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3,023,150 BATH FOR THE PRODUCTION OF METAL ELECTROPLATES

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19 Claims. (Cl. 204-44)

This invention relates to an electroplating bath and process for obtaining full bright metal electrodeposits. The invention more particularly relates to brightening compounds for such an electroplating process which are derivatives of sulfonic acids and which may be used in all types of electroplating baths.

Electroplating baths have previously been modified by the inclusion of organic sulfonic acids or organic sulfation products of various compounds. While the prior art compounds have effected some improvement in the brightness characteristics of electrodeposits, they have usually not produced commercially desirable electrodeposits individually and were used with supplemental brightening agents to obtain the desired results.

Where brightening agents of the prior art obtained bright electrodeposits individually, such as for example the brightening agents disclosed in United States Patent No. 2,830,014, the brightening agents were limited in their use to a specific type of electroplating bath and in their operating conditions.

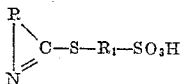
It is, therefore, an object of this invention to provide brightening agents for electroplating baths which will produce full bright, ductile electrodeposits in all types of electroplating bath solutions.

It is a further object to provide electroplating bath compositions of the acid, alkaline or cyanide type from which full-bright electrodeposits may be obtained.

Another object is to provide a process for producing full-bright electrodeposits over a broader range of operating conditions.

These and other objects of our invention will become apparent as the description thereof proceeds.

We have now found that the above objects may be achieved and full-bright, firmly adhering metal electroplates may be obtained by adding to the baths, as special brightening agents, water-soluble organic sulfonic acids of the general formula



or water-soluble salts thereof. In this formula R represents a possibly substituted polymethylene chain with 3 to 6 carbon atoms and R₁ represents a bivalent hydrocarbon radical which may also have hydroxyl groups and/or halogen atoms attached thereto.

Examples of sulfonic acids or their salts which may be used as brightening agents in accordance with the present invention are the following:

- 2-S-Δ'-pyrrolinyl-(2')-mercapto-propane-sulfonic acid-1.
- 4-S-Δ'-pyrrolinyl-(2')-mercapto-butane-sulfonic acid-1.
- 3-S-(4'-methyl-Δ'-pyrrolinyl-2')-mercapto - propane - sulfonic acid-1.
- 3-S-Δ'-pyrrolinyl-(2')-mercapto-2-hydroxy - propane-sulfonic acid-1.
- 3-S-Δ'-pyrrolinyl-(2')-mercapto-2 - chloro - propane - sulfonic acid-1.
- 3-S-Δ'-piperideinyl-(2')-mercapto-propane-sulfonic acid-1.
- 3-S-Δ'-piperideinyl-(2')-mercapto-butane-sulfonic acid-1.
- Isocaprothiolactam-S-ethyl ester-ω-sulfonic acid.
- Isocaprothiolactam-S-n-propyl ester-ω-sulfonic acid.

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Isocaprothiolactam-S-n-butyl ester-ω-sulfonic acid.
Isocaprothiolactam-S-benzyl ester-2-sulfonic acid.
Isoenanthothiolactam-S-n-propyl ester-ω-sulfonic acid.

The production of these compounds takes place in accordance with known methods, for example, by reaction of the cyclic thioamides (thiolactams) with sultones or halogen alkane sulfonic acids or their salts in the molten state, advantageously in the presence of a little water, or by heating an aqueous or non-aqueous, for example alcoholic, solution or suspension of these reactants.

The stability of these compounds is very good, so that baths which contain these brightening agents can be maintained in operation for extended periods of time. As compared to the brightening agents of the principal patent, the compounds according to the present invention produce full-bright electroplates in the range of medium and lower current densities even at higher bath temperatures.

The baths may also be modified with wetting agents as well as with substances which are capable of typing up inorganic impurities contained in the water or the metal salts, such as amino compounds free from carboxyl groups in accordance with German Patent 1,000,204.

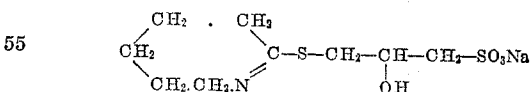
The novel brightening agents may be used in acid, cyanide and alkaline electroplating baths for the production of copper, zinc, cadmium, tin, brass, bronze, silver and gold electrodeposits of iron, iron alloys, copper, brass, zinc and other customary base metals. They are added to the baths in amounts of about 0.01 to 10 gm./liter.

The acid baths are operated at bath temperatures up to 60° C. within a current density range of 0.5 to 14 amp./dm.². If, in addition, thioamides or isothioamides which do not contain any sulfonic acid groups are added to the baths, full-bright metal electrodeposits can be obtained at temperatures around 60° C. even at current densities beginning at about 0 amp./dm.². In alkaline baths full-bright electroplates are obtained at current densities up to 40 amp./dm.² and at bath temperatures up to 90° C.

The following examples are given for the purpose of illustration and to enable persons skilled in the art to better understand and practice the invention and are not intended to be limitative.

Example I

When a customary acid copper bath, containing 220 gm./liter CuSO₄·5H₂O, 60 gm./liter H₂SO₄ and, as a wetting agent, 2 gm./liter of a condensation product of dodecyl alcohol and 10 mols ethylene oxide which has been 25% transformed into the sulfuric acid ester, was modified with 0.05 gm./liter of the sodium salt of isocaprothiolactam-S-hydroxy-propyl-ester-1'-sulfonic acid of the formula



and 2 gm./liter of the hydrochloride of 1,3-bis-(diethylamino)-propanol-2, full-bright copper electrodeposits were obtained on brass and other metallic bases at room temperature within a current density range of 0.5 to 8 amp./dm.².

Example II

When a cyanide zinc bath, containing 60 gm./liter zinc cyanide, 80 gm./liter sodium hydroxide and 40 gm./liter sodium cyanide, was modified with 4 gm./liter of the sodium salt of isocaprothiolactam-S-ethyl ester-ω-sulfonic acid, uniformly bright zinc electroplates were obtained on zinc and iron objects at room temperature within a current density range of 1 to 2 amp./dm.². Without the addition of the sulfonic acid salt the zinc electroplates

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were irregular and particularly dull within the medium and high current density range.

The sulfonic acid salt was obtained by admixing 12.9 parts by weight caprothiolactam with 21.1 parts by weight bromoethane-sodium sulfonate, adding 50 parts by weight of water and heating the mixture for a short period of time to about 105–110° C. until a clear solution was formed. Upon cooling, the sodium salt of isocaprothiolactam-S-ethyl ester- ω -sulfonic acid precipitated out in the form of yellow crystals with a yield of 13–15 parts by weight (=50–58% of theory).

Example III

A cyanide cadmium bath, containing 70 gm./liter cadmium cyanide, 50 gm./liter sodium cyanide and 30 gm./liter sodium hydroxide, was modified with 2.5 gm./liter of the internal salt of isocaprothiolactam-S-n-propyl ester- ω -sulfonic acid as a brightening agent. The cadmium electrodeposited at room temperature and at current densities between 2 and 6 amp./dm.² on sheet iron formed a full-bright, ductile plate.

The brightening agent used above was obtained by heating a mixture of 2.58 parts by weight caprothiolactam and 2.45 parts by weight propane sultone to 60° C. The temperature rose rapidly to 140 to 160° C. Upon cooling, the solidified melt thus obtained was dissolved in glacial acetic acid, the solution was concentrated slightly and was then triturated with ethyl acetate and acetone, whereby the internal salt of isocaprothiolactam-S-n-propyl ester- ω -sulfonic acid crystallized out as a grainy, faintly yellow substance. After washing the product with acetone and drying it, the salt was obtained with a yield of 4.1 parts by weight (79% of theory). After recrystallization from glacial acetic acid it melted at 257° C. (uncorrected).

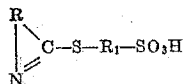
Example IV

Sheet steel was electroplated at room temperature and at a current density of 2–5 amp./dm.² in an acid zinc bath which contained 240 gm./liter zinc sulfate, 5 gm./liter sodium acetate, 5 gm./liter boric acid and as a brightening agent 3 gm./liter of the sodium salt of 4-S- Δ' -piperideinyl-(2')-mercapto-butane-sulfonic acid-1. The zinc electrodeposits thus obtained were full-bright.

While we have set forth specific embodiments and preferred modes of practice of our invention, it will be understood that the invention is not limited to these embodiments and that various changes and modifications may be made without departing from the spirit of the disclosure and the scope of the appended claims.

We claim:

1. An electroplating bath for producing bright electrodeposits of metals selected from the group consisting of copper, zinc, cadmium, tin, brass, bronze, silver and gold, comprising a solution of a salt of the metal to be deposited and as a brightening agent a water soluble sulfonic acid of the general formula



and water soluble salts thereof, wherein R represents a polymethylene chain and R₁ represents a bivalent hydrocarbon radical, said brightening agent being present in sufficient amount to obtain said bright electrodeposits.

2. The bath of claim 1 wherein the R polymethylene chain of the brightening agent is a substituted polymethylene chain.

3. The bath of claim 1 wherein the R₁ bivalent hydrocarbon radical of the brightening agent has substituents selected from the group consisting of hydroxyl groups and halogen atoms.

4. The bath of claim 1 comprising in addition a compound selected from the group consisting of thioamides

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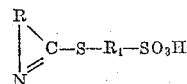
and isothioamides, said compound being free of sulfonic acid groups.

5. The bath of claim 1 wherein the bath is an acid bath.

6. The bath of claim 1 wherein the bath is an alkaline bath.

7. The bath of claim 1 wherein the bath is a cyanide bath.

8. An electroplating bath for producing bright electrodeposits of metals selected from the group consisting of copper, zinc, cadmium, tin, brass, bronze, silver and gold, comprising a solution of a salt of the metal to be deposited and as a brightening agent 0.01 to 10 gm./liter of a water soluble sulfonic acid of the general formula



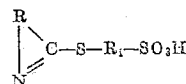
and water soluble salts thereof, wherein R represents a polymethylene chain and R₁ represents a bivalent hydrocarbon radical.

9. The bath of claim 8 wherein the brightening agent is the sodium salt of isocaprothiolactam-S-hydroxypropyl-ester-1'-sulfonic acid.

10. The bath of claim 8 wherein the brightening agent is the sodium salt of isocaprothiolactam-S-ethyl ester- ω -sulfonic acid.

11. The bath of claim 8 wherein the brightening agent is the sodium salt of 4-S- Δ' -piperideinyl-(2')-mercapto-butane-sulfonic acid-1.

12. A process for producing bright electrodeposits of metals selected from the group consisting of copper, zinc, cadmium, tin, brass, bronze, silver and gold, which comprises depositing said metal from an electroplating bath containing the metal to be deposited in the form of a salt in the presence of a brightening agent comprising a water soluble sulfonic acid of the general formula



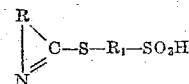
and water soluble salts thereof, wherein R represents a polymethylene chain and R₁ represents a bivalent hydrocarbon radical, said brightening agent being present in sufficient quantity to effect said brightening.

13. The process of claim 12 wherein the R polymethylene chain of the brightening agent is a substituted polymethylene chain.

14. The process of claim 12 wherein the R₁ bivalent hydrocarbon radical of the brightening agent has substituents selected from the group consisting of hydroxyl groups and halogen atoms.

15. The process of claim 12 wherein the bath contains in addition a compound selected from the group consisting of thioamides and isothioamides, said compound being free of sulfonic acid groups.

16. A process for producing bright electrodeposits of metals selected from the group consisting of copper, zinc, cadmium, tin, brass, bronze, silver and gold, which comprises depositing said metal from an electroplating bath containing the metal to be deposited in the form of a salt in the presence of 0.01 to 10 gm./liter of a brightening agent comprising a water soluble sulfonic acid of the general formula



and water soluble salts thereof, wherein R represents a polymethylene chain and R₁ represents a bivalent hydrocarbon radical.

17. The process of claim 16 wherein the brightening

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agent is the sodium salt of isocaprothiolactam-S-hydroxypropyl-ester-1'-sulfonic acid.

18. The process of claim 16 wherein the brightening agent is the sodium salt of isocaprothiolactam-S-ethyl ester-*w*-sulfonic acid.

19. The process of claim 16 wherein the brightening agent is the sodium salt of 4-S- Δ '-piperideinyl-(2')-mercapto-butane-sulfonic acid-1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,023,150

February 27, 1962

Wolf-Dieter Willmund et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 19, for "typing" read -- tying --; line 26, for "of iron" read -- on iron --.

Signed and sealed this 7th day of August 1962.

(SEAL)

Attest:

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Attesting Officer

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