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ELECTRODEPOSITION OF BRIGHT NICKEL

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This invention relates to the electrodeposition of bright nickel.

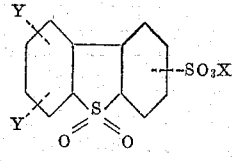
Nickel electrodeposits as plated are not bright in thicknesses substantially greater than those of very thin "strike" or "flash" coatings. It is possible to obtain bright deposits in substantial thickness with the use of bath additives. Addition agents useful as brighteners in nickel plating baths are generally divided into two classes on the basis of their predominant function. "Secondary brighteners" are materials which produce brightening and grain refining effects, resulting in semi-bright and lustrous deposits. The addition of "primary brighteners" together with the secondary brightener results in deposits that are "mirror-bright." Although many materials have been proposed as effective secondary brighteners, very few have had any successful commercial utilization. We have now discovered a new secondary brightener.

It is an object of this invention to provide an efficient process for electrodepositing bright and smooth nickel deposits.

Another object of this invention is to provide bath compositions for bright nickel plating.

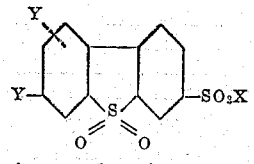
The invention also contemplates providing novel brighteners for use in nickel plating baths.

We discovered that sulfonated dibenzothiophene dioxide is an effective secondary brightener useful in a variety of nickel plating baths. When used in conjunction with a primary brightener, mirror-bright deposits are obtained. The sulfonated dibenzothiophene dioxide compounds have the following general formula:



wherein Y is hydrogen or SO_3X, and X is a cation whose presence in the bath is not deleterious and includes the alkali metals and the alkaline earth metals. X is preferably hydrogen, ammonium, sodium, potassium, nickel, cobalt, or magnesium. The sulfonated dibenzothiophene dioxide is used in amounts between 1 g./l. and 10 g./l., and preferably 2 g./l. and 6 g./l. in both bright and semi-bright baths.

Sulfonated dibenzothiophene dioxide may be synthesized by a number of routes. A preferred preparation is the sulfonation of diphenyl with fuming sulfuric acid (20% oleum) for about two hours, isolating and neutralizing. The reaction product is generally a mixture of the mono-, di-, and tri-substituted compounds (with the tri-substituted compound being present in major proportions) having the following general formula:



The mixed reaction product is an effective brightener. The mono-, di-, and tri-substituted compounds are each individually effective as brighteners. Sulfonated dibenzothiophene dioxide may also be synthesized by the hydrogen peroxide oxidation of dibenzothiophene followed by sulfonation with fuming sulfuric acid.

Conventional baths and processes for electroplating bright nickel are dscribed in "Principles of Electroplating and Electroforming," Blum and Hogaboom, pages 362–381, revised third edition, 1949, McGraw-Hill Book Co., Inc., New York; and "Modern Electroplating," edited by A. G. Gray, The Electrochemical Society, 1953, pages 299–355. The control and operating conditions, including the concentration of the bath ingredients, pH, temperature, cathode current density, etc., of these conventional baths are generally applicable to the present invention. Practically all baths for electroplating bright nickel contain nickel sulfate, a chloride, usually nickel chloride; a buffering agent, usually boric acid; and a wetting agent, e.g., sodium lauryl sulfate, sodium lauryl ether sulfate, and 7-ethyl-2-methyl-4-undecanol sulfate. Such types of baths include the well-known Watts-type bath and the high chloride type bath. Other bats contain as the source of the nickel a combination of nickel fluoborate with nickel sulfate and nickel chloride, or a combination of nickel fluoborate with nickel chloride. Typical Watts-type baths and high chloride baths are noted in Tables I and II.

TABLE I

Watts-Type Baths

Nickel sulfate	200 to 400 g./l.
Nickel chloride	30 to 75 g./l.
Boric acid	30 to 50 g./l.
Temperature	38 to 66° C.
pH	2.5 to 4.5 electrometric agitation.

TABLE II

High Chloride Baths

Nickel chloride	150 to 300 g./l.
Nickel sulfate	40 to 150 g./l.
Boric acid	30 to 50 g./l.
Temperature	38 to 66° C.
pH	2.5 to 4.5 electrometric agitation.

Sulfonated dibenzothiophene dioxide is compatible with a wide variety of primary brighteners. Preferred brighteners used in combination therewith include acetylenic alcohols and amides, 2-mercaptobenzimidazole and its amino substitution products, diethylene triamine and other polyamines (such as tetraethylene pentamine), triphenylmethane dyes, and such pyridine and quinaldine derivatives as: α-pyridinium-1-methylquinaldinium dimethosulfate, α,α'-(2,6-lutidinylene) bis(pyridinium iodide), and 1-(2-quinolylmethyl) pyridinium iodide. Effective bright plating baths have been developed utilizing the sulfonated dibenzothiophene dioxide as the secondary brightener, together with a primary brightener, and an auxiliary secondary brightener such as 2-butene-1,4-diol or N-vinyl-2-pyrrolidone, as illustrated in Examples 2 to 9, 13, 17 to 22, 27 and 28.

For the purpose of giving those skilled in the art a better understanding of the invention, illustrative examples are given. In each of the examples, an aqueous acidic nickel-containing bath was made up with the specified components. Electrodeposition was carried out by passing electric current through an electric circuit comprising an anode and a sheet metal or rod cathode, both immersed in the bath. The baths were agitated, usually by a moving cathode. The examples utilizing the sulfonated dibenzothiophene dioxide together with a primary brightener resulted in mirror-bright deposits. The deposite of Examples 16 and 26 wherein the secondary brightener was used alone resulted in fine-grained, uniformly semi-bright deposits having good ductility.

In Examples 1 through 16, the following standard Watts-type bath was used as a base solution:

Nickel sulfate	300 g./l.
Nickel chloride	60 g./l.
Boric acid	45 g./l.
pH	3.0 to 4.5.
Temperature	38° to 66° C.

Example 1

	Amount, g./l.
Sulfonated dibenzothiophene dioxide	4
4,4',4''-triaminotriphenylmethane	0.005
Sodium lauryl sulfate	0.5

Example 2

Sulfonated dibenzothiophene dioxide	1
Sodium 1,3,6 naphthalene trisulfonate	20
2-mercapto benzimidazole	0.01
N-vinyl-2-pyrolidone	0.5
Sodium lauryl sulfate	0.25

Example 3

Sulfonated dibenzothiophene dioxide	4
2-mercaptobenzimidazole	0.01
N-vinyl-2-pyrrolidone	0.2
Sodium lauryl sulfate	0.5

Example 4

Sulfonated dibenzothiophene dioxide	4
2-mercaptobenzimidazole	0.01
N-vinyl-2-pyrrolidone	1.0
Sodium lauryl sulfate	0.25

Example 5

Sulfonated dibenzothiophene dioxide	4
α-Phenyl propynol	0.01
Propargyl alcohol	0.005
2-butene-1,4-diol	0.2
Sodium lauryl sulfate	0.5

Example 6

Sulfonated dibenzothiophene dioxide	4
6-mercapto purine	0.0075
N-vinyl-2-pyrrolidone	0.2
Sodium lauryl sulfate	0.5

Example 7

Sulfonated dibenzothiophene dioxide	4
6-mercapto purine	0.0075
N-vinyl-2-pyrrolidone	1.0
Sodium lauryl sulfate	0.25

Example 8

Sulfonated dibenzothiophene dioxide	1
Sodium 1,3,6-naphthalene trisulfonate	10
N-vinyl-2-pyrolidone	0.5
Sodium lauryl sulfate	0.25

Example 9

Sulfonated dibenzothiophene dioxide	4
2-butyne-1,4-diol	0.01
2-butene-1,4-diol	0.2
Propargyl alcohol	0.005
Sodium lauryl sulfate	0.25

Example 10

Sulfonated dibenzothiophene dioxide	4
3-methyl-1-pentyne-3-ol	0.012
Sodium lauryl sulfate	0.25

Example 11

Sulfonated dibenzothiophene dioxide	6
2-methyl-1-butyne-2-ol	0.012
Sodium lauryl sulfate	0.25

Example 12

	Amount, g./l.
Sulfonated dibenzothiophene dioxide	5
Polyoxyethylated 2-butyne-1,4-diol 175	0.012
Sodium lauryl sulfate	0.25

Example 13

Sulfonated dibenzothiophene dioxide	4
2-butene-1,4-diol	0.26
Ethylnyl cyclohexanol	0.012
Sodium lauryl sulfate	0.25

Example 14

Sulfonated dibenzothiophene dioxide	4
5-sulfanilylindazole	0.005
Sodium lauryl sulfate	0.25

Example 15

Sulfonated dibenzothiophene dioxide	4
Phenylpropiolamine	0.2
Diethylene triamine	0.002
Sodium lauryl sulfate	0.25

Example 16

Sulfonated dibenzothiophene dioxide	4
Sodium lauryl sulfate	0.5

In Examples 17 through 26, the following high chloride aqueous bath was used as a base solution:

Nickel chloride	240 g./l.
Nickel sulfate	60 g./l.
Boric acid	45 g./l.
pH	3.0 to 4.5
Temperature	38° to 66° C.

Example 17

	Amount, g./l.
Sulfonated dibenzothiophene dioxide	4
2-mercaptobenzimidazole	0.01
N-vinyl-2-pyrrolidone	0.2
Sodium lauryl sulfate	0.25

Example 18

Sulfonated dibenzothiophene dioxide	4
2-mercaptobenzimidazole	0.01
N-vinyl-2-pyrrolidone	1.0
Sodium lauryl sulfate	0.5

Example 19

Sulfonated dibenzothiophene dioxide	6
6-mercaptopurine	0.01
N-vinyl-2-pyrrolidone	0.5
Sodium lauryl sulfate	0.5

Example 20

Sulfonated dibenzothiophene dioxide	4
5-amino-2-mercaptobenzimidazole	0.01
N-vinyl-2-pyrrolidone	0.2
Sodium lauryl sulfate	0.25

Example 21

Sulfonated dibenzothiophene dioxide	4
2-butene-1,4-diol	0.2
Sodium lauryl sulfate	0.25
2-butyne-1,4-diol	0.01

Example 22

Sulfonated dibenzothiophene dioxide	4
2-butene-1,4-diol	0.2
α-Phenyl propynol	0.01
Propargyl alcohol	0.005
Sodium lauryl sulfate	0.25

Example 23

Sulfonated dibenzothiophene dioxide	4
2-(2-quinolylmethyl)isoquinolinium iodide	0.04
Sodium lauryl sulfate	0.25

Example 24

	Amount, g./l.
Sulfonated dibenzothiophene dioxide	4
1 - [2 - (6 - methylquinolyl)methyl]pyridinium iodide	0.04
Sodium lauryl sulfate	0.25

Example 25

Sulfonated dibenzothiophene dioxide	4
1-(2-quinolylmethyl)pyridium iodide	0.04
Sodium lauryl sulfate	0.25

Example 26

Sulfonated dibenzothiophene dioxide	4
Sodium lauryl sulfate	0.25

In Examples 27 and 28 the following aqueous bath was used as a base solution:

Nickel chloride	250 g./l.
Nickel sulfate	45 g./l.
Boric acid	45 g./l.
pH	3.5.
Temperature	49° C.

Example 27

	Amount, g./l.
Sulfonated dibenzothiophene dioxide	4
2-butyne-1,4-diol	0.01
2-butene-1,4-diol	0.2
Sodium lauryl sulfate	0.5

Example 28

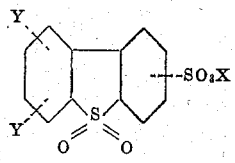
Sulfonated dibenzothiophene dioxide	4
2-butene-1,4-diol	0.2
2-propyne-1-ol	0.005
Sodium lauryl sulfate	0.5

The foregoing examples illustrate specific baths and processes, several being preferred. It is understood that the compositions and conditions may be varied. The sulfonated dibenzothiophene dioxide is also advantageously used in conjunction with another secondary brightener, as in Examples 2 and 8, to yield excellent bright deposits. The nickel from these baths may be applied to the usual basis metals including iron, steel, etc. They are preferably plated on copper or a copper alloy.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

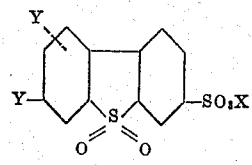
We claim:

1. In an aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of bright nickel, the improvement comprising incorporating therein as a brightener sulfonated dibenzothiophene dioxide having the structure



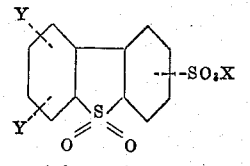
wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the group consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium, in an amount sufficient to cause the electrodeposition of bright nickel from said bath.

2. In an aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of bright nickel, the improvement comprising incorporating therein as a brightener between 1 g./l. and 10 g./l. of sulfonated dibenzothiophene dioxides having the structure



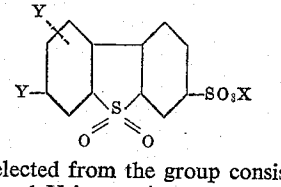
wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the group consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium, in an amount sufficient to cause the electrodeposition of bright nickel from said bath.

3. In an aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of mirror-bright nickel and containing a primary brightener, the improvement comprising incorporating therein as a secondary brightener between 1 g./l. and 10 g./l. of at least one sulfonated dibenzothiophene dioxide having the structure



wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the group consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium.

4. In an aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of mirror-bright nickel and containing a primary brightener, the improvement comprising incorporating therein as a secondary brightener between 2 g./l. and 6 g./l. of at least one sulfonated dibenzothiophene dioxide having the structure



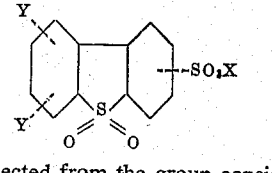
wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the class consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium.

5. The bath of claim No. 4 in which Y is hydrogen.

6. The bath of claim No. 4 containing in addition an auxiliary secondary brightener selected from the group consisting of N-vinyl-2-pyrrolidone and 2-butene-1,4-diol.

7. The bath of claim No. 4 in which the primary brightener is used in amounts between .005 g./l. and .1 g./l.

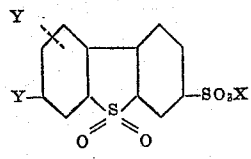
8. In the process of electrodepositing bright nickel from an aqueous acid electrolytic bath containing soluble nickel salts, the improvement comprising incorporating therein as a brightener at least one sulfonated dibenzothiophene dioxide having the structure



wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the class consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium in an amount sufficient to cause the electrodeposition of bright nickel from said bath.

9. In the process of electrodepositing mirror-bright nickel from an aqueous acid electrolytic bath containing soluble nickel salts and a primary brightener, the improve-

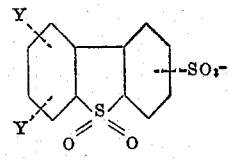
ment comprising incorporating therein as a secondary brightener between 1 g./l. and 10 g./l. of at least one sulfonated dibenzothiophene dioxide having the structure



wherein Y is selected from the group consisting of SO_3X and hydrogen, and X is a cation selected from the class consisting of hydrogen, ammonium, sodium, potassium, nickel, cobalt and magnesium.

10. An aqueous acid electrolytic bath containing soluble nickel salts for the electrodeposition of bright nickel, and

containing as a brightener a sulfonated dibenzothiophene dioxide anion having the structure



wherein Y is selected from the group consisting of SO_3^-, and hydrogen, in an amount sufficient to cause the electrodeposition of bright nickel from said bath.

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