

1

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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 the monoadduct bisulfite addition products of acetylenic compounds, when incorporated in a nickel electroplating bath which also contains one or more water-soluble acetylenic brightening compounds, are remarkably effective for promoting the formation of very bright and ductile electrodeposits of nickel over a wide current density range and, moreover, exert a pronounced leveling effect on the electroplate formed during the plating operation. The current density range over which bright deposits are formed, and the quality of the deposit may be further improved by incorporating one or more sulfo-oxygen "carrier" brightener compounds in the bath in conjunction with the bisulfite addition product and the water-soluble acetylenic brightener.

Theoretically, there are at least two possible bisulfite addition products which may be formed from a given acetylenic compound. Disregarding the numerous optical and geometrical enantiomorphs which chemical theory predicts may be formed, the addition of a bisulfite to an acetylenic bond proceeds in two successive stages, the first of which results in the formation of an initial bisulfite addition product which in turn reacts, in the second stage, to form a second bisulfite adduct. The extent of the reaction is dependent upon and therefore controlled by the molar proportions of bisulfite present in the reaction mixture. Although the proof of structure of each of the two adducts is far from conclusive, the initial bisulfite addition product of an acetylenic compound appears to be an α,β -unsaturated sulfonic acid (or sulfonate), which is capable of undergoing further addition in the presence of excess bisulfite to form the second adduct. The apparent structure of this second bisulfite addition product is that of a saturated disulfonic acid (or sulfonate), in which the sulfonic acid (or sulfonate) groups are vicinal.

Because almost any acetylenic compound can be made to undergo bisulfite addition, that is can be made to react with a compound capable of forming a chain-carrying sulfite radical to form one or more bisulfite addition products, no single common structural feature can be advanced to unequivocally characterize all of these adducts. At the present time, the only convenient characterization of the adducts is based on designating the proportionate amount of bisulfite (or of any compound capable of forming a chain-carrying sulfite radical) used in the reaction mixture. For example, the addition of a single equivalent of bisulfite to an acetylenic bond yields a compound which may be termed a "monoadduct," while further addition of a second equivalent of bisulfite to this compound results in the formation of a second adduct which, for convenience, is designated as a "biadduct," both adducts probably containing impurities.

Using a bisulfite addition product prepared by reacting a water-soluble acetylenic compound together with N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, we have found that it is possible to promote the formation of bright and even brilliant electrodeposits of nickel over very wide current density ranges when the bisulfite adduct is incorporated in an aqueous acidic nickel

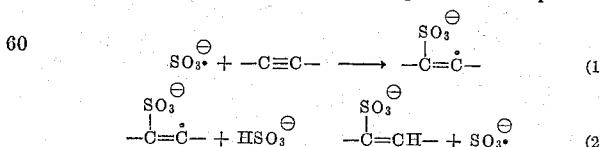
2

plating bath containing one or more water-soluble acetylenic brightener compounds. When the bisulfite adduct is incorporated in an aqueous acidic nickel plating bath which also contains one or more sulfo-oxygen "carrier" brightener compounds in conjunction with the acetylenic brightener, the current density range over which bright deposits are formed is extended still further, for the combined use of the bisulfite addition product, the water-soluble acetylenic brightener, and the sulfo-oxygen compound has been found to exert a synergistic effect on the brightening capacity of the bath as compared with the use of either of these additives by themselves.

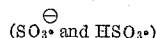
Only very small quantities of these bisulfite addition products are required in the plating bath for, in general, concentrations as low as 0.1 millimol per liter have been found to be effective. In many cases, however, at least 1 millimol per liter of the bisulfite addition products should be employed to secure the full benefit of their presence in the bath. There appears to be no critical upper limit on the concentration of these bisulfite addition products save solubility, but there is generally no advantage in employing more than 300 millimols per liter, and in most plating baths substantially the full benefit of its presence is achieved with 50 millimols per liter, or even less.

Any bisulfite addition product prepared by reacting a water-soluble acetylenic compound with N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, may be selected for inclusion in the plating solution. Particularly satisfactory results have been obtained by using the bisulfite addition products prepared from α -substituted or α,α' -disubstituted acetylenic compounds, both of which contain a functional group on a carbon atom vicinal to the acetylenic bond. It is of course necessary that the particular α -substituted or α,α' -disubstituted acetylenic compound used to prepare the bisulfite adduct contains at least one acetylenic bond which is neither sterically nor electronically hindered from undergoing reaction with a chain-carrying sulfite radical, and that the bisulfite adduct be capable of being dissolved in acid without undergoing decomposition.

Preparation of the bisulfite addition products is generally accomplished by refluxing an aqueous solution containing both the acetylenic compound and an alkali metal bisulfite (or sulfite) until most of the bisulfite (or sulfite) ions have been consumed. The rate at which bisulfite ion is consumed in the reaction mixture may be accelerated by passing gaseous oxygen through the mixture or by adding a trace amount of a free radical initiator (i.e., benzoyl peroxide) to the reactants; the rate is sharply diminished, on the other hand, by adding trace amounts of free radical inhibitors such as hydroquinone and similar antioxidants, to the reaction mixture. From these observations, it may be concluded that bisulfite addition to an acetylenic bond occurs primarily by a radical chain process, in which the chain-carrying steps may be postulated as proceeding via the following reaction sequence:



The exact nature of the chain-carrying sulfite radical is not actually known, since a similar chain involving $\text{HSO}_3^{\cdot}$ can be written. Both species



have been proposed for the autoxidation of bisulfite and sulfite ions by oxygen, and hence either may be the transitory intermediate which adds to the acetylenic bond. No

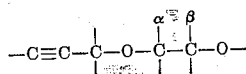
matter what the transitory intermediate radical, however, any compound which is capable of forming a chain-carrying sulfite radical may be used to form the bisulfite adduct. The term "compound capable of forming a chain-carrying sulfite radical" denotes the alkali metal or metal bisulfites, sulfites, and metabisulfites, as well as sulfurous acid or gaseous sulfur dioxide. All of these compounds may be used to form bisulfite adducts of acetylenic compounds which, in turn, may be used in nickel plating baths in accordance with this invention.

Even though all of the available evidence indicates that bisulfite addition to an acetylenic bond is radical in nature, and that consequently the predominant product formed when excess bisulfite is used is the corresponding vicinal disulfonic acid (or disulfonate), the possibility that bisulfite or sulfite ions form charge-transfer complexes with acetylenic bonds, or that bisulfite or sulfite ions undergo ionic addition to an acetylenic bond, cannot be completely dismissed.

After the bisulfite adduct has been prepared, the reaction mixture may be added directly (or decolorized and then added directly) to the nickel plating bath or, alternatively, the bisulfite addition product may be recovered from the reaction mixture (either by crystallization or precipitation), and then added to the plating bath, the same plating results being obtained in either case. Although the bisulfite addition products may be used in concentrations as high as 300 millimols per liter, or even more, there is no particular advantage to be gained from the higher concentrations, and the biadducts are preferably used in the range of concentrations from about 1 to about 50 millimols per liter, or even in the relatively narrow range from 1 to 10 millimols per liter.

Although all water-soluble acetylenic compounds, particularly those which contain one or more oxygen atoms, exert some degree of leveling on nickel plating baths and may therefore be used in the bath in combination with the bisulfite adduct, our experience has indicated that the water-soluble reaction products prepared via a base-catalyzed addition of a hydroxy-substituted acetylenic compound to an epoxide generally exhibit a more pronounced leveling effect on the bath during the plating operation than do any of the other water-soluble acetylenic brighteners. These alkynol-epoxide adducts, when incorporated in a nickel plating bath in combination with various bisulfite monoadducts in accordance with the invention, give a very high degree of leveling and a very wide bright plating range of current densities. Moreover, electroplates formed from baths containing the alkynol-epoxide adduct and a bisulfite monoadduct exhibit an unusually high tolerance to the presence of metallic impurities in the bath, such as copper and zinc, and have notably great ductility and a remarkably low internal stress.

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 acetylenic 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:

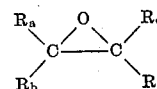


Where the reaction product is prepared from an alkynol in which one or more hydroxy groups are several carbons removed from the acetylenic bond, then this β -oxyethoxy grouping will be correspondingly removed from the acetylenic bond.

Only relatively small quantities of these alkynol-epoxide reaction products are required in the plating bath, when they are used in conjunction with a bisulfite monoadduct brightener in accordance with the invention, for the presence in the molecule of both an acetylenic bond and a β -oxyethoxy grouping appears to exert a pronounced leveling effect on the electroplate formed during the plating operation. In general, concentrations of the alkynol-epoxide reaction products as low as 0.1 millimol per liter are effective, but in many cases at least 1 millimol 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 50 millimols per liter, and in most plating baths substantially the full benefit of its presence is achieved with 10 millimols per liter or less.

Any alkynol-epoxide reaction product prepared via a base-induced reaction between a hydroxy-substituted 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, 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 together with the bisulfite monoadduct. 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 containing a bisulfite adduct.

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



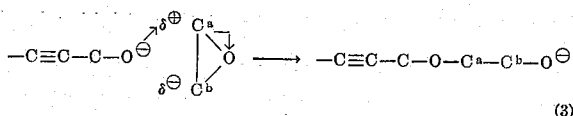
in which each of R_a and R_b are substituents of the group consisting of hydrogen, alkyl, alkenyl, mononuclear aryl and aralkyl groups, and hydroxy-substituted, alkoxy-substituted, and epoxy-substituted alkyl and alkenyl groups, and each of R_c and R_d are substituents of the group consisting of hydrogen,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

Preparation of the alkynol-epoxide reaction products is generally accomplished by inverse addition of the

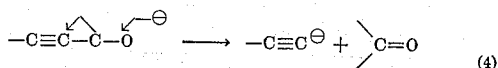
5

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, in turn, 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 and secondary or tertiary, then absent steric hindrance the anion will attack that epoxide carbon which possesses the highest fractional positive charge (δ^+), as shown by the following reaction sequence:



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:



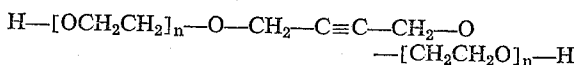
This side reaction may be prevented by employing mild reaction conditions when a strongly basic catalyst is employed, or by a mild base, such as triethylamine, when more vigorous reaction conditions are necessary to complete the reaction.

Among the most satisfactory acetylenic brightening agents are those prepared by reacting either an α -hydroxy or an α,α' -dihydroxy acetylenic compound with either ethylene oxide or epi-chlorohydrin. These adducts readily dissolved 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 carboxylic acid "carrier" additives are the α,α' -di-(polyoxy)-2-butyne obtained upon the reaction of 2-butyne-1,4-diol with ethylene oxide and with epichlorohydrin.

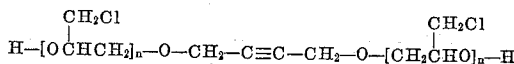
2-butyne-1,4-diol reacts with ethylene oxide in the presence of a base to form a 1,4-di-(hydroxypolyethoxy)-

6

2-butyne which is structurally characterized by the formula



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



n in both formulas being an integer from 1 to 20. The leveling effect of both of these reaction products in combination with various bisulfite monoadducts in nickel plating baths is especially pronounced.

The compounds listed in Table I are examples of sulfo-oxygen compounds which, when used in the plating bath in conjunction with a water-soluble acetylenic compound and the monoadduct bisulfite addition product of the same or a different acetylenic compound, extend the current density range over which the formation of ductile and bright nickel electro-deposits may be obtained. These sulfo-oxygen compounds may be used over a very wide range of concentrations ($\frac{1}{4}$ to 80 grams per liter), but preferably are used in an amount in the range from about 1 to about 20 grams per liter.

TABLE I

Organic Sulfo-Oxygen Compounds

- (1) Unsaturated aliphatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:
 - Sodium vinyl sulfonate, $\text{H}_2\text{C=CHSO}_3\text{Na}$
 - Sodium allyl sulfonate, $\text{H}_2\text{C=CHCH}_2\text{SO}_3\text{Na}$
 - 2-phenylethylene sulfonic acid, $\text{C}_6\text{H}_5\text{CH=CHSO}_3\text{H}$
- (2) Mononuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:
 - Benzene monosulfonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$
 - Sodium benzene monosulfonate, $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$
 - Nickel benzene monosulfonate, $(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Ni}$
 - Sodium p-toluene monosulfonate, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$
 - p-Chlorobenzene sulfonic acid, $\text{ClC}_6\text{H}_4\text{SO}_3\text{H}$
 - Sodium p-chlorobenzene sulfonate, $\text{ClC}_6\text{H}_4\text{SO}_3\text{Na}$
 - Sodium p-bromobenzene sulfonate, $\text{BrC}_6\text{H}_4\text{SO}_3\text{Na}$
 - 1,2-dichlorobenzene sulfonic acid, $\text{Cl}_2\text{C}_6\text{H}_3\text{SO}_3\text{H}$
 - 1,2- or 2,5-dichlorobenzene sulfonate sodium salt, $\text{Cl}_2\text{C}_6\text{H}_3\text{SO}_3\text{Na}$
 - Sodium m-benzene disulfonate, $\text{C}_6\text{H}_4(\text{SO}_3\text{Na})_2$
 - m-Benzene disulfonic acid, $\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$
 - Nickel m-benzene disulfonate, $\text{C}_6\text{H}_4(\text{SO}_3)_2\text{Ni}$
 - o-Sulfobenzoic acid monoammonium salt, $\text{HOOC---C}_6\text{H}_4\text{SO}_3\text{NH}_4$
 - 1-amino-2,5-benzene disulfonic acid, $\text{H}_2\text{NC}_6\text{H}_3(\text{SO}_3\text{H})_2$
 - o-Aminobenzene sulfonic acid, $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$
- (3) Mononuclear aromatic sulfinic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:
 - Sodium benzene sulfinic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{Na}$
 - Sodium p-toluene sulfinic acid, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Na}$
- (4) Mononuclear aromatic sulfonamides and sulfonimides:
 - Benzene sulfonamide, $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$
 - p-Toluene sulfonamide, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$
 - o-Sulfobenzene imide, $\text{C}_6\text{H}_4\text{CONHSO}_2$
 - Benzyl sulfonamide, $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{NH}_2$
 - Benzene sulfinic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{NHOH}$
 - N,N-dimethyl-p-toluene sulfonamide, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)_2$
 - N,N-dicarboxyethyl benzene sulfonamide, $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{COOH})_2$

- (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,
 $H_2N.C_{10}H_4(SO_3H)_3$
- (6) Heterocyclic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof:
 Thiophene sulfonic acid, $C_4H_3S.SO_3H$
 Sodium thiophene sulfonate, $C_4H_3S.SO_3Na$
 2-(4-pyridyl)ethyl sulfonic acid, $C_5H_4N.C_2H_4SO_3H$

For the most part only the free sulfonic acids are listed in Table I. 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.

The following examples are illustrative of the effectiveness with which the monoadduct bisulfite addition products of acetylenic compounds may be used in conjunction with water-soluble acetylenic brightener compounds in accordance with this invention. In each example, Watts nickel plating bath having the following basic composition was used:

	Grams per liter
Nickel sulfate, $NiSO_4 \cdot 7H_2O$	300
Nickel chloride, $NiCl_2 \cdot 6H_2O$	45
Boric acid, H_3BO_3	40

After adjusting the pH of the bath to 4.5 with sulfuric acid and adding varying quantities of either a water-soluble acetylenic brightener, a monoadduct bisulfite addition product or an acetylenic compound, a sulfon-oxygen "carrier" brightening compound, or various combinations of these additives, an electrodeposit of nickel was formed on a brass cathode in a Hull cell, using air agitation, a bath temperature of 60° C., and a total current of 2 amperes.

EXAMPLE I

Upon the addition of 0.3 gram per liter of 1,4-di-(β -hydroxy-ethoxy)-2-butyne to the basic Watts plating solution described above, a bright nickel electrodeposit was formed over only a portion of the brass cathode, the deposit exhibiting a striking feather-like pattern in which alternate areas of the nickel electroplate possessed variable thickness.

EXAMPLE II

The bisulfite addition product of 2-butyne-1,4-diol was prepared by refluxing equimolar proportions of 2-butyne-1,4-diol (in the form of a 36 percent aqueous solution) and sodium bisulfite. After refluxing the reaction mixture for about 7½ hours, it was diluted with water, treated with activated carbon and filtered, yielding a very light yellow solution. Titration of an aliquot of the filtrate with standard iodine-potassium iodide reagent, using starch as an indicator, showed that only 2.6 mol percent of the original sodium bisulfite had remained unreacted. From both the infrared spectrum and the chemical properties of the bisulfite addition product, it was adduced that the predominant product formed during the reaction was sodium 1,4-dihydroxy-2-butene-2-sulfonate. The bisulfite addition product could be used in nickel plating baths without further purification, or it could be precipitated or crystallized from solution and

then redissolved in the plating bath, the plating results being the same in either case.

When 0.2 gram per liter of the resulting bisulfite addition product was incorporated in the standard Watts plating solution described above, to which had been added 0.3 gram per liter of 1,4-di-(β -hydroxyethoxy)-2-butyne, the resultant electrodeposit was very bright over a very wide current density range and exhibited only a slight amount of the freakiness and skip plating which characterized the electroplate produced in Example I.

The addition of 4 grams per liter of sodium benzenesulfonate to this bath increased the current density range over which bright deposits are formed, but did not decrease the slight degree of skip plating or freakiness obtained. Increasing the concentration of the sodium 1,4-dihydroxy-2-butene-2-sulfonate (the monoadduct bisulfite addition product of 2-butyne-1,4-diol) to 0.4 gram per liter completely eliminated all traces of skip plating or freakiness from the electrodeposit.

EXAMPLE III

The pronounced leveling effect exerted upon the electroplate formed from a bath which contains both an acetylenic brightener and a monoadduct bisulfite addition product of the same or a different acetylenic compound is illustrated by the four examples set forth in Table II below. In each of these examples, an electrodeposit of nickel was formed on a roughened steel panel having a roughness value (root mean square value in microinches) of from about 18 to about 24, using a bath temperature of 60° C., air agitation, and a current density ranging from 3.2 to 6.4 amperes per square decimeter.

TABLE II

35 Leveling Effect Upon Using the Bisulfite Addition Product of 2-Butyne-1,4-Diol and 1,4-Di-(β -Hydroxyethoxy)-2-Butyne in Bright Nickel Plating Baths

	Bath No			
	1	2	3	4
A. Bath Composition (g/l):				
Benzenesulfonamide	1	1	1	1
Sodium benzenesulfonate	3	1	1	3
Sodium 1,4-dihydroxy-2-butene-2-sulfonate	0.4	0.4	0.4	0.4
1,4-Di-(β -hydroxyethoxy)-2-butyne		0.14	0.14	0.14
B. Operating Conditions:				
Plating time (minutes)	20	20	20	20
Current density (amps./dm ²)	3.2	3.2	6.4	6.4
pH	4.5	4.5	4.5	4.5
Temperature (° C.)	60	60	59	60
C. Character of Electrodeposit:				
Surface roughness before plating (micro-inches)	20.6	22.3	18.2	24.2
Surface roughness after plating (micro-inches)	11.2	7.6	4.5	4.5
Reduction in surface roughness (percent)	45.5	66.0	76.0	81.5

EXAMPLE IV

When as little as 5 milligrams per liter of copper (in the form of a stable, acid soluble copper compound) are added to a Watts nickel plating solution containing 4 grams per liter of sodium benzenesulfonate and 0.15 gram per liter of 2-butyne-1,4-diol, the resultant electrodeposit is discolored by a dark area in the low current density zone of a Hull cell panel. Similar hazes and discolorations are also produced when the bath is contaminated with other metallic impurities, such as zinc. The addition to the bath of only 0.09 gram per liter of sodium 1,4-dihydroxy-2-butene-2-sulfonate (the bisulfite adduct described in Example II) completely eliminates the discolorations on the test panel produced by the presence of copper or zinc impurities in the bath.

EXAMPLE V

Using a basic Watts nickel plating bath described above, to which had been added 8 grams per liter of sodium benzenemonosulfonate, 0.1 gram per liter of so-

dium 1,4-dihydroxy-2-butene-2-sulfonate (the bisulfite adduct described in Example II), and 0.1 gram per liter of 2-butyne-1,4-diol, a very bright nickel electrodeposit was formed over the current density range of from less than 1 to more than 9 amperes per square decimeter, using a bath temperature of from 40° to 75° C., and a bath pH of from 2.8 to 5, with or without agitation. The electroplates possessed a smoothness greater than that of the basis metal on which it was deposited, low stress and good ductility.

EXAMPLE VI

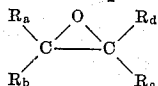
To a dilute aqueous solution of 1,4-di-(β -hydroxyethoxy)-2-butyne was added an equimolar quantity of sodium bisulfite and the reaction mixture refluxed for about 7 hours. After cooling, the solution was further diluted with water, treated with activated carbon, and filtered under suction, yielding an almost colorless filtrate. The predominant product formed during the reaction was sodium 1,4-di-(β -hydroxyethoxy)-2-butene-2-sulfonate.

An electrodeposit of nickel was formed on a Hull cell test panel, using a basic Watts bath having substantially the same composition (in nickel sulfate, nickel chloride, and boric acid) described previously. The deposit formed at a bath temperature of 60° C. and at a pH of 3.1 to 3.5 was matte and slightly stressed. Upon adding 0.4 gram per liter of the resulting bisulfite adduct, 0.3 gram per liter of 1,4-di-(β -hydroxyethoxy)-2-butyne, 4 grams per liter of sodium benzenesulfonate, 0.8 gram per liter of benzenesulfonamide, and 0.4 gram per liter of sodium saccharin, a bright to brilliant electrodeposit was formed under the same plating conditions.

In the foregoing examples of the invention, the mono-adduct bisulfite addition products of acetylenic compounds 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 bisulfite addition product is dissolved in other types of aqueous acidic nickel electroplating baths. For example, the bisulfite 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 the aqueous acidic solvent. Consequently the invention is applicable to electrodeposition from any aqueous acidic solution of one or more nickel salts.

We claim:

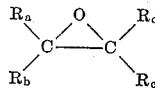
1. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.1 to about 50 millimols per liter of a water-soluble bisulfite addition product of a water-soluble acetylenic compound and N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical and being selected from the group consisting of sulfurous acid, sulfur dioxide, and the alkali metal and metal bisulfites, sulfites, and metabisulfites, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, and (b) from about 1 to about 50 millimols per liter of a water-soluble reaction product of a base-catalyzed reaction of a hydroxy-substituted 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 hydroxy-substituted acetylenic compound, 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.

2. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.1 to about 50 millimols per liter of a water-soluble bisulfite addition product of a water-soluble acetylenic compound and N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical and being selected from the group consisting of sulfurous acid, sulfur dioxide, and the alkali metal and metal bisulfites, sulfites, and metabisulfites, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, (b) from about 1 to about 50 millimols per liter of a water-soluble reaction product of a base-catalyzed reaction of a hydroxy-substituted 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 hydroxy-substituted acetylenic compound, 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, and (c) from about 1/4 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.

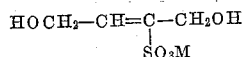
3. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.1 to about 50 millimols per liter of a water-soluble bisulfite addition product of a water-soluble acetylenic compound and N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical and being selected from the group consisting of sulfurous acid, sulfur dioxide, and the alkali metal and metal bisulfites, sulfites, and metabisulfites, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, and (b) from about 1 to about 25 millimols per liter of 2-butyne-1,4-diol.

4. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 0.1 to about 50 millimols per liter of a water-soluble bisulfite addition product of a water-soluble acetylenic compound and N times an equivalent weight of a compound capable of forming a chain-carrying sulfite radical and being se-

11

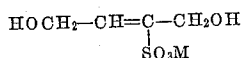
lected from the group consisting of sulfurous acid, sulfur dioxide, and the alkali metal and metal bisulfites, sulfites, and metabisulfites, where N is equal to the number of acetylenic bonds per molecule of the acetylenic compound, and (b) from about 1 to about 50 millimols per liter of 1,4-di-(β -hydroxyethoxy)-2-butyne.

5. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 1 to about 50 millimols per liter of a compound represented by the formula



in which M is a cation substituent selected from the group consisting of hydrogen, alkali metals, ammonium, magnesium, and nickel, and (b) from about 1 to about 50 millimols per liter of 2-butyne-1,4-diol.

6. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 1 to about 100 millimols per liter of a compound represented by the formula

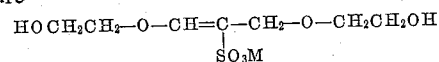


in which M is a cation substituent selected from the group consisting of hydrogen, alkali metals, ammonium, magnesium, and nickel, and (b) from about 1 to about 50 millimols per liter of 1,4-di-(β -hydroxyethoxy)-2-butyne.

7. The process for producing a bright nickel deposit substantially smoother than the basis metal to which

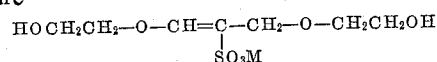
12

it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 1 to about 50 millimols per liter of a compound represented by the structure



in which M is a cation substituent selected from the group consisting of hydrogen, alkali metals, ammonium, magnesium, and nickel, and (b) from about 1 to about 50 millimols per liter of 2-butyne-1,4-diol.

8. The process for producing a bright nickel deposit substantially smoother than the basis metal to which it is applied which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved (a) from about 1 to about 50 millimols per liter of a compound represented by the structure



in which M is a cation substituent selected from the group consisting of hydrogen, alkali metals, ammonium, magnesium, and nickel, and (b) from about 1 to about 50 millimols per liter of 1,4-di-(β -hydroxyethoxy)-2-butyne.

References Cited in the file of this patent

UNITED STATES PATENTS

30	2,427,280	Hoffman	Sept. 9, 1947
	2,712,522	Kzrdos	July 5, 1955
	3,002,903	Foulke et al.	Oct. 3, 1961

FOREIGN PATENTS

35	1,231,332	France	Apr. 11, 1960
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