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3,457,146

PROCESS OF ELECTRODEPOSITING NICKEL AND ELECTROLYTE AND ADDITIVE COMPOSITION THEREFOR

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Claims priority, application France, Oct. 8, 1964,

Patent 1,418,245

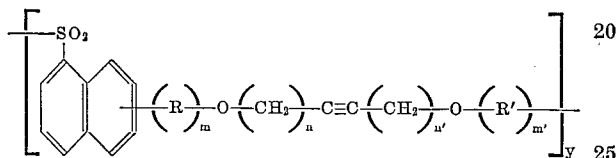
Int. Cl. C23b 5/46, 5/08

U.S. Cl. 204—49

13 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous acid nickel electroplating baths containing as a brightener a compound having a molecular structure which includes one or more units of the formula:



wherein R and R' are from the group of oxymethylene and oxyethylene, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of at least 1.

This invention relates to novel condensation reaction products of a naphthosultone and an acetylenically unsaturated glycol, and more especially to new and improved nickel electroplating baths containing such condensation reaction products, as additives, novel compositions containing the condensation reaction products herein and especially well suited as brightener additives for the baths, and an improved method for electroplating nickel involving the use of the new baths herein. Additionally, this invention relates to the condensation reaction products per se, and a novel method for the preparation of such products.

It is known in the prior art to utilize in nickel electroplating baths unreacted acetylenically unsaturated glycols, such as butynediols. However such glycol additives have the drawback of giving good results only at slow plating speeds. Likewise the addition to the baths of unreacted acetylenically unsaturated sulfonic acids has been proposed for instance by U.S. Patents 3,002,903 and 3,002,904 and by German Patent 1,017,873. Such baths however do not permit one to obtain bright, thin deposits of nickel.

One object of this invention is to provide new and improved nickel electroplating baths for providing bright nickel deposits.

Another object is to provide novel condensation reaction products of a naphthosultone, for instance a 1,8-naphthosultone, with an acetylenically unsaturated glycol, eminently well suited as a brightener additive for nickel electroplating baths.

A further object is to provide new compositions containing such new condensation reaction products and especially well suited as brightener additives for nickel electroplating baths.

2

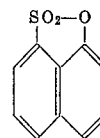
A further object is to provide a new and improved process for the preparation of the novel condensation reaction products herein.

An additional object is to provide an improvement in the method for electroplating nickel.

Additional objects and advantages will be readily apparent as the invention is hereinafter described in detail.

In accordance with the present invention, it has now been found that by the addition to the prior nickel electroplating baths of the condensation reaction product of a naphthosultone with an acetylenically unsaturated glycol, nickel electroplating baths are attained which produce extremely bright or brilliant deposits and such is the case even when the nickel deposits are thin deposits.

The naphthosultone herein is the inner anhydride of the corresponding hydroxynaphthalene sulfonic acid. Thus the 1,8-naphthosultone is the inner anhydride of 1-hydroxynaphthalene-8-sulfonic acid, and the 1,7-naphthosultone is the inner anhydride of 1-hydroxynaphthalene-7-sulfonic acid. The 1,8-naphthosultone has the formula:

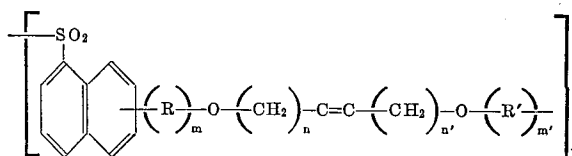


The condensation reaction is carried out with the naphthosultone and acetylenically unsaturated glycol present in at least those amounts required to stoichiometrically react to form the condensation reaction product herein. Usually the naphthosultone and acetylenically-unsaturated glycol are reacted together in equimolar portions to form the condensation reaction product.

The prior nickel plating baths which are improved upon by the present invention contain water as solvent or continuous phase, and a water-soluble compound of nickel, for instance a nickel salt such as the sulfate, sulfamate or fluoborate of nickel. In addition these acid baths usually contain chloride ions to enable anode corrosion, boric acid, a stabilizer for the bath, one or more levelling agents, and one or more depressants of surface tension or wetting agents.

In place of the known levelling agent or agents, the novel condensation reaction product or products of naphthosultones and heterocyclic aromatic compounds containing one or more five-membered heterocyclic rings including at least one ring nitrogen atom and one or more labile hydrogen atoms can be added to the bath as levelling agent. Such levelling agents are disclosed and claimed in copending U.S. patent application Ser. No. 492,266, entitled, "Nickel Electrodepositing Baths and Novel Condensation Reaction Products as Levelling Agents Therefor," filed Oct. 1, 1965.

The condensation reaction product herein has a molecular structure including one or more units of the formula:

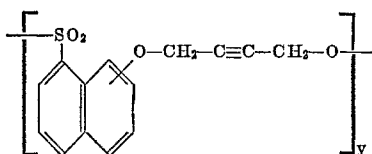


wherein R and R' are oxymethylene or oxyethylene and are the same, m and m' are each an integer of 0-1; n and n' are each an integer from 1-2; and y is an integer of at

3

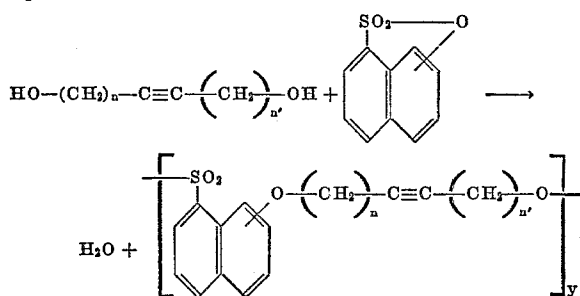
least 1 and typically as high as 100 and even higher. The exact value of y corresponds to the molecular weight of the particular condensation reaction product obtained at the particular reaction temperature and time of the condensation reaction.

When butynediol, e.g. 2-butyne-1,4-diol is the glycol condensed with the naphthosultone, the product obtained has a molecular structure including one or more units of the formula:



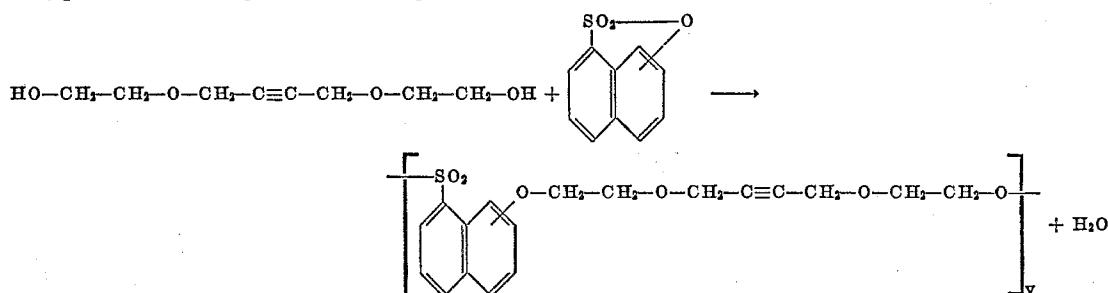
wherein y has a value as aforesaid.

The condensation reaction of the acetylenic glycol and the naphthosultone herein is illustrated by the following equation:



wherein n , n' and y have the value aforesaid.

The condensation reaction of the acetylenically-unsaturated glycol, the bis-hydroxyethylether of 2-butyne-1,4-diol, proceeds according to the following reaction:



wherein y has the value aforesaid.

Acetylenically-unsaturated glycols suitable for the condensation reaction herein include the mono-acetylenically unsaturated glycols and especially those having 4-8 inclusive carbon atoms per molecule, for instance the butynediols, e.g. 2-butyne-1,4-diol, 1-butyne-1,4-diol, as well as pentynediols and hexynediols, and derivatives of such unsaturated glycols, for instance the bis-hydroxyethylether of butynediol which itself is a mono-acetylenically unsaturated glycol although containing ether linkages. Exemplary of the naphthosultones suitable for the condensation reaction are 1,8-naphthosultone and 1,7-naphthosultone.

The naphthosultones herein are prepared by the intramolecular condensation of the corresponding hydroxynaphthalene sulfonic acid, and the 1,8-naphthosultone is obtainable in commerce. The acetylenically unsaturated glycols, the butynediols, are also obtainable in commerce, as are the bis-hydroxyethylethers of butynediols.

Nickel electroplating baths improved upon by the present invention contain, in addition to water as solvent or continuous phase, the following:

- (1) nickel ions, as sulfate, sulfamate, or fluoborate.
- (2) chloride ions, to permit anode corrosion.
- (3) boric acid.
- (4) a stabilizer, such as saccharine, paratoluenesulfonamide, hexammine, or cyanuric acid,

4

(5) at least one levelling agent.

(6) at least one depressant of surface tension, such as lauryl sulfate.

In addition, in accordance with this invention, the bath comprises at least one bath-compatible condensation reaction product compound of a sultone, for example the naphtho-1,8 sultone, with the acetylenically unsaturated glycol, i.e. the glycol as such, e.g. a butynediol, or a derivative of the unsaturated glycol and especially the bis-hydroxyethylether of the butynediol, in a proportion of preferably from about 0.05 to about 2 g./l.

Such a bath is preferably operated as follows:

- (1) mechanical agitation of the cathode bar.
- (2) a temperature of 20-70° C., depending on the concentration of nickel ions and of the desired plating speed, this temperature being preferably between 55 and 70° C.
- (3) pH of 3.0-5.5, preferably about 5.0.
- (4) current density of 2-15 amps/dm.², optimally 5-7 amps/dm.² for a bath temperature of 65° C.

The novel condensation reaction product herein can be added to the plating bath either as such or when in solution in an inert, i.e. non-reactive with respect to the constituents of the plating bath, liquid solvent. Exemplary of the inert liquid solvent is water. However any inert liquid solvent which is compatible with the electroplating bath can be utilized. The proportions of the condensation reaction product in such additive agent composition can be varied over wide limits, and do not form a part of this invention. It will suffice to point out that with higher smaller quantities of such addition agent composition are required to be added to the bath to obtain the desired concentration therein of such product, than when lower concentrations of the condensation reaction product are present in the additive agent composition.

The preparation process for preparing the condensation

reaction products herein comprises, in its broader aspects, heating a mixture of the naphthosultone and the acetylenically unsaturated glycol to an elevated reaction temperature below 95° C., and maintaining the mixture at the reaction temperature until its viscosity increases appreciably and the mixture becomes of a syrupy consistency, which is indicative of the condensation reaction having occurred. The thus-treated mixture is then cooled to ambient temperature, for instance by being permitted to cool down or by indirect heat exchange with a cooling fluid, e.g. cooling water.

More specifically the preparation process involves gradually heating a mixture of the naphthosultone and acetylenically unsaturated glycol, usually in equimolar portions, to an elevated temperature below 65° C., preferably of the order of 50° C., to effect dissolution of the naphthosultone in the glycol. The thus-obtained solution is then heated to a reaction temperature above 65° C. but below 95° C., preferably of the order of 80° C., and the solution maintained at a reaction temperature within the range stated until the solution becomes of a syrupy consistency which typically requires about 4 hours time. The thus-treated mixture is then cooled to room temperature.

The following examples further illustrate the invention but are not restrictive thereof. In the examples, the aque-

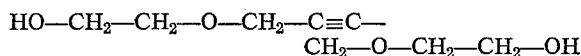
ous nickel plating bath compositions are given with amounts of ingredients being in grams per liter, along with operating conditions:

Example.....	1	2	3	4	5	6	7
NiSO ₄ ·7H ₂ O.....	330	370	330	330	250	0	0
Nickel sulfamate.....	0	0	0	0	0	400	400
NiCl ₂ ·6H ₂ O.....	80	45	80	85	45	40	40
H ₃ BO ₃	40	40	40	40	25	40	40
Saccharin.....	0.1	0.5	0.3	1	1	0.1	0.5
Paratoluenesulfonamide.....	0.1	0.1	0.1	0	0	0.1	0.1
Cyanuric acid.....	0.1	0	0.1	0	0	0.2	0.1
Compound A.....	0.5	1	0	0	0.5	0.2	0.15
Compound B.....	0	0	0.5	0.3	0	0	0
pH.....	4.5	4.0	4.5	5.0	5.5	3.5	3.5
Temperature (° C.).....	65	65	65	65	40	60	65
Current density (a./dm. ²).....	5-7	5-7	5-7	5-7	2.5	10-15	10-15

Compound A: Product of the condensation reaction of equimolar portions of bis-hydroxyethylether of butynediol and of 1,8-naphthosultone.

Compound B: Product of the condensation reaction of equimolar portions of butynediol and of 1,8-naphthosultone.

The formula of bis-hydroxyethylether of 2-butyne-1,4-diol is:



The preparation of Compounds A and B, and more generally, of the condensation reaction product compounds of this invention takes place as follows, by a method which itself comprises part of this invention:

Into a reflux retort, are added in stoichiometric amounts the acetylenically unsaturated glycol, e.g. butynediol or the bis-hydroxyethylether of butynediol, and the naphthosultone, e.g. 1,8-naphthosultone. First, the mixture is gradually heated to about 50° C. thereby dissolving the 1,8-naphthosultone, and then the mixture is heated to about 80° C. and maintained at that temperature for 4 hours; whereby the viscosity increases until the liquid becomes syrupy. The temperature of the mixture is then returned to ambient or room temperature. The solution thus obtained is useable directly as a brightener under the conditions cited above.

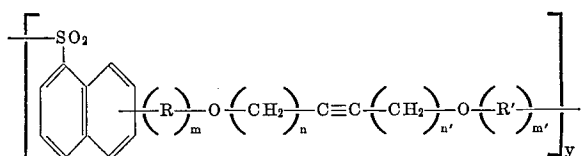
Of the above examples, those baths containing Compound A give the better results; in particular, nickel electroplating baths containing Compound A produce nickel deposits which are brighter and better levelled at 15 microns thickness than those produced from baths containing Compound B to 20 microns thickness.

In all examples, baths containing brighteners of this invention produce extremely brilliant deposits even when quite thin.

By comparison, nickel electroplating baths were prepared which were identical to those containing Compound A, but in which the compound was replaced by equivalent quantities of unreacted bis-hydroxyethylether of butynediol and of 1,8-naphthosultone as such (i.e., not subjected to the aforementioned condensation reaction). The nickel deposits obtained from such baths were semi-bright, cloudy and non-levelled, and were of no commercial importance.

What is claimed is:

1. A composition comprising a solution in an inert liquid solvent of a compound having a molecular structure including at least one unit of the formula:



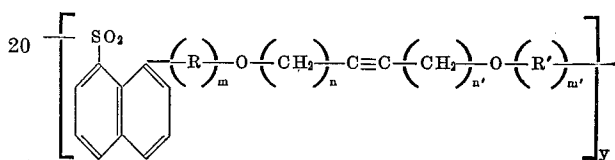
wherein

R and R' are selected from the group consisting of oxymethylene and oxyethylene and are the same, m and m' are each an integer of 0-1,

n and n' are each an integer of 1-2, and y is an integer of value of at least 1.

2. The composition of claim 1 wherein the compound

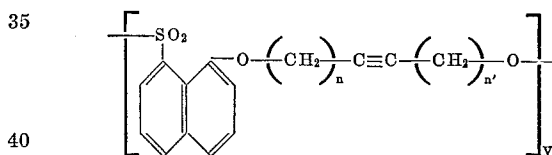
has a molecular structure including at least one unit of the formula:



wherein

R and R' are selected from the group consisting of oxymethylene and oxyethylene and are the same, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of value of at least 1.

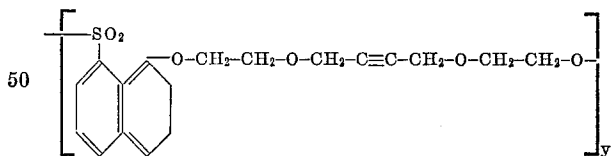
3. The composition of claim 2 wherein the compound has a molecular structure including at least one unit of the formula:



wherein

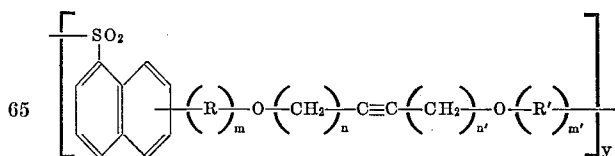
n and n' are each an integer of 1-2, and y is an integer of value of at least 1.

4. The composition of claim 2 wherein the compound has a molecular structure including at least one unit of the formula:



wherein y is an integer of value of at least 1.

5. In a method for the electroplating of nickel, the improvement which comprises effecting the electroplating of the nickel from an aqueous acidic nickel electroplating bath containing a source of nickel ions and as a brightener a compound having a molecular structure including at least one unit of the formula;



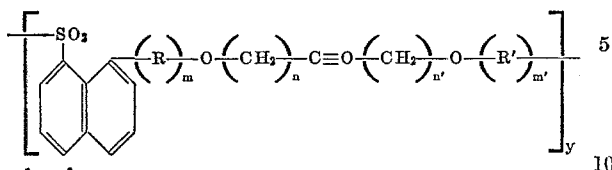
wherein

R and R' are selected from the group consisting of oxymethylene and oxyethylene and are the same, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of value of at least 1.

said compound being present in the bath in an amount sufficient to impart brightness to the nickel electroplate.

7

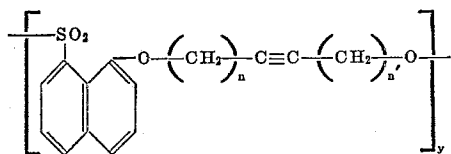
6. The method of claim 5 wherein the compound has a molecular structure including at least one unit of the formula:



wherein

R and R' are selected from the group consisting of oxy-methylene and oxyethylene and are the same, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of value of at least 1, said compound being present in the bath in an amount sufficient to impart brightness to the nickel electroplate.

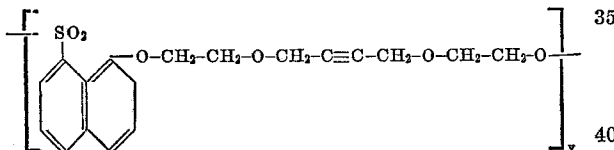
7. The method of claim 6 wherein the compound has a molecular structure including at least one unit of the formula:



wherein

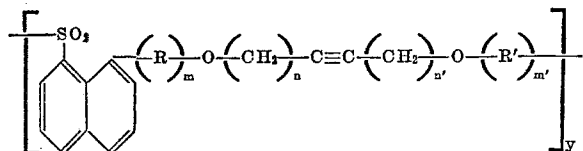
n and n' are each an integer of 1-2, and y is an integer of value of at least 1.

8. The method of claim 6 wherein the compound has a molecular structure including at least one unit of the formula:



wherein y is an integer of value of at least 1.

9. An aqueous acidic nickel electroplating bath containing a source of nickel ions and as a brightener a compound having a molecular structure including at least one unit of the formula:



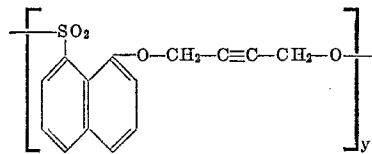
wherein

R and R' are selected from the group consisting of oxy-methylene and oxyethylene and are the same, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of value of at least 1,

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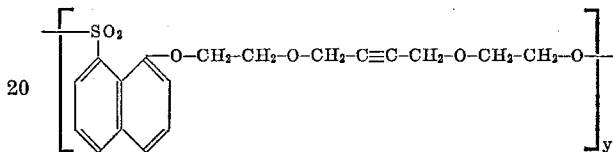
said compound being present in the bath in an amount sufficient to impart brightness to the nickel electroplate.

10. The nickel electroplating bath of claim 9 wherein the compound has a molecular structure including at least one unit of the formula:



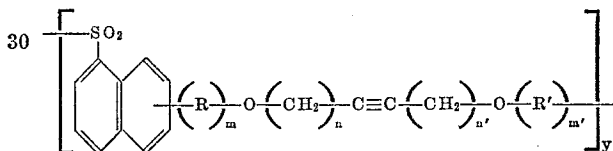
wherein y is an integer of value of at least 1.

11. The aqueous acidic nickel electroplating bath of claim 9 wherein the compound has a molecular structure including at least one unit of the formula:



wherein y is an integer of value of at least 1.

12. An aqueous acidic nickel electroplating bath containing a source of nickel ions and as a brightener a compound having a molecular structure including at least one unit of the formula:



wherein

R and R' are selected from the group consisting of oxy-methylene and oxyethylene and are the same, m and m' are each an integer of 0-1, n and n' are each an integer of 1-2, and y is an integer of value of at least 1,

said compound being present in the bath in an amount sufficient to impart brightness to the nickel electroplate.

13. The electroplating bath of claim 12 wherein the brightener is contained therein in amount of approximately 0.05 to 2 g./l.

References Cited

UNITED STATES PATENTS

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JOHN H. MACK, Primary Examiner

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U.S. Cl. X.R.

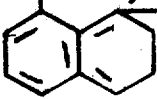
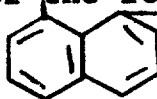
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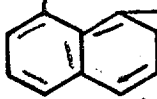
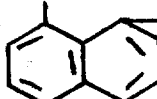
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,457,146 Dated July 22, 1969

Inventor(s) Jean Louis Levasseur

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 36, after "products" and before "as", the comma should be deleted. Column 2, line 28, "sulfone" should read -- sultone --. Column 5, line 23, that portion of the formula reading "2-butylene- 1, 4-" should read -- 2-butyne-1, 4- --; line 48, "to" should be --at--. Column 6, line 50, that portion of the formula reading " " should read --  --.

Column 7, line 5, that portion of the formula reading "-C≡O-" should read -- -C≡C- --; line 37 that portion of formula reading " " should read --  --.

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