

ELECTRODEPOSITION OF SILVER FROM THE IODIDE BATH*

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ABSTRACT

Silver has been electrodeposited on copper from a complex iodide solution. The deposits are white, dense and adherent, and the bath is comparable to the cyanide bath (without brightener) in respect of quality of deposit, electrode efficiency, current density and throwing power. The optimum conditions are: silver 20–40 g./L., iodide 400–600 g./L., c.d. 0.2–1.6 amp./dm.² and temperature 26–60° C. Ammonium sulfate and sodium thiosulfate as additions give semi-bright deposits.

INTRODUCTION

Silver is commonly electrodeposited from the cyanide bath because of the many advantages it possesses over other baths. But the bath suffers from some important disadvantages, namely, its poisonous nature and instability. In view of this, several attempts have been made to find substitutes for the cyanide bath used in industrial electroplating. A wide range of plating solutions have been tried in this connection: nitrate, sulfate, fluoride, fluoborate, ethyl sulfonate, thiosulfate, thiocyanate, thiourea, sulfate. The iodide bath has been studied by Schlotter,^{1, 2} Fleetwood and Yntema,³ Alpern and Toporek⁴ and Levin.⁵

Investigations have been started in this laboratory on the electrodeposition of a number of metals and alloys from solutions free from cyanide. The electrodeposition of silver and silver-lead alloy from the iodide bath has been briefly reported in preliminary notes by Rama Char and co-workers.^{6, 7, 8} The present paper gives a detailed account of the work on the electrodeposition of silver from the iodide bath which is simpler in composition than those attempted by the previous workers.

The Plating Solution

The solution was prepared by dissolving freshly precipitated silver iodide in a solution of alkali iodide: $\text{AgI} + \text{KI} \rightarrow \text{K}(\text{AgI}_2)$. The solubility

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of silver iodide in potassium iodide solution increases with increase in the concentration of the latter. Because of the high solubility of alkali iodides in water, it is possible to maintain a fairly high concentration of silver in the plating bath. Keeping in view the cost, drag out losses, throwing power and the necessity for a high free iodide content, it is advisable to maintain the metal content in the range 20 to 40 g./L.

An alkali iodide concentration of 400 to 600 g./L. is suitable and provides the necessary free iodide for good anode corrosion. Increase in the free iodide concentration helps in keeping down the silver ion concentration, increases the conductivity and cathode polarization, and improves the throwing power of the solution.

EXPERIMENTAL

The chemicals used for the plating solutions were of the C.P. variety: B.D.H., Johnson & Sons, Merck. Fresh solutions were used for each experiment.

The cathodes were cut from a 1/32" copper sheet. Each cathode was 1" × 3" and submerged to a depth of 2" in the plating solution, the electrode surface area submerged being 4".² Two anodes of pure silver 1/8" thick of the same dimensions as the cathode were used and placed symmetrically at a distance of 1" on either side of the cathode.

The copper cathode was first scrubbed well with emery paper and then given a dip and a scouring in an alkaline solution of the following composition, to remove the grease: sodium carbonate 40 g./L., trisodium phosphate 13 g./L., caustic soda 13 g./L., sodium silicate 6.25 g./L. It was then rinsed in running water and dipped into an acid mixture in order to remove oxide scales: sulfuric acid (Sp. gr. 1.84) 380 ml., nitric acid (Sp. gr. 1.38) 72 ml., hydrochloric acid (Sp. gr. 1.17) 5 ml., water 400 ml. After another rinse in water and alcohol, the cathode was dried and used for deposition.

The plating experiments were carried out in 250 ml. beakers containing 200 ml. of the solution. The electrodes were freely suspended from metallic hooks attached to brass terminals located on a wooden bar. The bar was capable of being raised, lowered or clamped in any convenient position above the plating bath. The beaker containing the plating solution was kept immersed in an electrical thermostat whose temperature could be adjusted to $\pm 1^\circ\text{C}$. When necessary, a mechanical stirrer was used to agitate the solution. The current was drawn from a 6-volt battery through a rheostat and a milliammeter. The bath voltage was measured with a voltmeter connected across the electrode terminals and generally stood between

0.1 to 0.3 volts. The time of deposition was 15 minutes. The electrodes were weighed before and after each experiment and the electrode efficiencies calculated.

The pH of the solution was determined with the glass electrode and Leeds and Northrup pH meter. The conductivity was measured by the Kohlrausch method, an induction coil serving as the source of alternating current and a head-phone as the null point detector. The direct method of Haring⁹ was employed for measuring the cathode polarization. The values were reproducible to 0.005 volts.

The experiments were carried out with plating solutions containing potassium as well as sodium iodide but the results for sodium iodide have been recorded here only in the form of a comparative table. The temperature was 26° C.

EXPERIMENTAL RESULTS

Silver ion concentration

The silver ion concentration was determined by measuring the static potential of silver in the plating solution against a saturated calomel reference electrode. It was of the order of 10^{-18} N for solutions of the composition: Ag 20, 30, 40 g./L., KI 500, 600 g./L. Fleetwood and Yntema³ obtained a value of 10^{-17} N for a bath containing silver, sodium iodide and citric acid, and Levin⁵ a value of 10^{-16} N for the plating composition: Silver sulfate, ammonia, potassium iodide and sodium pyrophosphate. In the cyanide bath, the silver ion concentration ranges from 10^{-17} to 10^{-20} N. The value of the instability constant $K = (\text{Ag}^+)/(\text{I}^-)^2/(\text{AgI}_2^-)$ of the silver iodide complex was of the order of 10^{-16} as against 10^{-15} reported by Fleetwood and Yntema, and 10^{-22} for the argento-cyanide complex ion. As in the cyanide bath, immersion deposition was minimised in the iodide bath due to complex formation which reduced the metal ion concentration.

Electrodeposition

Variation of concentration.—The electrodeposition was carried out with various concentrations of iodide and silver and the results obtained are given in Table I.

The cathode efficiency was practically 100% till the limiting c.d. (*i.e.*, the maximum value up to which deposits with the desired properties can be obtained at 100% efficiency under a given set of conditions) was reached beyond which it fell and the deposits were burnt. Variation in the iodide content, keeping silver content constant, had practically no effect on the electrode efficiency, quality of deposit and the limiting c.d. Increase in the

TABLE I

Ag g./L.	KI g./L.	c.d. amp./dm. ²	Efficiency % Cathode	Efficiency % Anode	Appearance of electrodeposit
20	400	0.2	100	102	Good (smooth, white, adherent)
		0.4	100	102	
		0.6	100	100	”
		0.8	88	101	”
		1.0	46	100	Slightly granular along edges Grey, burnt
20	500	0.2	100	102	Good
		0.4	100	102	”
		0.6	100	102	”
		0.8	89	100	Slightly granular
		1.0	45	100	Grey, burnt
20	600	0.2	100	102	Good
		0.4	100	102	”
		0.6	100	102	”
		0.8	90	102	Traces of granulation
		1.0	49	100	Grey, burnt
25	600	0.6	100	102	Good
		0.8	100	102	”
		1.0	100	101	”
		1.2	63	100	Grey, burnt
30	600	0.6	100	102	Good
		0.8	100	102	”
		1.0	100	101	”
		1.2	100	100	”
		1.4	74	100	Slightly granular
		1.6	53	96	Grey, burnt
40	600	0.8	100	100	Good
		1.4	100	100	”
		1.6	92	96	Slightly granular
		1.8	51	95	Grey, burnt

silver content, keeping iodide constant, increased the limiting c.d. Deposits which were smooth, white, thick (10^{-3} in.), adherent and readily polishable were obtained over a wide c.d. range from 0.2 to 1.4 amp./dm.² They were as good as those obtained from the cyanide bath (without brightener). The adherence of the deposit to the basis metal as found by bending and breaking tests was excellent. The anode corrosion was good in all the baths, the anode efficiency values being slightly higher than 100% in some cases. Satisfactory deposits were also obtained on copper flashed steel cathodes.

The deposits on copper cathodes were analysed and the silver content was found to be 100%.

Some experiments were carried out by using different salts of silver-iodide, nitrate and sulfate, for preparing the bath (Ag 20 g./L., KI 600 g./L.). There was no difference in the performance of the bath freshly prepared or aged for 4 months, except with the nitrate. In the latter case, the cathode efficiency was slightly less and the bath tended to decompose on standing.

Temperature.—The iodide bath can be safely worked at higher temperatures, if desired. Experiments performed at 40 and 60° C. with baths of the composition: Ag 20, 30 g./L., KI 600 g./L. showed that there was no deterioration in the cathode efficiency or the quality of the deposit. Increase in temperature improved anode corrosion and raised the limiting c.d. to 1.6 amp./dm.² A low concentration bath can, therefore, be used at higher plating speeds.

Agitation.—It was found that, in the bath of the composition: Ag 20 g./L., KI 600 g./L., agitation increased the limiting current density from 0.6 to 1.4 amp./dm.²

Addition agents.—The iodide bath appears to be satisfactory from a number of considerations. It does not, however, give bright deposits as does the silver cyanide bath containing carbon disulfide as brightener. A study was made of the effect of the addition to the bath: Ag 20 g./L., KI 500 g./L., of a large number of substances (concentrations ranging from 1 to 60 g./L.) to see whether any beneficial effects could be obtained: potassium nitrate, sulfate, carbonate, thiocyanate, hydroxide; ammonium hydroxide, carbonate, nitrate, sulfamate, thiocyanate; rochelle salt, sodium thiosulfate, barium chloride, glycine; oxalic, lactic, mandelic, tartaric, citric, succinic and sulfuric acids; di- and tri-ethanolamine; thiourea, methylene blue, carbon disulfide. To the bath containing Ag 20 g./L., NaI 500 g./L., which also gives good quality deposits, the following substances were added: sodium nitrate, sulfate, pyrophosphate, borate, acetate, ethyl xanthate, isopropyl xanthate, thiosulfate; ferrous sulfate, selenium oxide, citric acid.

The observed results can be summarized by classifying the addition agents in a general way under three categories with respect to their effect on the electrodeposition: (a) Improvement: ammonium sulfamate (5 and 20 g./L.) and sodium thiosulfate (1 g./L.) gave semi-bright deposits at 0.6 amp./dm.², but the brightness was not comparable to that of deposits from the cyanide bath using carbon disulfide; (b) Lowering of cathode efficiency and/or deterioration in the quality of the deposit: oxalic, citric and succinic acids, ammonium nitrate and (c) no change: the rest of the additions.

Conductivity, cathode polarization and throwing power.—Table II gives the conductivity, cathode polarization (range) and throwing power of the bath. The polarization values give a general idea of the variations but should not be considered as very accurate in view of the difficulties in reproducibility. The throwing power of the bath was good. Satisfactory deposits were obtained on the reverse side of the cathode when only one anode was used and the plating solution threw well into the recesses of irregularly shaped cathodes. The values given below were calculated according to the equation of Schlotter-Korpiun.¹⁰

TABLE II

Ag g./L.	KI g./L.	Sp. conductivity mhos/cm. ³	Cathode polarization range volts (c.d. 0.4–1.4 amp./dm. ²)	Throwing power at 6×10^{-3} amp./cm. ²
20	400	0.2569	0.025–0.110	2.71
20	500	0.2957		3.46
20	600	0.3362		4.08
30	600	0.3147		2.57
40	600	0.3114		

An increase in the metal concentration decreased the conductivity, polarization (individual values not given in table) and throwing power, whereas an increase in iodide content increased all these factors. The cathode polarization was very low and burning occurred at about 0.1 volt. Addition of ammonium sulfamate and sodium thiosulfate had little effect on the conductivity, polarization and throwing power.

The throwing power was the same as that for the cyanide bath (composition in Table III) where it is of the order of 3.7. It was also calculated from the equation of Gardam¹¹ by substituting, as an approximation, the inter-electrode distance for l_2 in the equation. At a c.d. of 6.0×10^{-3} amp./cm.² (where the cathode polarization—log c.d. relationship was roughly linear) the throwing power for the iodide bath (Ag 20 g./L., KI 600 g./L.) was 61% as against 67% (experimental) for the cyanide bath.

Comparison between iodide and cyanide baths.—The following table gives a relative idea of the performance of the iodide and cyanide baths for the electrodeposition of silver.

TABLE III

Composition	Cathode efficiency: 100%			Quality of deposit: Good.
	Iodide Bath	Iodide Bath	Cyanide Bath	
	Ag 20 g./L. NaI 672 g./L.	Ag 20 g./L. KI 600 g./L.	Ag 20 g./L. Total KCN 45.8 g./L. K ₂ CO ₃ 22 g./L.	
(Ag ⁺) g. ion/L.	.. 3.16 × 10 ⁻¹⁸	4.57 × 10 ⁻¹⁸	1.10 × 10 ⁻²⁰	
Sp. conductivity mhos/cm. ³	0.2328	0.3362	0.0538	
c.d. range (stirred) amp./dm. ²	.. 0.2-1.4	0.2-1.4		
„ (unstirred)	.. 0.2-0.4	0.2-0.6	0.2-0.6	
Cathode polarization volts (0.4-1.0 amp./dm. ²)	0.045-0.110 (0.4-0.8 amp./dm. ²)	0.045-0.105	0.200-0.900	
Bath voltage volts	.. 0.10-0.25	0.10-0.25	0.40-1.40	
Throwing power, Schlotter-Korpiun at 6 × 10 ⁻³ amp./cm. ²	} 3.33	4.08	3.69	

The potassium iodide bath has a higher conductivity and a slightly higher c.d. (unstirred) and throwing power than the sodium iodide bath. As regards the quality of the deposit, there is no difference. Similar observations have been made in the cyanide bath.

The most striking points of difference between the potassium iodide and the cyanide baths are in regard to conductivity and cathode polarization. Polarization in the iodide bath is very small compared with that in the cyanide bath, but the conductivity is much greater and the bath voltage low. It is as good as the cyanide bath in respect of c.d. range for good plating, cathode efficiency, quality of deposits and throwing power.

DISCUSSION

The electrodeposition of silver from the complex potassium or sodium silver iodide bath gives smooth, fine-grained deposits and the silver ion concentration is low. The simplicity in composition together with the 100% current efficiencies facilitate the control of the bath.

The previous workers on the silver iodide bath have employed some additions in order to obtain satisfactory deposits. Schlotter^{1, 2} used halide acids and colloids like gelatin and the deposits were white, yellow or golden

yellow in colour depending upon the amount of the iodine contamination. Fleetwood and Yntema³ added citric and tartaric acids, the operating conditions being 1.0 amp./dm.² (stirring), 25° C., cathode current efficiency less than 90% and the deposits creamwhite to yellow. Alpern and Toporek⁴ used acids like citric, acetic, maleic, sulfuric and hydrochloric and stated that the stability of the complex increases and the metal ion concentration decreases as the pH is lowered (3.0 to 0.65). Further, they reported that there is an improvement in the cathode efficiency and the quality of the deposit at low pH. The maximum value of the cathode efficiency was 95% (stirring) at 23° C., pH 1.7, 1 to 1.8 amp./dm.² The experiments of Levin⁵ were conducted at a pH of 8.2 by the addition of ammonia and sodium pyrophosphate, 0.36 (17° C.) to 1.18 (60° C.) amp./dm.², 100% efficiency.

The addition of the substances named above did not effect any improvement in the present iodide bath which by itself gave good quality deposits. It is not advisable to use acids as they have a tendency to decompose the bath. E.M.F. measurements showed that the silver ion concentration and the instability constant of the complex do not change appreciably when the pH was varied from 8.15 (about the value at which the bath is worked) to 0.75, 1.3, 1.55, 12.85, 13.15. There appeared to be no definite relationship between pH on the one hand and the cathode efficiency or quality of the deposit on the other. A low pH was not necessarily the criterion. The effect of the addition of various substances to the bath (in this investigation) was of a specific character.

Smooth, fine-grained deposits are generally expected from complex salt baths with a low metal ion concentration. The cathode polarization during deposition from such solutions is high and the throwing power is good. The iodide bath has a low silver ion concentration and gives such deposits but the cathode polarization is extremely low and the throwing power is good. It appears that polarization may not have much significance in the iodide bath.

SUMMARY

1. The iodide bath for silver gives good deposits on copper at 100% cathode and anode efficiencies over a wide range of experimental conditions: Ag 20–40 g./L., KI or NaI 400–600 g./L., c.d. 0.2–1.6 amp./dm.², temp. 26–60° C.

2. The bath is simple and stable.

3. The conductivity of the bath is very high and the cathode polarization low as compared with the cyanide bath.

4. The current density range and throwing power of the two baths are of the same order.

5. Ammonium sulfamate and sodium thiosulfate act as semi-brighteners.

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