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**“IMPROVEMENTS IN OR RELATING TO THE ELECTRODEPOSITION OF HIGH SPEED  
BRIGHT HARD SILVER.”**

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN  
INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

*The following specification describes the nature of this invention :—*

*This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and Mrs. MALATHY PUSHPAVANAM, Senior Laboratory Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, both Indian citizens.*

This invention relates to the improvements in or relating to the electrodeposition of high speed hard bright silver plating from cyanide bath.

Hitherto it has been proposed to electrodeposit silver from cyanide baths containing —

1. Carbon disulphide
2. Condensation product of carbon disulphide with acrolein or with a ketone
3. Ammonium thiosulphate
4. Compounds of selenium
5. Antimony complex with glycerol or triethanolamine as additives.

This is open to the objection that these addition agents cannot be used at high current densities, i.e. upto 11 A/dm<sup>2</sup> and most of them except antimony additive give only soft deposit. All the three mentioned conditions, viz. high current density, hard and bright, have not yet been tried in a single bath.

The object of this invention is to obviate these disadvantages by using a brightener which will produce bright and hard deposits at higher current density.

This invention mainly consists in producing hard, bright silver deposit at a higher current density from cyanide baths using silver cyanide, potassium cyanide and potassium carbonate with the antimony compound and a wetting agent. Pure 99% silver anodes are used. Cathodes may be either brass or copper.

The following typical examples are given to illustrate the invention :

*Example 1*

Silver cyanide :	60 g/l
Potassium cyanide :	70 g/l
Potassium carbonate :	20 g/l
Antimony addition compound :	1 g/l
Wetting agent :	0.4 ml/l
pH	12-13
Temperature :	30°-35°C
Current density :	11 A/dm <sup>2</sup>
with vigorous stirring Thickness :	35 microns

*Example 2*

Silver cyanide :	50 g/l
Potassium cyanide :	90 g/l
Potassium carbonate :	30 g/l
Antimony addition compound :	0.5 g/l
Wetting agent :	0.2 ml/l
Potassium antimonyl tartrate :	5 g/l
pH	12.5-13.5
Temperature :	35°-40°C
Current density :	8 A/dm <sup>2</sup>
with vigorous stirring Thickness :	35 microns

The following are among the main advantages of the invention :

1. Needs no polishing or buffing.
2. Hard deposits which are scratch-resistant (Hardness : 175 kg/mm<sup>2</sup> at load 50 gms)
3. Works at high current density (11 A/dm<sup>2</sup>)

*Dated this 2nd day of May, 1972*

R. BHASKARPAI  
PATENTS OFFICER,  
COUNCIL OF SCIENTIFIC &  
INDUSTRIAL RESEARCH.

**THE PATENTS ACT 1970  
COMPLETE SPECIFICATION  
(SECTION 10)**

**“IMPROVEMENTS IN OR RELATING TO THE ELECTRO-DEPOSITION OF HIGH SPEED BRIGHT  
HARD SILVER”**

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN  
REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

*The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :*

*This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and Mrs. MALATHY PUSHPAVANAM, Senior Laboratory Assistant, both of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, both Indian citizens.*

This invention relates to improvements in or relating to the electrodeposition of high speed bright hard silver.

Hitherto it has been proposed to electrodeposit silver from cyanide baths containing various brighteners. They are :

- (i) carbon disulphide
- (ii) condensation products of carbon disulphide with acrolin or ketones
- (iii) ammonium thiosulphate
- (iv) compounds of selenium or antimony complexes with glycerol or triethanolamine.

**Price : TWO RUPEES**

The main drawback of these brighteners is that the operating current density is very low, namely 1-2 A/dm<sup>2</sup>. Moreover, they are able to produce only soft deposits though they are bright at low current densities.

So, the main object of this invention is to combine both high current density bright plating with hardness. We are successful in producing bright deposits at a current density of 10 A/dm<sup>2</sup>. The hardness value was 180 kg/mm<sup>2</sup>.

According to the present invention, there is provided a process for the electrodeposition of bright hard silver deposits on articles by silver plating from a silver cyanide bath containing turkey red oil and potassium antimonyl tartrate characterised in that an antimony reaction product prepared by reacting antimony trichloride, carbon disulphide, diethylamine in presence of petroleum ether the compounds being mixed at 0°C, then stirred for two hours at room temperature and then refluxed for two hours in a water bath with carbon disulphide and diethylamine is added to the bath whereby brightness and hardness is imparted to the deposit further characterised in that a bath of the following ingredients is prepared : silver cyanide : 50-80 g/l, potassium cyanide : 50-90 g/l, potassium carbonate : 5-30 g/l, antimony reaction product : 0.1-5 g/l, turkey red oil : 0.1-3 ml/l, potassium antimonyl tartrate : 1-5 g/l.

The proportion of the ingredients may be

Silver cyanide :	60-65 g/l ;
Potassium cyanide :	70-75 g/l
Potassium carbonate :	10-20 g/l
Antimony reaction product :	0.5-1 g/l
Turkey red oil :	0.4-0.6 ml/l
Potassium antimonyl tartrate :	0.5-1 g/l;

Silver cyanide (60 g/l), potassium cyanide (70 g/l) and potassium carbonate (20 g/l) may be used 2-5 g/l of potassium antimonyl tartrate may be present. The bath is operated with continuous circulation or stirring or cathode rod movement. A brilliant deposit is obtained at wide current density range from 0.5 to 10 A/dm<sup>2</sup>.

The conventional cyanide silver bath was used with the following composition :

Silver cyanide :	60 g/l
Potassium cyanide :	70 g/l
Potassium carbonate :	20 g/l

The silver cyanide was prepared from silver nitrate. The brightener used is antimony carbon disulphide-diethylamine condensation product. This product produces bright deposit. When measured with glass reflectance meter with silver coated glass as a standard, it comes upto 95-98%. At the same time, the effect of antimony improves the hardness. Such a condensation product which produces bright hard and high speed plating has not yet been tried in silver plating.

The preparation of the antimony condensation product : Carbon disulphide and diethylamine are mixed in petroleum ether solution at 0°C. Then antimony trichloride is added gradually with stir-

ring. All the compounds are added the equimolar ratio. After the reaction of the three compounds are over, the mixture is stirred for two hours at room temperature. The mixture is then refluxed for two hours in a water bath. So far, antimony is complexed only with glycerol or triethanolamine. This additive has the combined effect of both sulphur and antimony. 1 g/l of this additive is enough to produce bright deposits. This compound is soluble in rectified spirit or benzene. Turkey red oil is used as wetting agent. The concentration of the wetting agent should be 0.2 to 0.8 ml/l. The pH of the bath was maintained at 12-13. Room temperature is enough to produce good deposits. Vigorous stirring is required. The addition of potassium antimonyl tartrate was found to increase the brightness.

A thickness of 35 microns has been tried. The current efficiency is 100%. The bath works at a wide current density range from 0.5 A/dm<sup>2</sup> to 10 A/dm<sup>2</sup>.

The invented process produces bright silver deposits at a current density greater than the normal current densities. Moreover, the deposits are harder and the hardness is 180 kg/mm<sup>2</sup>. A new antimony reaction product is used which enhances both the hardness and brightness of the deposit.

#### Example 1

The plating was carried out in a three-litre scale with a pure 99.9% silver anodes. In order not to get burnt deposits at the edge, the anode current density was maintained in such a way that it did not exceed 2-2.5 A/dm<sup>2</sup>. The following compositions were used :

Silver cyanide :	60 g/l
Potassium cyanide :	70 g/l
Potassium carbonate :	20 g/l

The bath was stirred well with a mechanical stirrer near the cathode or to and fro motion of the cathode was applied. 1 g/l of the antimony carbon disulphide diethylamine reaction product dissolved in spirit was added. 0.2-0.8 ml/l turkey red oil was used. 2 g/l of potassium antimonyl tartrate was also added. The pH of the solution was 12-13. The bath worked at room temperature (30-32°C) itself. Cathode current density was 8-9 A/dm<sup>2</sup>.

#### Example 2

The plating was also carried out under these conditions :

Silver cyanide :	50 g/l
Potassium cyanide :	90 g/l
Potassium carbonate :	30 g/l
Antimony reaction product :	0.5 g/l
Wetting agent :	0.2 ml/l
Potassium antimonyl tartrate :	5 g/l
Cathode current density :	10 A/dm <sup>2</sup>
Temperature :	45°C

This composition of the brightener gives bright deposits even upto 10 A/dm<sup>2</sup> and the hardness is 180 kg/mm<sup>2</sup>. This increased hardness is required to produce increased abrasion and wear resistance. In the case of other additives, it is reported that the hardness of the deposits get reduced to the normal values, i.e. to the value of soft silver after a lapse of

time. But in our deposits, the hardness remains the same even up to five months. The combined effects of hardness, brightness and high speed plating are the main advantages of the invention. Since this bath works at a higher current density, the total operating time to get a specific thickness gets reduced which results in the increased output per day. The hardness gives high wear resistance to the deposit.

To sum up, we say that the conventional silver cyanide bath with the new brightener which we have developed gives a very bright, hard silver deposit and the bath also works at a wide current density range up to 10 A/dm<sup>2</sup>. This current density is greater than the normal current density using other additives.

#### Noteworthy Features

1. A process for the production of high speed, hard, bright silver deposit with a hardness of 180 kg/mm<sup>2</sup> in a bath containing silver cyanide, potassium cyanide, potassium carbonate, turkey red oil and an antimony additive compound.

2. The bath may contain silver cyanide : 60 g/l, potassium cyanide : 70 g/l, potassium carbonate : 20 g/l, turkey red oil : 1 ml/l and antimony additive compound : 1 g/l.

3. The preparation of a new antimony trichloride, carbon disulphide, diethylamine reaction product in presence of petroleum ether, the compounds being mixed at 0°C. then stirred for 2 hours at 30°C, and then refluxed for 2 hours in water bath.

#### WE CLAIM :—

1. A process for the electrodeposition of bright hard silver deposits on articles by silver plating from a silver cyanide bath containing turkey red oil and potassium antimonyl tartrate characterised in that an antimonyl reaction product prepared by reacting antimony trichloride, carbon disulphide, diethylamine in presence of petroleum ether the compounds being mixed at 0°C., then stirred for two hours at room

temperature and then refluxed for two hours in a water bath with carbon disulphide and diethylamine is added to the bath whereby brightness and hardness is imparted to the deposit further characterised in that a bath of the following ingredients is prepared: silver cyanide : 50-80 g/l, potassium cyanide : 50-90 g/l, potassium carbonate : 5-30 g/l, antimony reaction product : 0.1-5 g/l, turkey red oil : 0.1-3 ml/l, potassium antimonyl tartrate: 1-5 g/l.

2. A process as claimed in Claim 1 wherein the proportion of the ingredients is : silver cyanide : 60-65 g/l, potassium cyanide : 70-75 g/l, potassium carbonate 10-20 g/l, antimony reaction product : 0.5-1 g/l, turkey red oil : 0.4-0.6 ml/l, sodium antimonyl tartrate : 0.5-1 g/l.

3. A process as claimed in Claim 1 or 2 wherein are present silver cyanide : 60 g/l, potassium cyanide : 70 g/l and potassium carbonate : 20 g/l.

4. A process as claimed in any of the preceding Claims wherein 2-5 g/l of potassium antimonyl tartrate is present.

5. A process as claimed in any of the preceding Claims wherein the bath is operated with continuous circulation of stirring or cathode rod movement.

6. A process as claimed in any of the preceding Claims wherein a brilliant deposit is obtained at a wide current density range from 0.5 to 10 A/dm<sup>2</sup>.

7. A process for the electrodeposition of bright hard silver deposits on articles substantially as hereinbefore described.

*Dated this 19th day of June, 1973.*

Sd/-

ASSTT. PATENTS OFFICER,  
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