

UNITED STATES PATENT OFFICE

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ELECTRODEPOSITION OF SILVER

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This invention relates to the electrodeposition of silver and has for its main object to provide a plating bath from which hard bright deposits of silver of any desired thickness can be obtained.

5 Present practice in silver plating from cyanide baths produces a matt deposit which requires polishing to develop a bright lustrous surface and this polishing not only adds to the cost of plating but removes a considerable proportion of silver
10 which is lost.

It is well known that the addition of organic sulphides, such as carbon disulphide, to the normal plating bath tends to produce smoother and brighter deposits of silver but the advantages to
5 be obtained are not sufficiently marked nor so constant as to warrant its use being generally adopted.

It is also well known that silver plating baths containing excessive amounts of free alkali metal cyanide produce very hard matt deposits which
20 are difficult and costly to polish. For this reason the amount of free alkali metal cyanide is usually kept down to the minimum required for satisfactory plating.

25 We have now found that the advantage to be obtained by the use of organic sulphides selected from the group carbon disulphide and mercaptans which are soluble in the bath, in respect to brightness of deposit and the advantage of increased
30 amounts of free alkali metal cyanide as regards hardness of deposit can be combined and considerably enhanced by the further addition to the normal plating bath of a colloidal solution of a detergent. The term detergent in the specification and claims means an alkali metal salt
35 of a soap-forming acid, such as a monobasic saturated or unsaturated carboxylic or hydroxycarboxylic acid of the aliphatic series containing not less than eight carbon atoms in the molecule, or of an alkali metal salt of a sulphonic acid
40 derived from one of the said soap-forming acids or from the corresponding alcohol. The addition made to a cyanide bath to produce a bright silver plate may thus consist of any of the commercial
45 forms of soap, including sulphonated soaps. All these compounds tend to hydrolyze in solution with the production of a small quantity of the free acid in a colloidal form which appears to be adsorbed to a small extent by the deposit, thus
50 producing a fine-grained structure consisting of almost sub-microscopic crystals.

When a soap is used, the amount required depends on the nature of the soap, but should be sufficient to produce a permanent lather when
55 the solution is shaken and should of course not exceed the solubility of the soap in the solution. When the bath is made up with soft water, about 0.1 ounce of soap per gallon is sufficient, but when made up with hard water more is required
60 since part is converted into the corresponding

calcium or magnesium compound which forms a silky precipitate and gives the bath an opalescent appearance which, however, does not interfere with the production of bright silver plates. A small quantity of glycerine or of a glycol may be added to the bath to reduce still further the grain size of the deposit. Obviously, the soap may be produced in situ in the bath by the addition of free acid, as for example sulphonated acid in the form commonly known as Turkey red oil.

Deposits obtained from the improved baths according to this invention are much harder than those obtained in the ordinary silver bath and have a brilliant white lustre which requires little or no polishing. There are therefore no losses
15 of silver due to polishing and silver plating costs are consequently very substantially reduced.

The free alkali metal cyanide content of the plating bath may vary within wide limits, for example from 1 to 16 ounces per gallon, with
20 corresponding effects upon the hardness of the deposited silver.

The sulphide brightening solution is added to the plating solution from time to time as required. This brightening solution is prepared by saturating a portion of the plating liquor or alternatively
25 an alkali metal cyanide solution with carbon disulphide and returning the sulphide solution obtained to the plating bath.

The following examples will further illustrate
30 how the said invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

A bath is prepared as follows:—

	Ounces per gallon
Silver (as $\text{KA}_2(\text{CN})_2$)	2.0
Free potassium cyanide	8.0
Turkey red oil	0.75
Sulphide brightening solution (obtained as described above)	0.75

Example 2

A bath is prepared as follows:—

	Ounces per gallon
Silver (as $\text{KA}_2(\text{CN})_2$)	3.0
Free potassium cyanide	6.0
Castile soap (sodium oleate)	3.0
Sulphide brightening solution (obtained as described above)	0.75

The baths described are preferably operated at room temperature and with a current density between 1 and 8 amperes per square foot. Higher
55 current densities tend to produce "burnt deposits".

What we claim is:—

1. A process for the electrodeposition of silver, in the form of hard bright deposits requiring 60

little or no polishing, from an alkali metal cyanide bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide and an organic sulphide of the group consisting of carbon disulphide and mercaptans which are soluble in the bath, which consists in adding to the said bath a colloidal solution of an alkali metal salt of an acid of the group consisting of aliphatic acids containing no less than eight carbon atoms in the molecule, sulphonic acids derived from said aliphatic acids, and sulphonic acids derived from the alcohols corresponding to said aliphatic acids.

2. A process for the electrodeposition of silver, in the form of hard bright deposits requiring little or no polishing, from an alkali metal cyanide bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide and an organic sulphide of the group consisting of carbon disulphide and mercaptans which are soluble in the bath, which consists in adding to the said bath a commercial soap, including sulphonated soaps.

3. In the process of electrodepositing silver from a bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide, an organic sulphide of the group consisting of carbon disulphide and mercaptans which are soluble in the bath and an alkali metal salt of an acid of the group consisting of aliphatic acids containing no less than eight carbon atoms in the molecule, sulphonic acids derived from said aliphatic acids, and sulphonic acids derived from the alcohols corresponding to said aliphatic acids, the step of introducing the organic sulphide in the form of a sulphide brightening solution prepared by saturating a portion of the plating liquor with carbon disulphide and returning the sulphide solution to the plating bath.

4. In the process of electrodepositing silver from a bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide, an organic sulphide of the group consisting of carbon disulphide and mercaptans which are soluble in the bath and an alkali metal salt of an acid of the group consisting of aliphatic acids containing no less than eight carbon atoms in the molecule, sulphonic acids derived from said aliphatic acids, and sulphonic acids derived from the alcohols corresponding to said aliphatic acids, the step of introducing the organic sulphide in the form of a sulphide brightening solution prepared by saturating an alkali metal cyanide solution with carbon disulphide and returning the sulphide solution to the plating bath.

5. A plating bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide, an organic sulphide of the group consisting of carbon disulphide and mercaptans soluble in the bath, and an alkali metal salt of an acid of the group consisting of aliphatic acids containing no less than eight carbon atoms in the molecule, sulphonic acids derived from said aliphatic acids, and sulphonic acids derived from the alcohols corresponding to said aliphatic acids.

6. A plating bath comprising a potassium argento-cyanide, an excess of free potassium cyanide, carbon disulphide and Turkey red oil.

7. A plating bath comprising a potassium argento-cyanide, an excess of free potassium cyanide, carbon disulphide and commercial sodium oleate (castile soap).

8. A process for the electrodeposition of silver, in the form of hard bright deposits requiring little or no polishing, from an alkali metal cyanide bath comprising an alkali metal argento-cyanide, an excess of free metal cyanide, and an organic sulphide of the group consisting of carbon disulphide and mercaptans soluble in the bath, which consists in adding to the said bath an alkali metal salt of an acid of the group consisting of aliphatic acids containing no less than eight carbon atoms in the molecule.

9. A process for the electrodeposition of silver in the form of hard bright deposits requiring little or no polishing, from an alkali metal cyanide bath comprising an alkali metal argento-cyanide, an excess of free alkali metal cyanide and an organic sulphide of the group consisting of carbon bisulphide and mercaptans which are soluble in the bath, which consists in adding to the said bath a colloidal solution of an alkali metal salt of a soap forming acid which tends to hydrolyze in solution with the production of a small quantity of the free acid in a colloidal form which appears to be adsorbed to a small extent by the deposit, thus producing a fine grained structure consisting of almost sub-microscopic crystals, said soap forming acid being selected from the group consisting of monobasic saturated or unsaturated carboxylic or hydroxycarboxylic acids of the aliphatic series containing not less than eight carbon atoms in the molecule, sulphonic acids derived from the said aliphatic acids, and sulphonic acids derived from the alcohols corresponding to said aliphatic acids.

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CERTIFICATE OF CORRECTION.

Patent No. 2,113,517.

April 5, 1938.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 9, before the word "acid" insert ricinoleic; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 31st day of May, A. D. 1938.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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