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3,366,557

ELECTRODEPOSITION OF NICKEL

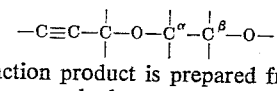
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8 Claims. (Cl. 204—49)

This invention relates to electroplating and, more particularly, to electrodepositing nickel from an aqueous nickel-plating bath. The invention is based on the discovery that water-soluble reaction products prepared by base-catalyzed additions of various alkynols to epoxides are remarkably effective for promoting the formation of bright and ductile nickel electrodeposits over a wide current density range when incorporated in a nickel electroplating bath, particularly in conjunction with various sulfo-oxygen compounds.

The electrodeposition of nickel from a plating bath containing a sulfo-oxygen "carrier" brightener additive generally produces a semi-bright deposit at the cathode, particularly at the lower current densities. Increasing the current density frequently decreases the overall brightness of the deposit and often induces the formation of haze, especially at the low and middle current density ranges. When, however, a small quantity of an alkynol-epoxide adduct, prepared via a base-catalyzed addition of hydroxy-substituted acetylenic compound to an epoxide, is incorporated in the plating bath together with a sulfo-oxygen compound, the brightness capacity of the bath is extended, and the electrodeposit is ductile and bright over a wide current density range.

Because almost any hydroxy-substituted acetylenic compound can be made to react in the presence of a base with an epoxide, absent steric hindrance either of the hydroxy group or of the oxirane ring, no single common structural feature can be advanced to unequivocally characterize all of the reaction products which are prepared by a base-induced reaction between an alkynol and an epoxide and which may be used in a nickel-plating bath in accordance with the invention. Structural characterizations of several of these reaction products, which have been used successfully in nickel-plating baths, have been made on the basis of structural similarities between the alkynols used to prepare these reaction products. For example, where the reaction product is prepared by a base-induced addition of an α-hydroxy aceylenic compound to an epoxide, then the common structural feature of all such adducts is the presence of a β-oxyethoxy group on the carbon atom vicinal to the acetylenic bond, as represented by the following structural formula:

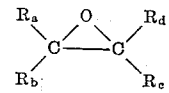


Where the reaction product is prepared from an alkynol in which one or more hydroxy groups are several carbons removed from the acetylenic bond, then this β-oxyethoxy grouping will be correspondingly removed from the acetylenic bond.

Only relatively small quantities of the alkynol-epoxide reaction products are required in the plating bath, especially when they are used in conjunction with a sulfo-oxygen "carrier" brightener, for the presence in the molecule of both an acetylenic bond and a β-oxyethoxy grouping appears to exert a pronounced synergistic effect on the brightening capacity of the sulfo-oxygen compound. In general, concentrations of the alkynol-epoxide reaction products as low as 0.1 millimole per liter are effective, but in many cases at least 1 millimole per liter should be employed to secure the full benefit of their presence in the bath. There appears to be no critical upper limit on the concentration of these alkynol-epoxide adducts save solubility, but there is no advantage generally in employing more than 250 millimoles per liter, and in most plating baths substantially the full benefit of its presence is achieved with 100 millimoles per liter or less.

Any alkynol-epoxide reaction product prepared via a base-induced reaction between a hydroxy-substituted acetylenic compound and an epoxide and which is capable of being dissolved in an aqueous solution of either acid or base and does not undergo decomposition upon protonation or in the presence of a nucleophile may be selected for inclusion in the plating solution. Particularly satisfactory results have been obtained by using additives (reaction products) prepared from α-hydroxy-substituted acetylenic compounds, the only limitations being that the α-hydroxy acetylenic compound used to prepare the additive contain at least one hydroxy group on a carbon atom vicinal to the acetylenic bond and that this hydroxy group be sufficiently unhindered to form an alkoxide ion and react with an oxirane ring. If these two conditions are met, then any α-hydroxy acetylenic compound, including those which are polyols, polyacetylenic, or both, or even contain other functional groups, may be used to form an adduct which is suitable for inclusion in a nickel-plating bath.

A preferred process according to this invention for producing bright nickel deposits comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about 0.1 to about 250 millimoles per liter of a water-soluble reaction product of a base-catalyzed addition of an α-hydroxy acetylenic compound with from N to xN times an equivalent weight of an epoxide, where N is an integer from 1 to 20 and x is equal to the number of hydroxy groups per molecule of the acetylenic compound. The epoxides used in preparing this reaction product are structurally represented by the formula



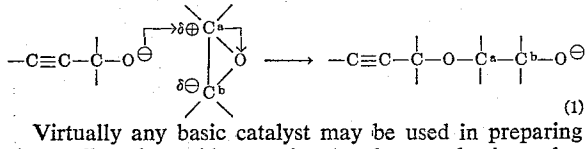
in which each of R_a and R_b are substituents of the group consisting of hydrogen, alkyl, alkenyl, mononuclear aryl and aralkyl groups, and hydroxy-substituted, alkoxy-substituted, and epoxy-substituted alkyl and alkenyl groups, and each of R_c and R_d are substituents of the group consisting of hydrogen, chloromethyl, carboxy, cyano, mononuclear aryl, alkyl, alkenyl, alkoxy, alkenoxy, and hydroxy-substituted, alkoxy-substituted, alkenoxy-substituted, and epoxy-substituted alkyl, alkenyl, alkoxy, and alkenoxy groups. To obtain alkeynol-epoxide reaction products which are readily soluble in aqueous solution, the chain length of each of the oxirane substituents (R_a, R_b, R_c, and R_d) of the particular epoxide used to prepare the reaction product preferably should contain not more than from 5 to 7 carbon atoms. However, if these oxirane substituents contain a sufficient number of hydrophilic groups, then the number of carbon atoms in the oxirane substituents does not materially affect the water solubility of the resultant alkynol-epoxide reaction product.

The effect of these alkynol-epoxide reaction products on the brightening capacity of various sulfo-oxygen compounds is especially pronounced when they are used in the nickel plating solution together with from ¼ to 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 sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of these acids, and mononuclear aromatic sulfonamides and sulfonimides.

Preparation of the alkynol-epoxide reaction products is generally accomplished by inverse addition of the epoxide to a reaction mixture of the alkynol and a catalytic amount

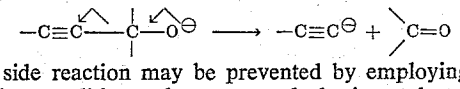
of base. Inverse addition of the epoxide to the alkynol, rather than the converse, is the most frequently used technique since it affords close control over the number of recurring polyoxy groups in the end-product. Other reaction techniques have been used to prepare the alkynol-epoxide adducts, including simultaneous addition of both reactants to a solution of base or initial polymerization of the epoxide followed by reaction with the alkynol, but in general they are difficult to control and do not yield uniform products.

Although the reaction between an alkynol and an epoxide is conveniently termed an "addition," and although the term "adducts" is used interchangeably in the specification with "reaction products," since no elimination (or condensation) of water occurs during the reaction and in a sense the end-product is the additive of the reactant moieties, the reaction is properly classified as a nucleophilic aliphatic substitution which proceeds via the formation of an acetylenic alkoxide anion which attacks one of the epoxide carbons and causes nucleophilic fission of the oxirane ring. Because the reaction is a nucleophilic aliphatic substitution, and is generally of second-order kinetics (S_N2), certain generalizations can be made which will enable prediction of the structure of the reaction products. For example, the acetylenic alkoxide anion preferentially attacks the primary epoxide carbon, if one is present, in a higher epoxide rather than secondary or tertiary carbon. Where both epoxide carbons are secondary or tertiary, then absent steric hindrance the anion will attack that epoxide carbon which possesses the highest fractional positive charge ($\delta\oplus$), as shown by the following reaction sequence:



(1)

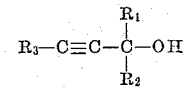
Virtually any basic catalyst may be used in preparing these alkynol-epoxide reaction products, selection of a suitable catalyst being dependent upon the particular alkynol used in the reaction. Where α-hydroxy acetylenic compounds are used to prepare the additives, then the basicity of the catalyst becomes important, since under certain conditions the anion of an α-hydroxy acetylenic compound is capable of undergoing a reverse-Favorskii reaction or cleavage into an acetylide ion and a carbonyl, as illustrated by the following reaction:



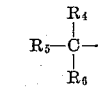
(2)

This side reaction may be prevented by employing mild reaction conditions when a strongly basic catalyst is employed, or by using a mild base, such as triethylamine, when more vigorous reaction conditions are necessary to complete the reaction.

The alkynol-epoxide reaction products prepared from α-hydroxy acetylenic compounds have been found to be unusually effective brightening agents, especially when used in a plating bath in conjunction with various sulfo-oxygen compounds. Particularly satisfactory results have been obtained using reaction products (alkynol-epoxide adducts) prepared from α-hydroxy acetylenic compounds having a structure represented by the formula

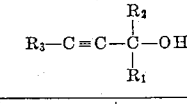


in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and R_3 is a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, hydroxy-substituted, alkoxy-substituted, and amino-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, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and R_6 is a substituent of the group consisting of hydroxy, alkoxy, formoxy, alkanoxy, and halogen. Where R_3 is a substituted-alkyl group having the above structural configuration, in which R_6 is a hydroxy group, then the alkynol is termed an α,α'-dihydroxy acetylenic compound, since both carbon atoms vicinal to the same acetylenic bond contain free hydroxy groups. The compounds listed in Table I are examples of various α-hydroxy acetylenic compounds from which effective brightening agents may be prepared.

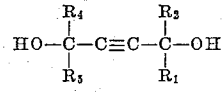
TABLE I.—α-HYDROXY ACETYLENIC COMPOUNDS



Compound	R_1	R_2	R_3
3-butyne-1,2-diol	$-CH_2OH$	$-H$	$-H$
3-methyl-1-butyn-3-ol	$-CH_3$	$-CH_3$	$-H$
3-methyl-1-pentyn-3-ol.	$-C_2H_5$	$-CH_3$	$-H$
2-propyn-1-ol	$-H$	$-H$	$-H$
2,5-dimethyl-1-octen-3-yn-5-ol.	$-C_3H_7$	$-CH_3$	$-C(CH_3)=CH_2$
6-amino-2,4-hexadiyn-1-ol.	$-H$	$-H$	$-C\equiv C-CH_2NH_2$
3-methyl-1-nonyn-3-ol.	$-C_6H_{13}$	$-CH_3$	$-H$
2,4-hexadiyne-1,6-diol	$-H$	$-H$	$-C\equiv C-CH_2OH$
4-methoxy-2-butyn-1-ol.	$-H$	$-H$	$-CH_2OCH_3$
2-(N,N-diethylamino)-3-hexyn-5-ol.	$-CH_3$	$-CH_3$	$-CH_2CH_2N(C_2H_5)_2$
4-chloro-2-butyn-1-ol	$-H$	$-H$	$-CH_2Cl$

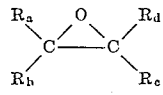
Table II sets forth examples of α,α'-dihydroxy acetylenic compounds which may be used to prepare the alkynol-epoxide reaction products which, in turn, may be employed successfully in embodiments of this invention.

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



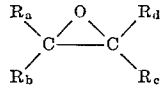
Compound	R_1	R_2	R_4	R_5
2-butyne-1,4-diol	$-H$	$-H$	$-H$	$-H$
2,5-dimethyl-3-hexyne-2,5-diol	$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$
4,7-dimethyl-5-decyn-4,7-diol	$-C_3H_7$	$-CH_3$	$-CH_3$	$-C_3H_7$
3,6-dimethyl-1,7-octadien-4-yne-3,6-diol	$-C_3H_3$	$-CH_3$	$-CH_3$	$-C_3H_3$
1,8-di-[N,N-di-(β-hydroxyethyl)amino]-3,6-dimethyl-4-octyne-3,6-diol.	$-C_2H_4N(C_2H_4OH)_2$	$-CH_3$	$-CH_3$	$-C_2H_4N(C_2H_4OH)_2$
2,5-diphenyl-3-hexyne-2,5-diol	$-C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_5$
1,1,4,4-tetraphenyl-2-butyne-1,4-diol	$-C_6H_5$	$-C_6H_5$	$-C_6H_5$	$-C_6H_5$

The epoxides used in preparing the alkynol-epoxide reaction products are structurally characterized by the formula



in which R_a, R_b, R_c, and R_d are the substituents hereinbefore specified. Upon reaction with the alkynol and nucleophilic fission of the oxirane ring, the epoxide moiety is transformed in the reaction product into a chain of recurring β-oxyethoxy groupings, the number of such groupings in the molecule being dependent upon the proportions of alkynol and epoxide employed in the reaction. As a general rule, the most satisfactory brightening agents are those which are prepared by reacting the alkynol with from N to xN times an equivalent weight of epoxide, where N is an integer from 1 to 20 and x is equal to the number of free hydroxy groups in the alkynol molecule. Table III sets forth examples of the epoxides which have been reacted with various alkynols, including those listed in Tables I and II, to form additives which may be used successfully in embodiments of this invention.

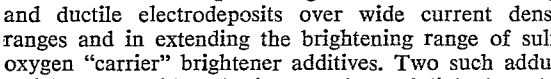
TABLE III.—EPOXIDES



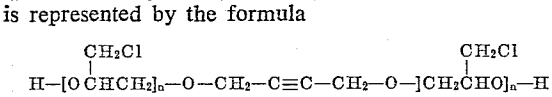
Compound	R_a	R_b	R_c	R_d
Ethylene oxide	—H	—H	—H	—H
Propylene oxide	—H	—H	—H	—CH_3
Epichlorohydrin	—H	—H	—H	—CH_2Cl
Butadiene monoxide	—H	—H	—C_2H_3	—H
Butadiene dioxide	—H	—H	—C_2H_3O	—H
Allyl glycidyl ether	—H	—H	—$CH_2(C_3H_5O)$	—H
Isopropyl glycidyl ether	—H	—H	—C_3H_7O	—H
2,3-epoxybutane	—CH_3	—H	—H	—CH_3
Styrene oxide	—H	—H	—H	—C_6H_5
Di-(1,2-dimethyl-1,2-epoxypropyl) ether	—CH_3	—CH_3	—CH_3	—$(C_5H_9O)O$
1,2-epoxypentane	—H	—H	—H	—C_3H_7
α,β-Epoxypropionic acid	—H	—H	—H	—COOH
α,β-Epoxypropionitrile	—H	—H	—H	—CN

Among the most satisfactory 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 both acidic and basic 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 extending the brightening range of sulfo-oxygen "carrier" brightener additives. Two such adducts which are notably effective 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-chloromethylethoxy)]-2-butyne, the structure of which is represented by the formula



n in both formulas being an integer from 1 to 20. The brightening effect of both of these reaction products in combination with various sulfo-oxygen compounds in nickel plating baths is especially pronounced.

The compounds listed in Table IV are examples of sulfo-oxygen compounds which, when used in the plating bath in conjunction with an alkynol-epoxide reaction product, extend the current density range over which the formation of ductile and bright nickel electrodeposits may be obtained. These sulfo-oxygen compounds may be used over a very wide range of concentrations (for example, from ¼ to 80 grams per liter), but preferably they are used in an amount in the range from about 1 to about 20 grams per liter.

TABLE IV.—ORGANIC SULFO-OXYGEN COMPOUNDS

(1) Unsaturated aliphatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Sodium vinyl sulfonate, $H_2C{=}CHSO_3Na$
Sodium allyl sulfonate, $H_2C{=}CHCH_2SO_3Na$

(2) Mononuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Benzene monosulfonic acid, $C_6H_5SO_3H$
Sodium benzene monosulfonate, $C_6H_5SO_3Na$
Nickel benzene monosulfonate, $(C_6H_5SO_3)_2Ni$
Sodium p-toluene monosulfonate, $CH_3C_6H_4SO_3Na$
p-Chlorobenzene sulfonic acid, $ClC_6H_4SO_3H$
Sodium p-chlorobenzene sulfonate, $ClC_6H_4SO_3Na$
Sodium p-bromobenzene sulfonate, $BrC_6H_4SO_3Na$
1,2-dichlorobenzene sulfonic acid, $Cl_2C_6H_3SO_3H$
1,2- or 2,5-dichlorobenzene sulfonate sodium salt, $Cl_2C_6H_3SO_3Na$
Sodium m-benzene disulfonate, $C_6H_4(SO_3Na)_2$
m-Benzene disulfonic acid, $C_6H_4(SO_3H)_2$
Nickel m-benzene disulfonate, $C_6H_4(SO_3)_2Ni$
o-Sulfobenzoic acid monoammonium salt, $HOOC{-}C_6H_4SO_3NH_4$
1-amino-2,5-benzene disulfonic acid, $H_2NC_6H_3(SO_3H)_2$
o-Aminobenzene sulfonic acid, $H_2NC_6H_4SO_3H$

(3) Mononuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Sodium benzene sulfinate, $C_6H_5SO_2Na$
Sodium p-toluene sulfinate, $CH_3C_6H_4SO_2Na$

(4) Mononuclear aromatic sulfonamides and sulfonimides:

Benzene sulfonamide, $C_6H_5SO_2NH_2$
p-Toluene sulfonamide, $CH_3C_6H_4SO_2NH_2$
o-Sulfobenzoic imide, $C_6H_4CONHSO_2$
Benzyl sulfonamide, $C_6H_5CH_2SO_2NH_2$
Benzene sulfhydroxamic acid, $C_6H_5SO_2NHOH$
N,N-dimethyl-p-toluene sulfonamide, $CH_3C_6H_4SO_2N(CH_3)_2$
N,N-dicarboxyethyl benzene sulfonamide, $C_6H_5SO_2N(C_2H_4COOH)_2$

(5) Binuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

2-naphthalene monosulfonic acid, $C_{10}H_7SO_3H$
1,5- or 2,7-naphthalene disulfonic acid, $C_{10}H_6(SO_3H)_2$
Nickel 1,5- or 2,7-naphthalene disulfonate, $C_{10}H_6(SO_3)_2Ni$
Sodium naphthalene trisulfonate, $C_{10}H_5(SO_3Na)_3$
Naphthalene trisulfonic acid, $C_{10}H_5(SO_3H)_3$
Diphenyl p,p'-disulfonic acid, $HSO_3C_6H_4—C_6H_4SO_3H$
2-naphthol-3,6-disulfonic acid, $HOC_{10}H_5(SO_3H)_2$
Sodium 2-naphthol-3,6-disulfonate, $HOC_{10}H_5(SO_3Na)_2$
1-naphthylamine-3,6,8-trisulfonic acid, $H_2N\cdot C_{10}H_4(SO_3H)_3$

(6) Heterocyclic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:

Thiophene sulfonic acid, $C_4H_3S\cdot SO_3H$
Sodium thiophene sulfonate, $C_4H_3S\cdot SO_3Na$
2-(4-pyridyl)ethyl sulfonic acid, $C_5H_4N\cdot C_2H_4SO_3H$

For the most part, only the free sulfonic acids are listed in Table IV. However, the alkali metal, ammonium, magnesium, and nickel salts of these acids are in all cases the full equivalent of the corresponding sulfonic acid, and may be used in its place in carrying out the process of the invention.

Table V summarizes the preparation of the reaction products of four different epoxides with 2-butyne-1,4-diol which were employed in carrying out the examples of the invention that are set forth below. Each of the compounds listed in Table V was prepared by reacting 1.0 mole of 2-butyne-1,4-diol with 2.0 moles of the epoxide in the presence of from 0.5 to 5 percent by weight of a basic catalyst. The basicity of the catalyst as well as the reaction conditions employed were sufficiently mild so that the danger of a reverse-Favorskii reaction (which would have resulted in the cleavage of 2-butyne-1,4-diol to acetylene and formaldehyde) was precluded. A fifth compound, 1,4-di-(β,γ-epoxypropoxy)-2-butyne, was prepared by dehydrohalogenating an aliquot portion of 1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne, which was initially prepared by reacting epichlorohydrin with 2-butyne-1,4-diol.

a temperature of 65° C. Mild agitation of the bath was provided in each case. As indicated in Table VI, each of the epoxide adducts was employed in a solution free from a sulfo-oxygen compound, and again in a solution in which 15 grams per liter of sodium naphthalene-1,3,6-trisulfonate had been dissolved.

TABLE VI.—BRIGHT NICKEL PLATING WITH 1,4-DI-(POLYOXY)-2-BUTYNES

Compound	Conc. (gm./l.)	Sodium naphthalene-1,3,6-trisulfonate (gm./l.)	Current Density Range (a.s.f.) of maximum brightness
1,4-di-(β-hydroxyethoxy)-2-butyne.	0.4	0.0	1 to 15.
	0.4	15.0	1 to 80.
1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne.	1.1	0.0	1 to 20.
	1.1	15.0	1 to 80.
1,4-di-(β,γ-epoxypropoxy)-2-butyne.	1.0	0.0	1 to 15.
	1.0	15.0	2 to 80.
1,4-di-(β-hydroxy-γ-butenoxy)-2-butyne.[1]	0.9	0.0	1 to 15.
	0.9	15.0	3 to 80.
1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne.[2]	1.3	0.0	4 to 10.
	1.3	15.0	6 to 80.

[1] Reaction product of 2-butyne-1,4-diol and two equivalents of butadiene monoxide; also contains 1,4-di(α-hydroxymethyl-β-propenoxy)-2 butyne as well as 1-(β-hydroxy-γ-butenoxy)-4-(α-hydroxymethyl-β propenoxy)-2-butyne.

[2] Reaction product of 2-butyne-1,4-diol and two equivalents of allyl glycidyl ether; also contains 1,4-di-(1'-hydroxymethyl-3'-oxa-5'-hexenoxy)-2-butyne as well as 1-(1'-hydroxymethyl-3'-oxa-5'-hexenoxy)-4-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne.

Although Table VI indicates that bright deposits are obtained when the epoxide adducts of alkynols are used alone (without the sulfo-oxygen compound), the current density range of maximum brightness in such cases is somewhat restricted. By way of contrast, when the electrodeposit was received on the test panel under identical plating conditions, but using a plating bath containing only the sulfo-oxygen compound, the deposit was semi-bright over a wide current density range and possessed a strong haze at the middle and low current density ranges. For optimum results, therefore, the plating bath should contain both the sulfo-oxygen compound and the epoxide-alkynol reaction product.

The effectiveness of various sulfo-oxygen compounds in providing a wide current density range over which bright

TABLE V.—PREPARATION OF 1,4-DI-(POLYOXY)-2-BUTYNES

Reactants			Products
Acetylenic Compound (moles)	Epoxide (moles)	Catalyst (percent)	
2-butyne-1,4-diol (1.0)	Ethylene oxide (2.0)	NaOH (5%)	1,4-di-(β-hydroxyethoxy)-2-butyne.
2-butyne-1,4-diol (1.0)	Epichlorohydrin (2.0)	Na_2CO_3 (5%)	1,4-di-(β-hydroxy-γ-chloropropoxy)-2-butyne.
2-butyne-1,4-diol (1.0)	Butadiene monoxide (2.0)	NaOH (3%)	(a) 1,4-di-(β-hydroxy-γ-butenoxy)-2-butyne (predominant product). (b) 1,4-di-(α-hydroxymethyl-β-propenoxy)-2-butyne. (c) 1-(β-hydroxy-γ-butenoxy)-4-(α-hydroxymethyl-β-propenoxy)-2-butyne.
2-butyne-1,4-diol (1.0)	Allyl glycidyl ether (2.0)	K_2CO_3 (0.5%)	(a) 1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne (predominant product). (b) 1,4-di-(1'-hydroxymethyl-3'-oxa-5'-hexenoxy)-2-butyne. (c) 1-(1'-hydroxymethyl-3'-oxa-5'-hexenoxy)-4-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne.

In each of the following examples of the invention, which are summarized in Tables VI and VII, the electrodeposit was formed from a Watts plating bath having the following basic composition:

	Grams per liter
Nickel sulfate, $NiSO_4\cdot 7H_2O$	300
Nickel chloride, $NiCl_2\cdot 6H_2O$	45
Boric acid, H_3BO_3	41.25

Table VI sets forth the results obtained when nickel was electrodeposited from the standard Watts plating bath which also contained one of the five epoxide adducts described in Table V. The pH of the bath was adjusted to about 3.4 in each case, and the electrodeposit formed at

deposits can be produced from a bath containing 1,4-di-(β-hydroxyethoxy)-2-butyne is illustrated by the examples set forth in Table VII below. Electroplates of nickel, deposited from a highly purified Watts plating bath (pH=3.4) containing 300 grams per liter of nickel sulfate ($NiSO_4\cdot 7H_2O$), 45 grams per liter of nickel chloride ($NiCl_2\cdot 6H_2O$), 41.25 grams per liter of boric acid (H_3BO_3), and 0.4 gram per liter of 1,4-di-(β-hydroxyethoxy)-2-butyne, increased in brilliance when a sulfo-oxygen compound was used in conjunction with the epoxide-alkynol adduct. Plating operations were carried out using mild air agitation and at a bath temperature of 65° C.

TABLE VII.—EFFECT OF 1,4-DI-(β-HYDROXYETHOXY)-2-BUTYNE[a] AND VARIOUS SULFO-OXYGEN COMPOUNDS ON BRIGHT NICKEL PLATING

Sulfo-Oxygen Compound	Conc. (gm./l.)	1,4-di-(β-hydroxyethoxy)-2-butyne (gm./l.)	Current Density Range (a.s.f.) of maximum brightness
Sodium vinylsulfonate	1.1	0.4	1 to 40.
p-Toluenesulfonamide	0.4	0.4	1 to 80.
Sodium benzene-1,3-disulfonate.	3.2	0.4	1 to 80.
	17.6	0.4	1 to 80.
o-Sulfobenzoic imide	0.5	0.4	1 to 80.

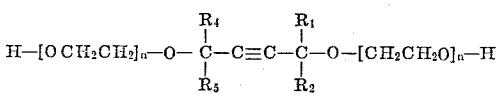
[a] Reaction product of 2-butyne-1,4-diol and two equivalents of ethylene oxide; may contain small quantities of polymeric condensates.

The general principle illustrated in Table VII, that the plating range of a bath containing an epoxide-alkynol adduct may be extended by the addition to that bath of a sulfo-oxygen compound, was repeatedly and consistently verified in another series of tests using a large number of epoxide-alkynol adducts and of sulfo-oxygen brightening addition agents.

In the foregoing examples of the invention, the reaction products of a base-catalyzed reaction of an α-hydroxy acetylenic compound with an epoxide were used successfully 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 epoxide-alkynol adducts are dissolved in other types of aqueous acidic or basic nickel electroplating baths. For example, the epoxide-alkynol adducts are beneficial when used in straight nickel sulfate baths, in straight nickel chloride baths, and in various other nickel plating baths based on using nickel formate, nickel sulfamate, or nickel fluoborate as the nickel salt which is dissolved in an aqueous acidic solvent. In other tests, bright to brilliant nickel electroplates were obtained from aqueous alkaline nickel plating baths containing the epoxide-alkynol adduct. Consequently, the invention is applicable to electrodeposition from any aqueous solution of one or more nickel salts.

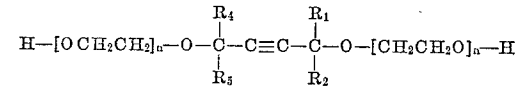
We claim:

1. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about 0.1 to about 250 millimoles per liter of an α,α′-di(polyoxy) acetylenic compound having a structure represented by the formula



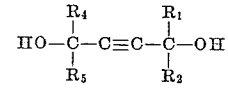
in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and n is an integer from 1 to 20.

2. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved 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, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 0.1 to about 250 millimoles per liter of an α,α′-di(polyoxy) acetylenic compound having a structure represented by the formula

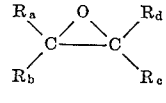


in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and n is an integer from 1 to 20.

3. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved 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, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 1 to about 100 millimoles per liter of a water-soluble reaction product of a base-catalyzed reaction of an α,α′-dihydroxy acetylenic compound with from N to xN times an equivalent weight of an epoxide, where N is an integer from 1 to 20 and x is equal to the number of hydroxy groups per molecule of the α,α′-dihydroxy acetylenic compound whereby both α and α′ hydroxy groups are converted into ether radicals, said α,α′-dihydroxy acetylenic compound having a structure represented by the formula



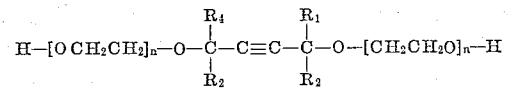
in which each of R_1 and R_2 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and said epoxide having a structure represented by the formula



in which each of R_a and R_b are substituents of the group consisting of hydrogen, alkyl, alkenyl, mononuclear aryl and aralkyl groups, and hydroxy-substituted, alkoxy-substituted, and epoxy-substituted alkyl and alkenyl groups, and each of R_c and R_d are substituents of the group consisting of hydrogen, chloromethyl, carboxy, cyano, mononuclear aryl, alkyl, alkenyl, alkoxy, alkenoxy, and hydroxy-substituted, alkoxy-substituted, alkenoxy-substituted, and epoxy-substituted alkyl, alkenyl, alkoxy, and alkenoxy groups.

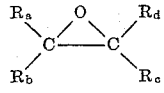
4. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mono-nuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 1 to about 100 millimoles

per liter of an α,α'-di(polyoxy) 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, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, each of R_4 and R_5 are substituents of the group consisting of hydrogen, alkyl, alkenyl, alkynyl, and hydroxy-substituted, alkoxy-substituted, and amino-substituted alkyl, alkenyl, and alkynyl groups, and n is an integer from 1 to 20.

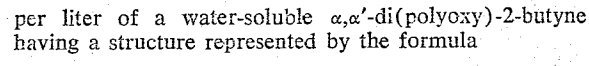
5. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mono-nuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 1 to about 100 millimoles per liter of a water-soluble reaction product of a base-catalyzed condensation of 2-butyne-1,4-diol with from N to 2N times an equivalent weight of an epoxide whereby both hydroxy groups of said 2-butyne-1,4-diol are converted into ether radicals, said epoxide having a structure represented by the formula



in which each of R_a and R_b are substituents of the group consisting of hydrogen, alkyl, alkenyl, mononuclear aryl and aralkyl groups, and hydroxy-substituted alkoxy-substituted, and epoxy-substituted alkyl and alkenyl groups, and each of R_c and R_d are substituents of the group consisting of hydrogen, chloromethyl, carboxy, cyano, mono-nuclear aryl, alkyl, alkenyl, alkoxy, alkenoxy, and hydroxy-substituted, alkoxy-substituted, alkenoxy-substituted, and epoxy-substituted alkyl, alkenyl, alkoxy, and alkenoxy groups, and where N is an integer from 1 to 20.

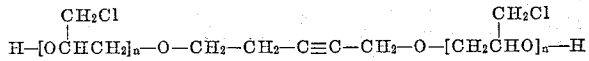
6. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved from about ¼ to about 80 grams per liter of a water-soluble sulfo-oxygen compound of the group consisting of unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, the alkali metal, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 1 to about 100 millimoles

per liter of a water-soluble α,α'-di(polyoxy)-2-butyne having a structure represented by the formula



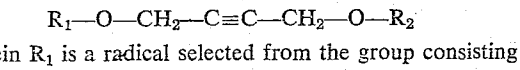
in which n is an integer from 1 to 20.

7. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt in which there is dissolved 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, ammonium, magnesium, and nickel salts of said acids, and mononuclear aromatic sulfonamides and sulfonimides, and from about 1 to about 100 millimoles per liter of a water-soluble α,α'-di(polyoxy)-2-butyne having a structure represented by the formula

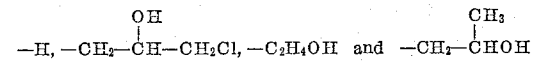


in which n is an integer from 1 to 20.

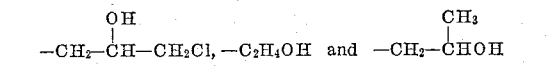
8. The process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous solution of at least one nickel salt characterized in that there is dissolved in the nickel plating bath at least about 1 millimole per liter of a compound of the formula



wherein R_1 is a radical selected from the group consisting of



and R_2 is a radical selected from the group consisting of



and sodium allyl sulfonate in an amount of at least about 0.3 gram/liter.

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UNITED STATES PATENT OFFICE

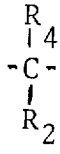
CERTIFICATE OF CORRECTION

Patent No. 3,366,557 January 30, 1968

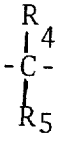
Donald Gardner Foulke et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 59, for "sulfonic" read -- sulfinic --; column 11, lines 3 to 6, for that portion of the formula reading



read



Signed and sealed this 1st day of April 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents