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BRIGHT NICKEL PLATING

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This invention relates to the use of thiophene sulfonic acid and derivatives thereof as brightening addition agents for aqueous, acid nickel plating solutions, to the method of electroplating from such solutions and the articles resulting therefrom, and also includes the simultaneous use of thiophene sulfonic acid and derivatives thereof with other brightening addition agents in aqueous acid nickel plating solutions.

In the last decade, great progress has been made in the art of bright nickel plating. (The term "bright" as used herein includes "fully bright" and "semi-bright.") Outstanding developments have been realized in connection with the use of aromatic sulfonic acids and their metal and amine derivatives such as sodium and nickel benzene sulfonates, sodium and nickel naphthalene sulfonates and saccharine, when used in connection with cooperating addition agents such as certain metals and dyes and other complex organic compounds.

We have now discovered that thiophene sulfonic acid and its alkali metal, nickel, and cobalt derivatives wherein the substituent replaces the hydrogen atom of the SO_3H group are excellent addition agents for use in bright nickel plating, either alone or in combination with other addition agents of the type indicated above. Accordingly, it is the principal object of our invention to provide new solutions and processes involving the use of thiophene sulfonic acid and its said substitution products as indicated.

The simplest form in which our invention may be realized involves a solution which may consist of water as the solvent and a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride and mixtures thereof together with boric acid or other suitable buffer such as formic acid or a formate and a small proportion of thiophene sulfonic acid or one of its substitution products indicated above. In this embodiment of our invention, thiophene sulfonic acid and the indicated substitution products produce semi-bright deposits of nickel in quite low concentration, that is, from about .005 to about .5 gram per liter. This is a very low concentration as compared to the quantity of aromatic sulfonates required. For example, benzene sulfonates and naphthalene sulfonates are not effective to produce semi-bright nickel deposits unless present in concentration of the order of one gram per liter and, even at such concentrations, the semi-bright deposit hardly compares with that of 0.1 gram per liter of thiophene sulfonic acid. Again, thiophene sulfonic acid and its indicated derivatives are effective to produce electroplating solutions having good bright throwing power, that is, ability to produce bright deposits in low cathodic areas. For this reason and because of its ability to mix with other bright plating solutions with-

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out losing the property of enhancing the bright throwing power of the solution, it is very useful for inclusion in plating solutions relying mainly upon benzene or naphthalene sulfonates or similar aromatic sulfonates and brighteners such as dyes and other complex organic compounds. In the case of such solutions, a small inclusion of thiophene sulfonic acid or one of its indicated derivatives improves the bright throwing power and also appears to enable the solution to tolerate a greater concentration of impurities of the kind which normally produce grey areas especially under conditions of low current density. This we attribute to the improved bright throwing power already mentioned.

The basic electroplating solution in connection with which our invention is best realized may be operated at pH 3.0 to 5.0 and may contain the following:

	Gram/liter
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ -----	150-350
$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ -----	20- 75
H_3BO_3 -----	20- 75

To the foregoing basic solution there may be added any suitable quantity (e. g. 0.1 to 1.0 gram per liter) of an anti-pit agent such as the sulfates of the aliphatic alcohols containing from 8-18 carbon atoms, suitably sodium lauryl sulfate. Of this latter material, we may use from about 0.1 gram per liter up to saturation, one gram per liter ordinarily being adequate. Under favorable conditions no anti-pit agent is used and good deposits are obtained without it.

To the above indicated basic solution we may add from .005 to .5 gram per liter of thiophene sulfonic acid or one of its indicated derivatives. It is to be understood that by thiophene sulfonic acid we mean a compound having the thiophene nucleus substituted by a sulfonic acid group in the alpha position with respect to the sulfur atom. This will result in the production of a semi-bright deposit, no other brightening addition agent being necessary to this result.

We may also add a group of cooperating addition agents, for example, (1) an organic brightener such as a dye or nitrile brightener and thiophene sulfonic acid or (2) an aromatic sulfonate, an organic brightener such as a dye or nitrile brightener and thiophene sulfonic acid.

The aromatic sulfonate brighteners may be, for example, the mono-, di and tri sulfonates of benzene, naphthalene and diphenyl, their alkali metal, nickel and cobalt salts and chloro, amino and methyl derivatives as well as the corresponding sulfonamides, and saccharine and its sodium salt. These may be used in proportions from 0.5 to 5.0 grams per liter. Specific examples are set forth in the following table:

Table I

1. Benzene mono-sulfonic acid ($C_6H_5SO_3H$)
 2. Benzene disulfonic acids ($C_6H_4(SO_3H)_2$)
 3. Sodium benzene monosulfonate
($C_6H_5SO_3Na$)
 4. Nickel benzene monosulfonate
($(C_6H_5SO_3)_2Ni$)
 5. Monochlor benzene monosulfonic acids
($ClC_6H_4SO_3H$)
 6. Benzene monosulfonamide ($C_6H_5SO_2NH_2$)
 7. Saccharine, sodium salt ($C_6H_4SO_2CONNa$)
 8. Dichloro benzene disulfonic acids
($Cl_2C_6H_2(SO_3H)_2$)
 9. 2,5 dibromo benzene sulfonic acid
($Br_2C_6H_3SO_3H$)
 10. Toluene sulfonic acids ($CH_3C_6H_4SO_3H$)
 11. Benzaldehyde sulfonic acid
($C_6H_4(CHO)SO_3H$)
 12. Diphenyl sulfonic acid ($C_6H_5C_6H_4SO_3H$)
 13. Benzene sulfonyl chloride ($C_6H_5SO_2Cl$)
 14. Para chloro benzene sulfonamide
($ClC_6H_4SO_2NH_2$)
 15. Xylene sulfonamide ($(CH_3)_2C_6H_3SO_2NH_2$)
 16. Para toluene sulfonamide
($CH_3C_6H_4SO_2NH_2$)
 17. Thiophene sulfonic acid ($C_4H_3S.SO_3H$)
 18. Diphenyl sulfone ($C_6H_5SO_2C_6H_5$)
 19. Alpha-naphthalene mono-sulfonate
 20. Beta-naphthalene mono-sulfonate
 21. Naphthalene disulfonates
 22. Naphthalene trisulfonates
 23. Sulfonated naphthalene
 24. o-Toluene sulfonamide.
- The auxiliary brighteners may be aliphatic nitriles containing from 1 to 10 carbon atoms, aromatic nitriles containing from 8 to 10 carbon atoms and aromatic amino compounds containing from 8 to 24 carbon atoms. These may be employed in proportion from .01 to 1.0 gram per liter in the case of the nitriles (Items 1-21 below) and in proportion from .005 to 0.1 gram per liter in the case of the dyes (Items 22-29 below). Specific examples are set forth in the following table.

Table II

1. Methyl cyanide (acetonitrile, CH_3CN)
2. Ethyl cyanide (propionitrile, C_2H_5CN)
3. Beta-chloro-propionitrile (ClH_2CCH_2CN)
4. Beta-bromopropionitrile (BrH_2CCH_2CN)
5. Alpha, alpha, beta-trichloropropionitrile
(ClH_2CCl_2CCN)
6. Ethylene cyanohydrin ($HOCH_2CH_2CN$)
7. Lactonitrile ($CH_3CHOHCN$)
8. Glycolonitrile ($HOCH_2CN$)
9. Chloralcyanohydrin ($Cl_3CCHOHCN$)
10. Acrylonitrile ($H_2C:CHCN$)
11. Beta-amino-propionitrile
($NH_2CH_2CCH_2CN$)
12. Cyano acetic acid ($HOOCCH_2CN$)
13. Ethyl cyanoacetate ($C_2H_5OOCCH_2CN$)
14. Isopropylcyanoacetate
($(CH_3)_2O_2CHOOCCH_2CN$)
15. Cyano-ethyl acetate
($NCCH_2CH_2OOCCH_3$)
16. Cyanoacetamide ($NCCH_2CONH_2$)

17. Butyl-cyano acetate ($C_4H_7OOCCH_2CN$)
 18. Succinonitrile ($((CH_2CN)_2)$)
 19. Benzonitrile (C_6H_5CN)
 20. Benzyl cyanide ($C_6H_5CH_2CN$)
 21. Benzylacetoneitrile ($C_6H_5C_2H_4CN$)
 22. (Fuchsin) p,p'-diamino - m - methyl fuchsonium chloride
 23. Triaminotolyl diphenyl methane hydrochloride (reduction product of fuchsin)
 24. Triaminotolyl phenyl carbitol hydrochloride (carbitol product of fuchsin)
 25. Mixture of reduction products and carbitol of fuchsin prepared as hereinafter explained
 26. Malachite Green (tetramethyl-p,p'-diaminotriphenylmethane)
 27. Rhodamine Orange (tetramethyl-diamino-acridine hydrochloride)
 28. Safranin Y (mixture of ms-phenylditolazonium chloride) and mo-o-tolyditolazonium chloride
 29. Methylene Blue or Calcozine Blue 2F EX (tetramethyldiaminodiphenazthionium chloride)
- Specific Example 23 of Table I above is such as may be produced by reacting 2 parts of 20% oleum on one part of naphthalene at 160° C. for two hours, neutralizing the resulting mixture with nickel carbonate, filtering and diluting to 26° Bé. Where quantities of "sulfonated naphthalene" are referred to hereinafter, it is to be understood that the quantity specified represents roughly the nickel-naphthalene-mixed sulfonate content of the mixture. Five cc. of the nickel neutralized reaction mixture is taken as equivalent to one gram of nickel-naphthalene-mixed sulfonates. This treatment produces, as is well known, a mixture containing nickel naphthalene mono-sulfonates, disulfonates and trisulfonates.
- We have found it most practical to prepare specific Example 25 of Table II given above in the following way: Fifty parts of the dye, 1,000 parts of water, 100 parts of granular nickel and 100 parts of hydrochloric acid are heated and mechanically stirred until the magenta color of fuchsin has practically disappeared. The mixture is then stirred with a small amount of activated carbon and filtered. The filtrate is made up to one liter and contains the equivalent of five grams of the original fuchsin per 100 cc.
- The following specific examples will serve to illustrate the invention:

Example I

- 55 $NiSO_4 \cdot 7H_2O$, 240 g.
 $NiCl_2 \cdot 7H_2O$, 40 g.
 H_3BO_3 , 40 g.
Nickel thiophene sulfonate, 0.15 g.
Water to make 1 liter
- 60 Temp., 140° F.
Current density, 50 A. S. F.
pH, 3.5
Character of deposit, semi-bright, ductile.

Example II

- 65 $NiSO_4 \cdot 7H_2O$, 240 g.
 $NiCl_2 \cdot 7H_2O$, 40 g.
 H_3BO_3 , 40 g.
- 70 Nickel thiophene sulfonate 0.5 g.
Water to make 1 liter
Temp., 140° F.
Current density, 50 A. S. F.
pH, 3.5
- 75 Character of deposit, semi-bright, ductile.

Example III

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 240 g.
 $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, 40 g.
 H_3BO_3 , 40 g.
 Thiophene sulfonic acid, 0.15 g.
 Ethylene cyanohydrin, 0.3 g.
 Water to make 1 liter
 Temp., 140° F.
 Current density, 50 A. S. F.
 pH, 3.5
 Deposit, fully bright; ductile.

Example IV

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 240 g.
 $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, 40 g.
 H_3BO_3 , 40 g.
 Thiophene sulfonic acid, .15 g.
 Reduced fuchsin, .005 g.
 Water to make 1 liter
 Temp., 140° F.
 Current density, 50 A. S. F.
 pH, 3.5
 Deposit, fully bright; ductile.

Example V

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 240 g.
 $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, 40 g.
 H_3BO_3 , 40 g.
 Thiophene sulfonic acid, 0.2 g.
 Reduced fuchsin, .005 g.
 Water to make 1 liter
 Temp., 140° F.
 Current density, 50 A. S. F.
 pH, 3.5
 Deposit, fully bright; ductile.

Example VI

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 240 g.
 $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, 40 g.
 H_3BO_3 , 40 g.
 Thiophene sulfonic acid, 0.15 g.
 Sulfonated naphthalene, 4 g.
 Reduced fuchsin, .005 g.
 Water to make 1 liter
 Temp., 140° F.
 Current density, 50 A. S. F.
 pH, 3.5
 Deposit was fully bright in spite of impurities which, with the same constituents except thiophene sulfonic acid, caused a gray deposit in recessed portions.

This example shows the type of solution which would result if thiophene sulfonate were used to treat a bright plating solution which, on account of impurities, exhibited low bright throwing power. We have found thiophene sulfonic acid and thiophene sulfonates useful for that purpose not only in solutions containing dye brighteners but also those containing nitrile brighteners. Accordingly, other dye brighteners or the nitrile brighteners may be substituted for reduced fuchsin in this example.

Having thus described our invention, what we claim is:

1. An aqueous, acid electroplating bath for production of a bright cathodic deposit of nickel, said bath essentially consisting of a nickel ion yielding material selected from the group consisting of nickel sulfate, nickel chloride and mixtures thereof, a buffer and, as an addition agent, a material of the class consisting of thiophene sulfonic acid and its alkali metal, nickel and cobalt derivatives wherein the metal atom replaces the hydrogen atom of the SO_3H group,

said addition agent being present in concentration from 0.005 to 0.5 gram per liter, the pH of said solution being from 3.0 to 5.0.

2. An electroplating bath according to claim 1 wherein is contained an additional brightening addition agent of the class consisting of aliphatic nitriles having from 1 to 10 carbon atoms and aromatic nitriles having from 8 to 10 carbon atoms.

3. An electrodeposition bath according to claim 2 wherein is also contained an aromatic sulfonate of the class consisting of the mono-, di and tri sulfonic acids of benzene, naphthalene and diphenyl, their alkali metal, nickel and cobalt salts, and chloro, amino and methyl derivatives, the corresponding sulfonamides, saccharine and its sodium salt.

4. An aqueous, acid electroplating bath for production of a bright cathodic deposit of nickel, said bath essentially consisting of a nickel ion yielding material selected from the group consisting of nickel sulfate, nickel chloride and mixtures thereof, a buffer and, as an addition agent, a material of the class consisting of thiophene sulfonic acid and its alkali metal, nickel and cobalt derivatives wherein the metal atom replaces the hydrogen atom of the SO_3H group said addition agent being present in concentration from 0.005 to 0.5 gram per liter, the pH of said solution being from 3.0 to 5.0, said bath also containing an additional brightening addition agent of the class consisting of aliphatic nitriles having from 1 to 10 carbon atoms and aromatic nitriles having from 8 to 10 carbon atoms, said nitriles being employed in concentrations of from 0.01 to 1.0 gram per liter.

5. An electrodeposition bath according to claim 4 wherein is also contained an aromatic sulfonate of the class consisting of the mono-, di and tri sulfonic acids of benzene, naphthalene and diphenyl, their alkali metal, nickel and cobalt salts, and chloro, amino and methyl derivatives, the corresponding sulfonamides, saccharine and its sodium salt.

6. An electrodeposition bath according to claim 1, the same containing from 0.01 to 1.0 gram per liter of ethylene cyanohydrin.

7. An electrodeposition bath according to claim 1, the same containing from 0.01 to 1.0 gram per liter of ethyl cyanoacetate.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,528,902

November 7, 1950

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 72, for "thiophane" read *thiophene*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of January, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,

Assistant Commissioner of Patents.