magnesium, cobalt, and nickel, and *n* is an integer from 1 to 3; and (b) from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, cobalt and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides.

7. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula

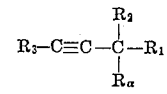


in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, magnesium, cobalt, and nickel, and *n* is an integer from 1 to 3; and (b) from about 0.1 to about 25 millimoles per liter of a leveling agent selected from the group consisting of (i) water-soluble acetylenic compounds, (ii) the bisulfite monoadducts of water-soluble acetylenic compounds, (iii) water-soluble olefinic compounds, (iv) hydrogen cyanamide, (v) acetyl-cyanamides, and (vi) quinolinium compounds.

8. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula



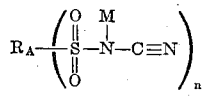
in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, ammonium, magnesium, and nickel, and *n* is an integer from 1 to 3; and (b) from about 0.1 to about 10 millimoles per liter of an α-substituted acetylenic compound having a structure represented by the formula



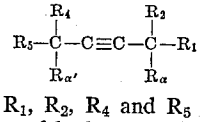
in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, R_3 is a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkynyl groups, and substituted-alkyl groups having the structural configuration

in which each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and each of R_a and R_a' are substituents of the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy, halogen, and polyoxy groups.

9. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula

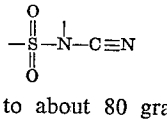


in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, ammonium, magnesium, and nickel, and *n* is an integer from 1 to 3; and (b) from about 0.1 to about 10 millimoles per liter of an α,α'-disubstituted acetylenic compound having a structure represented by the formula



in which each of R_1, R_2, R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and each of R_a and R_a' are substituents of the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy halogen, and polyoxy groups.

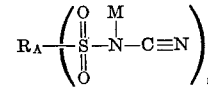
10. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide which contains the structural configuration.



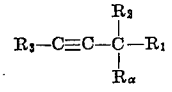
(b) from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, cobalt, and nickel salts of

said acids, and mononuclear aromatic sulfonamides and sulfonimides; and (c) from about 0.1 to about 10 millimoles per liter of a water-soluble acetylenic brightening compound.

11. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 25 millimoles per liter of a water-soluble N-cyanosulfonamide having a structure represented by the formula



in which R_A is a radical selected from the group consisting of (i) alkyl and substituted-alkyl radicals, (ii) mononuclear and binuclear aromatic and alkyl-, sulfo-, halo-, sulfoalkyl-, haloalkyl-, acetamido-substituted aromatic radicals, and (iii) heterocyclic radicals, M is a cation substituent of the group consisting of hydrogen, the alkali metals, magnesium, cobalt, and nickel, and *n* is an integer form 1 to 3; (b) from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, cobalt and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides; and (c) from about 0.1 to about 10 millimoles per liter of an α-substituted acetylenic compound having a structure represented by the formula

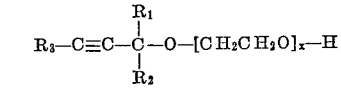


in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, R_3 is a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkynyl groups, and substituted-alkyl groups having the structural configuration

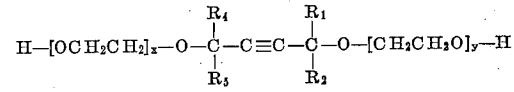
in which each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, and each of R_α and R_α' are substituents of the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy, halogen, and polyoxy groups.

12. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, m-benzene-di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides and the alkali metal, magnesium, cobalt, and nickel salts thereof; and (b) from about 0.1 to about 10 millimoles per liter of a water-soluble acetylenic brightening compound.

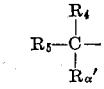
13. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, m-benzene-di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides and the alkali metal, magnesium, cobalt, and nickel salts thereof; (b) from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, magnesium, cobalt, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides; and (c) from about 0.01 to about 10 millimoles per liter of a water-soluble acetylenic compound selected from the group consisting of propargyl alcohol, 2-butyne-1,4-diol, 1-butyn-3-ol, 3-methyl-1-butyn-3-ol, α-polyoxy acetylenic compounds having a structure represented by the formula



and α,α'-di(polyoxy) acetylenic compounds having a structure represented by the formula

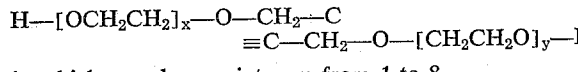


in which each of R_1, R_2, R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkynyl groups, R_3 is a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkynyl groups, and substituted-alkyl groups having the structural configuration



in which R_α' is a substituent of the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkenoxy, halogen, and polyoxy groups, and *x* and *y* are integers from 1 to 8.

14. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.01 to about 10 millimoles per liter of an N-cyanosulfonamide selected from the group consisting of benzene-N-cyanosulfonamide, m-benzene - di-(N-cyanosulfonamide), toluene-N-cyanosulfonamide, the halo-substituted derivatives of said N-cyanosulfonamides and the alkali metal, magnesium, cobalt, and nickel salts thereof; and (b) from about 0.01 to about 10 millimoles per liter of a water-soluble, α,α'-di(polyoxy)-2-butyne having a structure represented by the formula



in which *x* and *y* are integers from 1 to 8.

References Cited by the Examiner

UNITED STATES PATENTS

2,782,155	2/1957	Du Rose et al.	204—49
2,994,648	8/1961	Du Rose	204—49
3,002,904	10/1961	Foulke et al.	204—49
3,116,225	12/1963	Michael et al.	204—49

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