ELECTRODEPOSITION OF COPPER FROM THE DIETHANOLAMINE BATH*

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Received May 25, 1953

Copper has been electrodeposited on steel by using a complex copper diethanolamine solution. This bath does not deposit copper by immersion. The inclusion of rochelle salt improves the bath performance. The optimum conditions for satisfactory deposition are: copper oxalate 45 g./L., diethanolamine 68ml./L., rochelle salt 45 g./L., c.d. 1·2–1·6 amp/dm^2, pH 9·0 and temperature 24°C. The addition of sodium sulfate has some beneficial effect.

INTRODUCTION

The electrodeposition of copper from the mono-, di- and tri-ethanolamine baths has been briefly reported in preliminary notes by Rama Char and Shivaraman[1, 2] and the detailed work on the monoethanolamine bath presented in a recent communication.[3] Diethanolamine has been used for copper plating by Brockman and Whitley.[4] This paper gives the results on the deposition of copper from diethanolamine solutions. Electrodeposition from the triethanolamine bath will be reported in a subsequent paper.

THE PLATING BATH

When 1·5 ml. of diethanolamine was added to 1 g. of copper oxalate suspended in water, a clear blue solution was obtained due to complex formation. The copper oxalate: amine ratio remained the same over a wide range of concentration. The concentration of copper oxalate in the bath was in the range 10–120 g./L. (4–48 g./L. of copper).

EXPERIMENTAL

The diethanolamine (technical) was a product of Carbide and Carbon Chemical Corporation and the other chemicals were made by B.D.H. or Merck. The amine had a specific gravity of 1·093 at 24° C. and a pH of 12·7. It boiled, at 274° C. and had no smell of free ammonia. Mild steel cathodes and copper anodes were used. The plating time was 2·5 mins.

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* This paper is based on part of the thesis submitted by N. B Shivaraman for the Associateship of the Indian Institute of Science.

and the temperature 24° C. The experimental details were the same as described before.[3, 5]

EXPERIMENTAL RESULTS

Copper ion concentration.—The copper (cupric) ion concentration in the plating solutions was of the order of 10^{-10} N. The addition of 45 g./L. rochelle salt to the bath of the composition 45 g./L., copper oxalate, 68 ml./L., amine decreased the metal ion concentration from $7\cdot67 \times 10^{-10}$ to $1\cdot55 \times 10^{-11}$ N. The solutions used did not deposit copper on steel by immersion due to the low metal ion concentration.

Electrodeposition

Variation of concentration.—Electroplating was carried out over a wide range of concentration and c.d. and the results are recorded in Table I.

TABLE I. *pH:* 8·70–8·75

Copper oxalate g./L.	Amine ml./L.	c.d. amp/dm ^{2}	Bath voltage volts	Cathode efficiency %	Appearance of electrodeposit
20	30	0·4	2·2	109	Dull
		0·6	3·2	98	Fairly bright
		0·8	4·0	80	Burnt
30	45	0·4	2·1	118	Dull
		0·8	4·0	92	Fairly bright
		1·2	8·2	90	Edges rough
		1·6	9·8	88	Burnt
45	68	1·2	4·6	106	Dull
		1·6	5·0	100	Bright
		2·0	6·8	90	”
		2·4	8·2	91	Burnt
60	90	1·6	4·5	97	Dull
		2·4	6·7	92	Bright
		3·2	8·8	83	Burnt
75	113	1·6	4·3	90	Dull
		2·4	6·3	90	Bright
		2·8	7·8	92	”
		3·6	10·0	90	Burnt
90	135	1·6	3·9	98	Dull
		3·2	5·9	90	Bright
		4·8	8·8	80	Edges rough
120	180	2·4	4·3	70	Dull
		3·6	5·9	86	Bright
		4·8	8·1	88	”
		6·0	10·0	85	Edges rough

The cathode efficiency varied from 86–100% in the bright c.d. range 0·6–4·8 amp./dm.^{2} In a few cases, values over 100% have been obtained at low c.d. and in the dull plating range, probably due to deposition of cuprous copper. The deposits were quite adherent but treed at c.d. beyond 4·8 amp./dm.^{2} Higher metal concentrations enabled the use of higher c.d., the optimum bath composition being copper oxalate 45 g./L. and amine 68 ml./L. The bath voltage was rather high and the anode corrosion was good. Addition of 10–70 ml./L. of excess amine to the optimum concentration bath did not improve the conditions of deposition.

Rochelle salt bath.—The inclusion of rochelle salt (optimum concentration 45 g./L.) in the bath improved its performance though not to the same extent as in the deposition of copper from the monoethanolamine bath (Rama Char and Shivaraman[3]). Rochelle salt facilitated anode corrosion; reduced the bath voltage and minimized the fluctuations in voltage and current; increased the conductivity, cathode polarization and throwing power; reduced the copper ion concentration; and gave better quality deposits by eliminating treeing and increasing the brightness. The c.d. range and cathode efficiency remained practically the same. Table II gives the results obtained:

TABLE II. *pH*: 8·85–9·20

Copper oxalate g./L.	Amine ml./L.	Rochelle salt g./L.	c.d. amp./dm.^{2}	Bath voltage volts	Cathode efficiency %	Appearance of electrodeposit
45	68	15	0·8	2·3	98	Dull
			1·2	3·3	99	Bright
			1·6	4·3	97	”
			2·0	6·2	96	Edges rough
45	68	30	0·8	2·1	90	Dull
			1·2	2·5	97	Bright
			1·6	3·5	96	Edges rough
			2·0	4·1	91	”
45	68	45	0·8	2·1	88	Dull
			1·2	2·5	90	Bright
			1·6	3·3	94	”
			2·0	3·7	98	Edges rough
45	68	60	0·8	2·1	98	Dull
			1·2	2·5	100	Bright
			1·6	2·9	95	Edges rough
			2·0	3·5	90	Burnt
45	68	75	0·8	2·0	91	Dull
			1·2	2·5	100	Bright
			1·6	2·8	96	”
			2·0	3·4	94	Burnt

Temperature.—Higher temperatures were not conducive to the good working of the bath with and without rochelle salt, resembling the mono-ethanolamine bath in this respect.

Addition Agents.—In order to see whether the rochelle salt-amine bath could be improved, some inorganic salts were added to the optimum concentration bath 45 : 68 : 45 (Table II). Sodium sulfate (5–15 g./L.) increased the brightness of the deposit and lowered the bath voltage. With the addition of 10 g./L. of this salt, the cathode efficiency was 90–91% in the c.d. range 1·2–1·8 amp./dm.^{2}, the voltage being 2·1–2·6 volts. Potassium and ammonium sulfates were not as beneficial. Ammonium nitrate increased the c.d. range but decreased the cathode efficiency. With ammonium chloride there was a blackening of the anodes and the deposits were unsatisfactory.

Conductivity, cathode polarization and throwing power.—Table III gives the conductivity, cathode polarization (range) and throwing power of the bath.

TABLE III. *pH*: 8·7–9·0

Copper oxalate g./L.	Amine ml./L.	Rochelle salt g./L.	Sodium sulfate g./L.	Sp. Conductivity mhos./cm.^{3}	Cathode Polarisation range, volts (c.d. 0·8–2·0 amp./dm.^{2})	Throwing Power Schlotter-Korpiun[3] at $1 \cdot 6 \times 10^{-2}$ amp./cm.^{2}
45	68	..	..	0·0097	0·20–0·65	1·37
45	68	45	..	0·0272	0·38–0·88	2·45
45	68	45	10	0·0330	0·42–0·87	2·63

Rochelle salt increased the conductivity, polarization (individual values not given in table) and throwing power; these factors were further increased to a slight extent by the addition of sodium sulfate. The throwing power of the bath was satisfactory. Calculations from the equation of Gardam[3] gave values for the throwing power in the range 15–36% at a c.d. of $1 \cdot 2 \times 10^{-2}$ amp./cm.^{2}, as against the normal value of 30–40% for the cyanide bath.

DISCUSSION

The electrodeposition of copper from the complex diethanolamine bath yields smooth, fine-grained and bright deposits on steel. There is no immersion deposition due to the low copper ion concentration. The high cathode efficiency, comparative stability and ability for good working at the room temperature, are some of the advantages of this bath over the cyanide. Brockman and Whitley[4] used the plating composition: copper sulfate, sodium oxalate and diethanolamine, and obtained deposits which were adherent and bright but rougher than those from the triethanolamine bath. Investigations conducted in this laboratory have, however, shown that the performance of the diethanolamine bath is quite satisfactory as compared with that of the mono- and tri-ethanolamine baths.[1, 3, 6]

Rochelle salt improves the performance of the diethanolamine bath and the beneficial effects are somewhat on the lines obtained in the rochelle salt-copper cyanide bath.[7] A decrease in the metal ion concentration on addition of this salt is accompanied by the formation of brighter deposits. The effect of the addition of other ions is of a specific character. Small variations in pH are not of significance.

Complex salt plating baths generally give fine-grained and bright deposits due to the low metal ion concentration. The cathode polarization and throwing power in these solutions is high. In the diethanolamine bath, the copper ion concentration is low and such deposits are obtained. The cathode polarization is high. But the conductivity is lower, the cathode efficiency higher and the throwing power slightly less than that of the cyanide bath.[3] The polarization is increased by the addition of rochelle salt and sodium sulfate (to a little extent) which act as brighteners. Cathode polarization appears to have some significance in the deposition of copper from the ethanolamine bath.

SUMMARY

1. The copper oxalate-diethanolamine-rochelle salt bath gives good quality electrodeposits of copper directly on steel. The optimum conditions are: copper oxalate 45 g./L., diethanolamine 68 ml./L., rochelle salt 45 g./L., c.d. 1·2–1·6 amp./dm.^{2}, pH 9·0 and temperature 24° C.

2. The advantages of the amine bath over the cyanide are (*a*) higher cathode efficiency, (*b*) comparative stability, (*c*) non-poisonous nature. The conductivity and throwing power are not as good as that of the cyanide bath.

3. Sodium sulfate increases the brightness of the deposits.

The authors are thankful to Prof. K. R. Krishnaswami, Head of the Department of General Chemistry, for his keen interest in the work.

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