Bulletin of Electrochemistry 16 (3) March 2000, pp 136-139

0256-1654/2000/$ 3-50

ELECTRODEPOSITION OF SILVER FROM LOW CONCENTRATED CYANIDE ELECTROLYTES

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[Received: 4 May 1999 Accepted: 16 July 1999]

Silver is used as a deposit for decorative and aesthetic appeal on jewellery, hollowers, flatware etc. It is also used in engineering industries for various reasons like high heat and electrical conductivity and good antigalling property on bearings, electronic components like socket contacts, slip rings, switch gear and wave guides for radars etc. Usually, silver is electroplated from cyanide based electrolytes and these solutions contain higher concentrations of both silver and cyanide causing heavy pollution due to effluents. Also, silver being costly, it was considered worthwhile to investigate the feasibility of evolving a bath formula with low concentration of silver as well as cyanide with equivalent characteristic features to the concentrated baths. Experiments were carried out with different concentrations of silver and cyanide and the results are compared with that of conventional cyanide based baths.

Keywords: Sockets, contacts, slip rings, switch gear, wave guides for radars.

INTRODUCTION

Most of the decorative silver plating applications concern with electroplating of small household items, jewellery etc. Silver plating is used in various engineering industries like aircrafts as bearing materials, as intermediate materials for heavy duty bearings to prevent galling or seizing of metal surfaces under light loads etc. Its applications as hot gas seals in rocket engines, is yet another significant application in spacecrafts.

Electrical and electronic industries are the foremost now to apply silver on various components because of its outstanding electrical conductivity. Sockets, contacts, slip rings, switch gear, wave guide for radars etc are some of the components in electronics as using silver as a coating for better electrical and electronic conductivity.

Such a versatile metal was first electroplated from cyanide bath by Elkington [1-3]. Plating from cyanide electrolytes has not changed much even today [4]. The exact composition of the plating bath depends on the purpose for which plating is done. It varies from the very low metal concentration strike bath to the very high concentration high speed bath [5,6].

The major research in silver plating has been directed towards the use of various additives and brighteners in cyanide plating bath [7,8] and attempts to introduce non-cyanide systems [9-10]. The presently reported work on low silver low cyanide solutions was undertaken with a view of developing less polluting and less costly plating baths.

EXPERIMENTAL

The experiments were carried out in triplicate with copper specimens of 2.5 x 7.5 x 0.1 cm size. The pretreatment conditions adopted were as follows.

1. Degreasing with trichloroethylene
2. Alkaline cleaning using the following solution

Composition and operating conditions:

Sodium carbonate	20 g/l
Sodium hydroxide	7 g/l
Trisodium orthophosphate	9 g/l
Temperature	353 K

Duration	2 minutes
Current density	3 A/dm^2 (cathodic)
Anode	Stainless steel

3. Washing with running water
4. Dipping in 5% H_2SO_4 for 15 seconds
5. Washing with running water
6. Rinsing with distilled water

Hull cell experiments

Hull cell studies were carried out using different silver cyanide compositions to select the compositions for further studies like current efficiency. For Hull cell studies polished copper cathodes of size 10 x 7.5 x 2.5 cm were used and experiments carried out at room temperature by passing a cell current of 0.5 Amp for 5 minutes. The desirable current density (A/dm^2) was obtained by using the formula

$$C.D. = C \times (5.10 - 5.24 \log L)$$

where C = total current passing through the cell and L = the distance in cm of the point of interest from nearer end of the cathode.

Current efficiency studies

Current efficiency studies were carried out with two selected compositions using an assembly consisting of a soluble silver anode and copper cathode of equal size (5 x 2.5 x 0.1 cm) after usual pre-treatments. The specimens were weighed before and after electrodeposition cathodic current efficiency (CCE) was calculated as below.

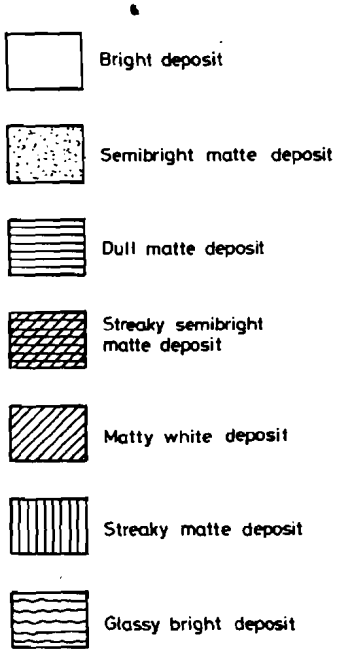

Fig. 1: Codes for Hull cell pattern of deposits

$$CCE\ (\%) = \frac{\text{Amount of metal deposited} \times 100}{\text{Amount of metal be deposited theoretically}}$$

Studies on characteristics of deposits — Adhesion

The bend test was carried out in order to qualitatively evaluate the adhesion of silver deposits. The plated samples from different electrolytes were bent at 180° which was repeated upto the point of fracture of the base metal.

Microhardness

The microhardness of electrodeposits of silver, obtained from different silver plating electrolytes at different conditions of current density were determined using a Russian made PMT-3 microscope hardness meter.

RESULTS AND DISCUSSION

Results of Hull cell studies

Fig. 1 to 4 relate to the patterns obtained in Hull cell studies. Fig. 2 corresponds to the patterns for the silver cyanide plating electrolyte for varying concentration of silver from 5 to 20 g/l at a fixed concentration of potassium cyanide namely 45 g/l at a cell current of 0.5 A for 5 minutes at 303 K. Fig. 3 shows the Hull cell pattern obtained from the bath containing silver (as cyanide) at 5 g/l with varying concentrations of KCN ranging from 15 to 100 g/l and at a cell current of 0.5 A at 303 K for a duration of 5 minutes. Fig. 4 shows the patterns obtained in the Hull cell experiments for the bath containing silver (as cyanide) at 15 g/l with potassium cyanide of varying concentrations from 15-100 g/l carried out at 303 K at a cell current of 0.5 A and for a duration of 5 minutes.

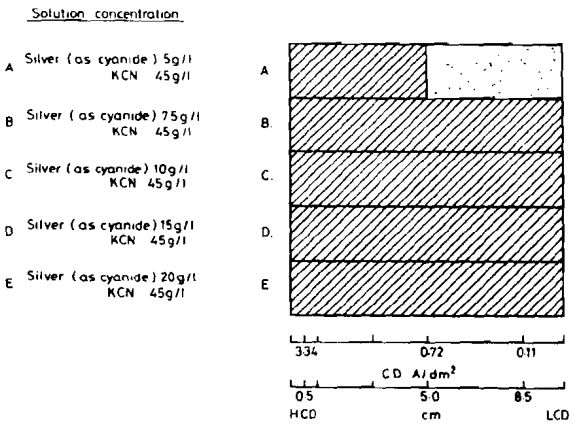

Fig. 2: Effect of varying concentration of silver in the cyanide bath solution. Cell current: 0.5 A. Time: 5 nts, Temp: 303 K

Effect of varying concentration of silver

From Fig. 2 it is clear that a semibright silver deposit is obtained over a current density range of 0.1-0.72 A/dm^2 from a bath containing silver (as cyanide) 5 g/l and KCN 45 g/l. Beyond this range upto 3.34 A/dm^2 the deposit is matty white. In the other silver concentrations namely 7.5-15 g/l matty white deposits are obtained over the entire current density range.

Effect of varying concentration of cyanide in the silver bath I

The patterns 3A to 3E indicate the possibility of obtaining a bright silver deposit for the current density range upto 0.33 A/dm^2 in the case of solutions containing silver as cyanide 5 g/l and KCN 25 g/l (Fig. 3) and also in the case of solution containing silver 5 g/l and KCN 50 g/l in which the current density range for the bright deposits get slightly reduced 0.18 A/dm^2 and below (Fig. 3C). In all the other cases, there are no indications for obtaining bright deposits.

Effect of varying concentrations of cyanide in the silver cyanide bath II

From Fig. 4 it is seen that a semibright deposit of silver is obtained in the case of the bath containing silver (as cyanide) 15 g/l and KCN 15 g/l over a current density range of 0.1 A/dm^2 (Fig. 4A). In the other baths with KCN concentration ranging from 25-100 g/l with the fixed concentration of silver as cyanide (15 g/l) the deposit is matty white over the entire current density range.

From the above Hull cell studies the following two compositions were selected for further studies.

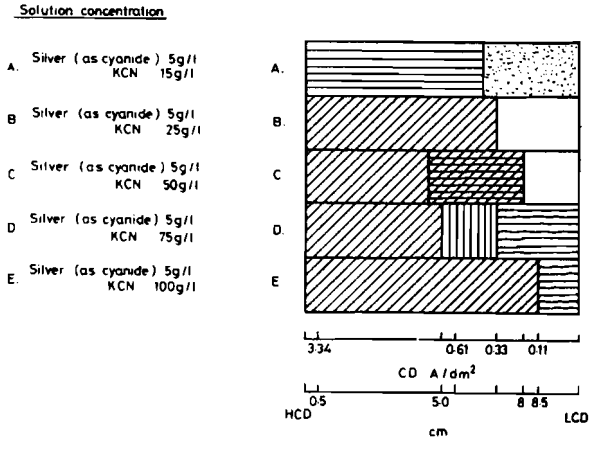

Fig. 3: Effect of varying concentration of cyanide in the silver cyanide bath I. Cell current: 0.5 A, Time: 5 mts, Temp: 303 K

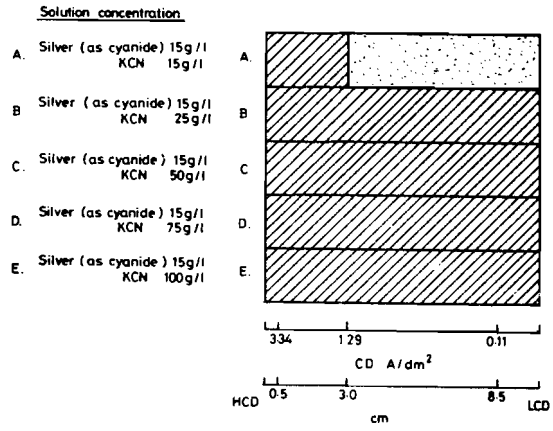

Fig. 4: Effect of varying concentration of cyanide in the silver cyanide bath II. Cell current: 0.5 A, Time: 5 mts, Temp: 303 K

Solution I

Silver (as cyanide)	5 g/l
Potassium cyanide	25 g/l

Solution

Silver (as cyanide)	15 g/l
Potassium cyanide	50 g/l

Results of current efficiency studies

From Table I, it may be noticed that the current efficiency values are varying from 50.7% to 36.4% for different current densities studied namely 0.25-0.75 A/dm^2. In general the current efficiency value decreases with increasing current density. Rate of build up shows an increase with increase in current density. Table II contains the results of studies on current efficiency obtained from bath containing silver (as cyanide) 15 g/l and KCN 50 g/l. It can be seen that the

TABLE I: Results on the studies of current efficiency with Bath I

Bath composition (g/l)		Current density (A/dm^2)	Current efficiency (%)	Rate of build up (μm/hr)
Silver (as cyanide):	5			
Potassium cyanide:	25	0.25	50.7	4.86
-do-		0.50	41.9	8.04
-do-		0.75	36.4	10.44

TABLE II: Results on the studies of current efficiency with Bath II

Bath composition (g/l)		Current density (A/dm^2)	Current efficiency (%)	Rate of build up (μm/hr)
Silver (as cyanide):	15			
Potassium cyanide:	50	0.25	96.0	9.18
-do-		0.50	65.1	12.50
-do-		0.75	58.1	16.72

current efficiency values are regularly decreasing with increasing current density. However, rate of build up increases with current density.

A comparison of Table I and II shows that the current efficiency is higher for bath containing 15 g/l silver as cyanide complex. At 0.25 A/dm^2 a current efficiency of 98% is obtained which decreases to 58% at 0.75 A/dm^2.

Nature of deposits

It was observed that the deposits obtained from the two baths under different conditions of current densities are uniformly matty white indicating good scope of such bath containing low concentration of silver as well as cyanide.

Deposit adhesion

The deposits obtained under conditions of different current densities (the thickness varying from 1.25 to 13.18 μm, when subjected to bend test, no peeling or blistering was observed on any of these deposits, thereby showing that the deposits are well adherent.

Microhardness of deposits

Table III contains the microhardness values of silver deposits obtained from the baths studied. In general, the microhardness values of the deposits from bath I and bath II are sufficiently harder than wrought silver (25 VHN) and comparable with deposits from conventional cyanide baths having higher concentration of silver.

CONCLUSION

From the investigations carried out, the following compositions of silver cyanide based electrolyte are found to be suitable for producing acceptable matty white and adherent deposits. The optimized compositions and the conditions are as follows:

Bath I

Silver (as cyanide)	5 g/l
Potassium cyanide	25 g/l
Temperature	303 K
Anode	Pure silver
Anode to cathode area	1:1
Current density	0.25-0.5 A/dm^2

TABLE III: Microhardness of silver deposits

Bath composition (g/l)		Current density (A/dm^2)	Microhardness (Kg/mm^2) VHN
Silver (as cyanide):	5		
Potassium cyanide:	50	0.50	44
-do-		0.75	55
Silver (as cyanide):	15		
Potassium cyanide:	50	0.25	60
-do-		0.50	62
-do-		0.75	68

Bath II

Silver (as cyanide)	15 g/l
Potassium cyanide	50 g/l
Temperature	303 K
Anode	Pure silver
Anode to cathode area	1:1
Current density	0.25-0.75 A/dm^2

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