United States Patent [19]

Beach et al.

[11] **3,907,876**

[45] **Sept. 23, 1975**

[54] **SYMMETRICAL ACETYLENIC SULFO-OXYGEN COMPOUNDS**

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Related U.S. Application Data

[60] Division of Ser. No. 268,039, June 30, 1972, Pat. No. 3,860,638, which is a division of Ser. No. 145,474, May 20, 1971, Pat. No. 3,699,016, which is a continuation-in-part of Ser. Nos. 592,742, Nov. 8, 1966, abandoned, and Ser. No. 860,008, Sept. 22, 1969, abandoned.

[52] **U.S. Cl.** ..... **260/513 R**

[51] **Int. Cl.²** **C07C 143/16**

[58] **Field of Search** ..... 260/513 R, 513 B

[56] **References Cited**

UNITED STATES PATENTS

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Assistant Examiner—Nicky Chan
Attorney, Agent, or Firm—Fay & Sharpe

[57] **ABSTRACT**

A novel class of brightening addition agents is disclosed for the electrodeposition of nickel from modified Watts type acid nickel plating baths. The novel class of addition agents consists of symmetrical hydroxy sulfonic lower alkanoxy acetylenic derivatives produced either by the boron trifluoride or similar Lewis acid catalyzed reaction of halogenated propylene and butylene oxides with symmetrical acetylenic diols having 4, 6, or 8 carbon atoms, or by first reacting the diols with ethylene, propylene or butylene oxides and then with epichlorohydrin. In either case, the resulting brightening agent are characterized by attachment to adjacent carbon atoms of the alkanoxy group of a sulfonic and an hydroxyl radical. Plating bath solutions incorporating the novel addition agents, and plating processes employing such solutions are also enclosed.

1 Claim, No Drawings

SYMMETRICAL ACETYLENIC SULFO-OXYGEN COMPOUNDS

PRIOR RELATED APPLICATIONS

This application is a division of our prior application Ser. No. 2,68,039, filed June 30, 1972 now U.S. Pat No. 3,860,638, which was a division of Ser. No. 145,474, filed May 20, 1971, now U.S. Pat. No. 3,699,016, which was a continuation-in-part of applications Ser. No. 592,742, filed Nov. 8, 1966 and Ser. No. 860,008, filed Sept. 22, 1969, both now abandoned.

BACKGROUND OF THE INVENTION

The prior art is replete with teachings respecting addition agents for modifying a standard acidic nickel plating bath of the Watts type to overcome the deficiencies of that bath in respect to the brightness, uniformity of appearance, leveling capabilities, corrosion resistance, ductility, etc., of the nickel deposit, and for overcoming low tolerance to cathode current density differences or changes invariably encountered in any practical commercial nickel plating operation. While the art of selecting suitable brightening agents for use in such baths has developed to a state where it is now possible to make some predictions regarding general suitability of a given type agent for a given application, the fact remains that the use of brightening agents in nickel plating is still largely an art and not a science. Discoveries of new agents having fewer of the disadvantages attending previously known agents, and possessing better properties than those prior known agents, is a highly empirical matter. Thus addition agents differing only slightly in chemical structure from previously known addition agents can and do produce vastly different results which are totally unpredictable. It is believed that the foregoing is especially true with respect to the novel addition agents herein disclosed.

Although the novel addition agents belong generally to the class of acetylenic organic compounds whose brightening effect in nickel electroplating solutions has been known for some years, this is yet another example of the fact that despite such general knowledge it is quite impossible to predict whether or not a particular member of that general class will be satisfactory, and still less possible to predict that any particular member will have outstanding advantages over others in the same class. As will be further demonstrated, the particular agents herein disclosed do possess unusual and unexpected advantages leading to nickel deposits of exceptional luster, uniform brightness, remarkable leveling power, good ductility and excellent corrosion resistance which make them especially desirable for use in mass production, highly automated plating installations of the type encountered in the automotive and appliance industries.

SUMMARY OF THE INVENTION

The novel class of addition agents which are the subject of this invention comprises the symmetrical hydroxy sulfonic lower alkanoxy acetylenic derivatives of the condensation product resulting either directly from the boron trifluoride or similar Lewis acid catalyzed reaction of halogenated propylene and butylene oxides with lower alkyl symmetrical acetylenic diols, or from first reacting the diols with ethylene, propylene or butylene oxide, followed by reaction with epichlorohydrin. In both cases of course the intermediate is sulfonated to substitute for the chloro or other halogen radical. The term lower alkyl symmetrical acetylenic diols is used herein to designate those having 4, 6 or 8 carbons with symmetrically oriented hydroxyl groups relative to the triple bond. The halogenated epoxides herein referred to comprise the chloro, bromo and iodo substituted propylene and butylene compounds. The brightening agents of this invention, more especially when used in combination with other additives of standard or known type, are found to possess unique properties useful as bright nickel plating bath adjuncts.

The novel addition agents as hereinabove briefly defined are believed to comprise chemically new compounds differing from any which have been proposed heretofore for use in bright nickel plating baths. These new agents give excellent performance within unusually broad addition agent concentrations and within wide current density ranges in a plating operation. This is of great practical importance because of the trend toward fully automated plating processes where continuous maintenance and adjustment to keep the plating process operating effectively and satisfactorily is and must be held to a minimum. Broad tolerance to variations in additive concentration in the bath is highly desirable as this simplifies the matter of automatic replenishment of the plating bath. Broad tolerance to current density changes is likewise allimportant since such changes occur inevitably over a rather wide range during the passage of articles through the electroplating bath in variably spaced relation to the electrodes therein. Due also to contour variations in the articles themselves, which necessarily place certain areas or points on such articles closer to the electrodes than others while passing through the bath, current density differences over the surface of the articles are always present.

It has been found to be a critical characteristic in the addition agents of the invention that the symmetry of the molecule be maintained at least to the extent that one hydroxyl and one sulfonate group be present on each end. It is further found to be critical that the hydroxyl and sulfonate groups be attached to adjacent carbons at a terminal alkyl group. The resulting symmetrical sulfonic hydroxy alkanoxy acetylenic derivatives produce uniquely good nickel plating results when used in a standard Watts bath, as aforesaid, and especially when used in conjunction with other known brightening agents, as will be described more fully hereinafter.

In using the new class of brightening agents it is found that while relatively small amounts in the plating bath will provide a full bright nickel deposit over a wide range of current densities, excess amounts of the agent do not interfere with the operation of the bath. For example, optimum concentration of one of the novel addition agents, namely 1, 4 di-(beta-hydroxy gamma-sulfonic propoxy)-2-butyne, is from about 0.35 to 1.5 grams per liter where air agitation of the bath is employed. Other novel addition agents within the class herein disclosed but of higher molecular weight are preferably employed at proportionately greater concentrations in solution. In all cases minimum effect is noted at a concentration of around 0.05 g/l but the plated deposit is usually dull at such lower amount. Apart from economic considerations, excess amounts up to the limit of solubility of the addition agent in the bath do not adversely affect the plating operation; gen-

erally 5.0 g/l represents the maximum and is far in excess of what is needed.

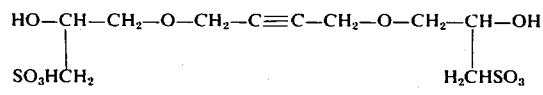
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The use of the novel agents by themselves in a Watts bath shows substantial improvement in the nickel deposit. Such a bath is shown in the following example:

Example I

	Grams/liter
$NiSO_4.6H_2O$	180–400
$NiCl_2.6H_2O$	8–120
H_3BO_3	8–50
1,4 di-(beta-hydroxy gamma-sulfonic propoxy)-2-butyne	0.35–1.5
pH	2.5–4.8
Temp.	30°–80°C

The brightener designated above is represented bby the following structural formula:



(1)

Maximum benefits of the invention are, however, secured by incorporating other well-known primary or "carrier" sulfo-oxy brighteners consisting of such agents as the benzene and naphthalene sulfonic acids, sulfomamides and sulfonimides in standard amount, usually from about 0.5 to 25.0 grams per liter of bath solution; also, a secondary brightener such as the known amine polyaryl methane group consisting of fuchsin, reduce fuchsin, p,p'-methylene dianiline or 2,2',4,4'-tetramine 5,5'-dimethyl diphenylmethane. The secondary brightener is commonly used in amounts of from 2 to 100 milligrams per liter. The novel symmetrical hydroxy sulfonic alkanoxy acetylenic compounds are fully compatible with such known addition agents and with mixtures of more than one additive from the same class.

As an illustration, a typical bath of preferred composition in accordance with the invention is given as follows:

Example II

	Grams/liter
$NiSO_4.6H_2O$	280
$NiCl_2.6H_2O$	60
H_3BO_3	45
Saccharin	2.5
Naphthalene disulfonic acid	4.0 – 8.0
1,4 di-(beta-hydroxy gamma-sulfonic propoxy)-2-butyne	0.8 – 1.5

The foregoing bath has a pH of around 3.8 to 4.2 which is the preferred range but this may vary in the course of the plating operation from as low as about 2.5 to as high as about 4.8 with completely satisfactory results.

Normally at the lower limits of the additive concentrations above specified, air agitation or the equivalent should be employed in the bath, otherwise higher concentrations of the additives will be necessary to get comparable results. Alternatively, cathode oscillation may be employed in which case the bath should preferably include a surfactant, for example 0.1 gram per liter of sodium lauryl sulfate.

The plating bath described is fully operative at temperatures from 30°C. to 80°C. with the preferred range being 55° to 60°C.

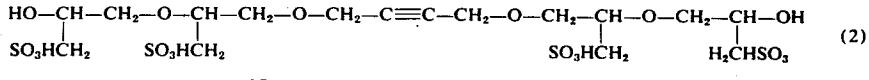
The resulting plate is of full, uniform brightness from areas of very low cathode current density up to just short of where "burning" occurs. This represents a range of current densities from as low as 1 amp. per square foot up to 150 amps. or more per square foot, which thus amply covers the range of conditions normally encountered in a practical plating operation.

The leveling capabilities of such a bath are outstanding. As a measurement of bath performance in this respect, a conductive master phonograph record or plaque is employed as the test substrate to be plated, in which there is accurately milled or scribed a groove of exactly 1 mil depth. This is then plated to provide a deposit of nickel exactly 1 mil thick. The leveling capacity of the bath is evaluated by comparing the thickness of the nickel deposit in the groove against the 1 mil deposit on the ungrooved (level) portion of the plaque. In the bath described the degree of leveling is around 85%. This compares, for example, with about 64% from a plating bath containing 0.2 g/l of butyne diol and 4.0 g/l of naphthalene trisulfonic acid, a typically standard plating bath in commercial use. Such a bath has generally required supplemental leveling agents to bring it up to an acceptable degree of leveling.

Ductility of the deposit is also one of the more important factors to be considered. The invention provides outstanding results in that the ductility of a nickel deposit using a bath composition as in Example II is rated at 0.11 to 0.12 on the standard Chrysler test. A standard value of 0.1 is considered as being commercially acceptable in this test. By comparison, the conventional butyne diol, napthalene trisulfonic acid bath above referred to produces a deposit whose ductility rating on the same test is down around 0.01.

By way of further comparison, a full bright deposit of excellent luster is obtained throughout a plating current density range of from 1 to at least 150 a.s.f. using the invention bath of Example II, as compared to a deposit that is generally fogged at all current densities using the conventional butyne diol addition agent.

The baths above described may be modified by substituting for some or all of the novel addition agent of Examples I or II a still further epoxylated derivative of 1,4 di-(beta-hydroxy gamma-sulfonic propoxy)-2-butyne. The hydroxy groups of the later can be further reacted with epichlorohydrin to add an additional beta-hydroxy gammasulfonic propoxy group to each end of the molecule. Such product is herein designated as 1,4 di-[beta(beta-hydroxy gamma-sulfonic propoxy) gamma-sulfonic propoxy]-2-butyne, and is represented by the following structural formula:



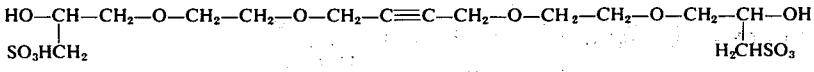
(2)

It is to be noted that this alternative addition agent (2) still maintains the positioning of hydroxyl and sulfonic groups on adjacent carbons at each end of the mole-

cule, which characterized the addition agent (1) first discussed. Addition agent (2) appears to enhance the brilliance of the deposit even more, probably on account of the extra sulfur which it introduces. The plating conditions employed remain substantially unchanged from the previous examples when using this compound, but the amount of brightener added to the bath in this case is preferably about one-third more. The over-all range is from about 0.35 to 3.0 grams per liter of bath solution.

EXAMPLE III

A compound similar to addition agent (2) but omitting the symmetric sulfonic groups interiorly of the chain is also useful and is represented by the formula:



(3)

This is obtained by first reacting buytne diol with ethylene oxide and then reacting the condensation product with epichlorohydrin. Further reaction is of course required to substitute the sulfonic group for the chloro radical on the intermediate product. Addition agent (3), when substituted for the novel brightening agents in Examples I and II, produces an exceptionally satisfactory nickel plating bath. The amount of brightener added is about the same as in Example II; that is, it is increased over the concentration recommended proportional to the increase in molecular weight.

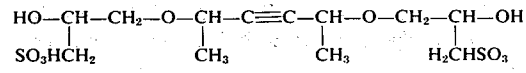
Other compounds in the novel class of addition agents include the sulfonated reaction products of hexyne diols and octyne diols with the halogenated epoxides.

The following examples are illustrative:

Example IV

	Grams/liter
$NiSO_4.6H_2O$	280
$NiCl_2.6H_2O$	60
H_3BO_3	45
Saccharin	2.5
Naphthalene disulfonic acid	4.0
Sulfonated reaction product of 3-hexyne 2,5-diol and epichlorohydrin	1.0

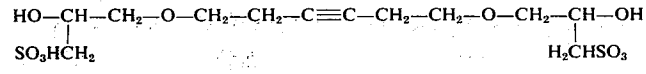
The hexyne additive is represented by the formula:



(4)

The concentration of additive (4) when used in the plating bath is again preferably increased over that given in Example I substantially proportionally to the increase in molecular weights of the additives, but other conditions of the plating bath remain the same.

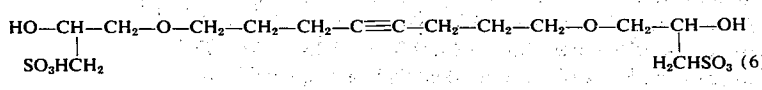
The resulting plate is of full, uniform brightness throughout a wide range of current cathode densities normally encountered in commercial plating operation, and the leveling capacity is excellent. The 3-hexyne 1,6-diol isomer may be used instead to give the corresponding unbranched reaction product. This is represented by the formula:



(5)

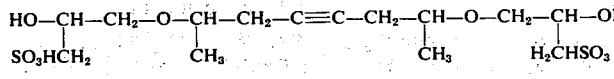
EXAMPLE V

The same plating bath as used in the preceeding examples is employed except that the acetylenic brightening agent is the sulfonated reaction product of 4-octyne, 1,8-diol and epichlorohydrin, represented by the structural formula:

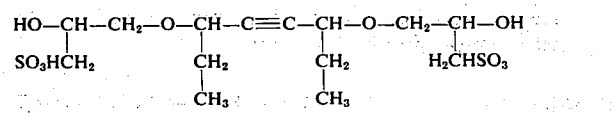


(6)

Similarly the sulfonated reaction products of epichlorohydrin and either of the 2,7 and 3,6 diol octyne isomers can also be used, alone or mixed. These are represented respectively by the formulas:



(7)

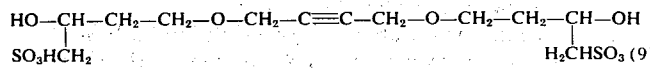


(8)

Concentrations in the plating bath are proportional on a molecular weight basis with those recommended for the novel agents in Examples I and II.

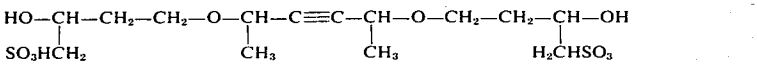
EXAMPLE VI

In place of using epichlorohydrin as the alkene oxide in reacting with the acetylenic diol, a halo butylene oxide such as chlorobutylene oxide can be employed. The sulfonated reaction product in this case will contain an additional carbon in the alkanoxy group and is typified by the following formula (where 1,4 butyne diol is the starting reactant):

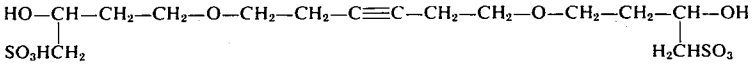


(9)

The hexyne and octyne diols will form corresponding reaction products. Where the starting reactants are chlorobutylene oxide and 3-hexyne 2,5-diol or 3-hexyne 1,6-diol, the corresponding products are, respectively:

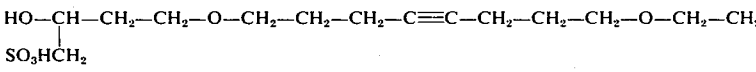


(10)

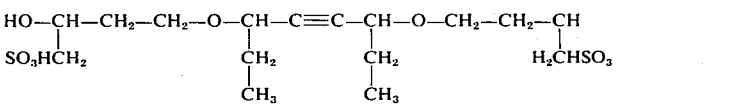


(11)

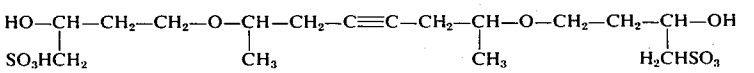
Similarly, for chlorobutylene oxide and 4-octyne 1,8 diol, or the 2,7 or 3,6 isomers, the resulting products are, respectively:



(12)



(13)

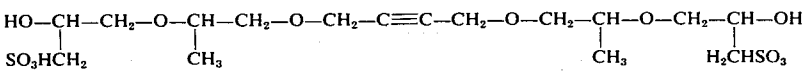


(14)

Again, concentration of these brightening agents in the plating bath is proportional to their molecular weights.

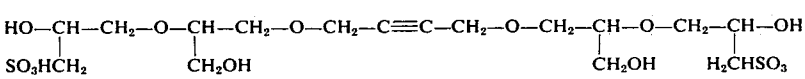
EXAMPLE VII

The reaction between symmetrical acetylenic diols and various alkene oxides to produce a first intermediate product having hydroxyl groups, which are then further reacted with epichlorohydrin and sulfonated, provides still another class of useful additives. Addition agent (3) of Example III above is illustrative, using ethylene oxide as the alkene oxide. This group retains the characterizing hydroxy-sulfonic radical arrangement discussed, and is further characterized by a double ether linkage on each side of the acetylenic carbons. Additional products of this type found to provide good results in plating baths are illustrated by the following which are obtained by reacting 2-butyne 1,4 diol first with an alkene oxide (or halo alkene oxide) and then epoxylating that intermediate again by reaction with epichlorohydrin. Typical are the following:



(15)

The alkene oxide use to derive this was propylene oxide.



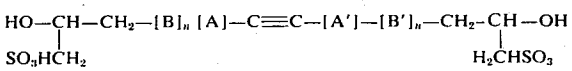
(16)

The alkene oxide in this case was epichlorohydrin.

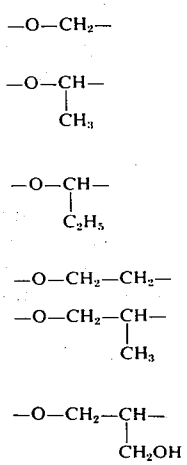
Similarly the various available methyl, ethyl, propyl, butyl and styrene oxides when reacted with symmetrical butyne diol yield corresponding products useful as brightening and leveling addition agents.

Polymerization of the alkanoxy grouping on the molecule chain of these compounds occurs depending on the relative concentrations of the alkene oxides and diols. However, as the length of the chain increases the solubility of the resulting product in the plating bath decreases and for practical purposes a polymerization number of about 3 appears to be the useful limit.

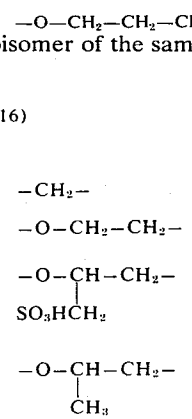
In summary, the class of novel addition agents can be represented by general structural formula:

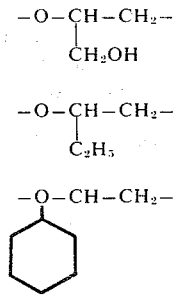


where A is



and A′ is the steroisomer of the same radical; and B is

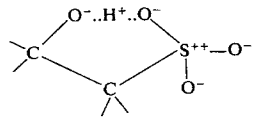




and B′ is the stereoisomer of the same radical; and where n is an integer of from 0 to 3.

The importance of the positioning of the hydroxyl and sulfonate groups on adjacent carbon atoms of the terminal alkanoxy groups has been mentioned. Further evidence of this is afforded by the following. For example, if the hydroxyl group is replaced by methoxy, ethoxy or even propoxy hydroxy (—O—C_3H_6—OH) groups so that there is no grouping of sulfonic and hydroxyl radicals on adjacent carbons, and these resulting compounds are substituted into the bath of Example II in place of the invention addition agents, the leveling values drop to 65–70% and the ductility drops to less than 0.01, with a striated and dark low current density deposit. The same is true if the sulfonate group is replaced by a hydroxyl group, as can be accomplished by reacting butyne diol with gylcidol to give the di-beta, gamma-hydroxy derivative.

It is clear that the combination of a hydroxyl group alpha to the sulfonate results in uniquely good plating performance. It would appear from this that the chemical structure involving the positioning of these two functional groups in unique and is the result of hydrogen and resonance bonding which occurs between the oxygens of the functional groups, as shown below, to produce the stable structure for the atoms (in acid solution):



The hydrogen which is effectively bonded to two oxygens thus maintains this six-membered ring structure in planar form. Substitution of other groups for the hydroxyl group destroys the hydrogen bonding; similarly, replacement of the sulfonate group by another hydroxyl group likewise destroys the possibilities for the foregoing unique structure stabilized by resonance and hydrogen bonding. Wherever such substitutions are made, the performance of the plating bath is adversely affected in one or more of the important factors of leveling, brilliance or ductility.

The importance of the symmetry of the molecule, the other requirement above mentioned of the novel addition agents, is further evidenced by the following. For instance, if propargyl alcohol is used in place of butyne diol in the epoxylating reaction, and then this reaction product sulfonated to substitute the sulfonic for the chloro group as before, and this final product is used in the plating bath described above, leveling drops to 70% and ductility is about 0.07, while the deposit is badly striated and dark in the low current density region. On the other hand, if one end of the starting butyne diol is blocked off with the methoxy group (thereby forming the mono methyl ether of butyne diol), and this is reacted in the manner described and the resulting material is used as an addition agent in the foregoing bath, the leveling value then drops to the order of 61%, ductility is about 0.1 but the deposit is dark throughout the medium and low current density plating ranges.

It may also be pointed out that the intermediate hydroxy chloro compound resulting from reaction of epichlorohydrin and butyne diol, which incidentally has very slight solubility in water, is a poor addition agent, probably on account of the chlorine groups. Using this as an addition agent in a standard nickel plating bath in amount of 1.1 g/l, together with 14.0 g/l of naphthalene trisulfonic acid, gives only 8% leveling, a ductility value less than 0.01 and black deposits throughout the medium and low current density plating range.

Thus, in brief, it is indicated that if either of the hydroxyl or sulfonate groups on adjacent carbons of the alkanoxy group is replaced, or if their relative positions are shifted, then ductility and color of nickel deposit are adversely affected. And if symmetry of the molecule of the addition agent is not maintained relative to the triple bond, then the color of the deposit falls below acceptable limits.

Production of the novel additives may be accomplished in various ways, however the following procedure affords advantages of simplicity and low cost and is accordingly preferred.

In producing 1,4-di (beta-hydroxy gamma-sulfonic propoxy)-2-butyne (i.e. addition agent (1) above), for each mole of 1,4-butyne diol there is employed at least 2.5 and preferrably 3.6 moles of epichlorohydrin in the starting mixture to ensure as complete a reaction as possible. Boron trifluride or other Lewis acid in ether is employed as a catalyst, and the reaction is effected by adding the epichlorohydrin dropwise to hold the reaction mixture temperature below 40°C. until all of the epichlorohydrin has been added. The mixture is then held for a further period to ensure complete reaction. The condensation product, that is, the intermediate product, resulting from this is a polymerized water insoluble compound, 1,4 di-(beta-hydroxy gamma-chloro propoxy)-2-butyne.

Thereafter, the intermediate thus obtained is refluxed with sodium sulfite solution containing 1 mole of the sulfite for each mole of epichlorohydrin originally employed. The sulfonation step is accomplished by first adding to the insoluble reaction product sufficient water to dissolve the sodium sulfite which is subsequently to be added. First however, the mixture is agitated and made neutral or basic with any suitable base. Then the sulfite is added, after which the mixture is refluxed and sulfonation proceeds smoothly. After about one or two hours at reflux, the process is shut down. The mixture is acidified, preferably to a pH of 1.0 to 2.0, and then heated to drive off residual sulfur dioxide.

Thereafter the solution is readjusted to a desired pH of 4 to 5, purified with carbon, filtered and is ready for use as the additive (1) in the plating bath, as described.

In producing the further epoxylated product (2), namely 1,4-di-[beta (beta-hydroxy gamma-sulfonic propoxy) gamma sulfonic propoxy]-2-butyne, the procedure is the same except that from 4 to 6 moles of epi-

chlorohydrin are reacted per mole of butyne diol in the starting mixture.

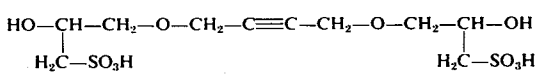
The same procedure just described is used in preparing the sulfonated reaction products of the hexyne and octyne diols, using either epichlorohydrin or chlorobutylene oxide (or the bromo or iodo substituted equivalents). Concentrations of these reactants should be proportioned on a molecular weight basis to the weights employed in the epichlorohydrinbutyne diol reaction.

The various addition agents incorporating the double ether linkage, such as addition agents (3), (15) and (16) above, are produced in similar manner except that the first reaction with butyne diol may employ an unhalogenated alkene oxide, and this reaction product then reacted further with a halogenated alkene oxide, in the manner described.

The addition agents may have the sulfonic group either in the acid form or as the alkali metal salt of the acid since this will hydrolyze in the acid solution of the plating bath to the sulfonic acid group.

What is claimed is:

1. A composition of matter having the following structural formula,



or the alkali metal salts thereof.

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