

ELECTRODEPOSITION OF COPPER FROM THE TRIETHANOLAMINE BATH

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ABSTRACT

Copper has been plated on steel from complex copper-triethanolamine solutions containing copper oxalate, nitrate, citrate, tartrate and carbonate which do not deposit copper by immersion. Good quality deposits are obtained over a wide range of operating conditions and the bath performance can be improved by the addition of nitrates, ammonium compounds and rochelle salt. The bath is comparable to the mono- and di-ethanolamine baths for copper deposition.

INTRODUCTION

The electrodeposition of copper from the mono-, di- and tri-ethanolamine baths and of brass from the triethanolamine bath has been briefly reported in preliminary notes by Rama Char and Shivaraman^{1, 2, 3} and the detailed work on the mono- and di-ethanolamine baths presented in recent communications.^{4, 5} Triethanolamine has been used for copper plating by Brockman and Brewer,⁶ Levin⁷ and Schweig.⁸ This paper gives the results on the deposition of copper from triethanolamine solutions.

THE PLATING BATH

The bath was prepared by the addition of triethanolamine to a solution or suspension of copper salt—oxalate, nitrate, citrate, tartrate and carbonate, a blue coloured complex being formed. The ratio of amine (in ml.) to salt (in g.) in 1 litre of solution was as follows over a wide range of concentration: oxalate 2.0 to 3.5, nitrate 3.0 to 3.5, citrate 3.0 to 5.0, tartrate 3.0 to 3.5, carbonate 3.0. In the case of carbonate, ammonia was also added to obtain a clear solution, the ammonia to salt ratio being 1.2-2.0.

EXPERIMENTAL

The triethanolamine (technical) was a product of the B.D.H. and the other chemicals were from B.D.H. or Johnson and Sons. Mild steel cathodes

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and copper anodes were used. The plating time was 2.5 minutes and the temperature 24° C. The experimental details were the same as described before.^{4, 9}

EXPERIMENTAL RESULTS

Copper Ion Concentration

The copper (cupric) ion concentration in all the plating solutions (without the addition agents) was in the range 10^{-10} to 10^{-13} N. The solutions did not deposit copper on steel by immersion due to the low metal ion concentration.

Electrodeposition

Variation of concentration.—The baths gave smooth, bright and adherent deposits, comparable to those from the cyanide bath, over a wide range of experimental conditions. Table I shows the effect of variation of concentration on the c.d., bath voltage and cathode efficiency. In all cases, the range has been recorded. For a given concentration of copper salt, the amine:salt ratio was as stated before.

TABLE I

	Oxalate	Nitrate	Citrate	Tartrate	Carbonate
Composition :					
Copper salt g./l.	10—120	10—120	10—90	10—120	10—75
Amine ml./l.	35—240	35—360	40—275	35—360	30—225
24% ammonia ml./l.	20—90
pH	8.13—8.50	8.30—8.70	8.95—9.0	8.50—8.74	9.45—9.85
c.d. amp./dm. ²	0.4—2.4	0.4—3.6	0.2—2.0	0.2—1.6	0.6—2.8
Bath voltage, volts	2.1—6.6	1.1—3.2	2.5—7.8	1.5—4.5	3.3—7.1
Cathode efficiency %	87—107	50—95	79—118	94—117	92—100

The cathode efficiency was in the majority of cases between 90–100%. In a few cases, values above 100% have been obtained at low c.d. The nitrate bath was characterised by very low efficiency. The anode corrosion and throwing power were good. The optimum composition for each bath is given in Table II below.

Plating Characteristics under Optimum Conditions

Table II gives the comparative performance of the optimum concentration baths containing various copper salts. The throwing power was calculated from the Schlotter-Korpiun equation.¹⁰

TABLE II

	Oxalate	Nitrate	Citrate	Tartrate	Carbonate
Composition :					
Copper salt g./l.	60	45	30	45	45
Amine ml./l.	150	135	150	135	135
24% ammonia ml./l.	50
pH	8.13	8.30	9.30	8.55	9.45
Copper concentration g./l.	24.00	11.70	10.29	12.28	20.43
Copper ion concentration N	7.90×10^{-11}	4.82×10^{-10}	1.51×10^{-12}	2.04×10^{-11}	2.29×10^{-13}
Sp. conductivity mhos/cm. ³	0.0079	0.0177	0.0034	0.0079	0.0072
c.d. amp./dm. ²	0.7—2.0	0.6—1.6	0.4—1.2	0.2—1.2	0.8—2.0
Cathode polarization volts	0.20—0.51	0.34—0.75	0.60—0.75	0.16—0.79	0.21—0.48
Bath voltage volts	2.1—5.0	1.2—2.2	2.9—5.8	1.5—3.8	2.1—5.5
Cathode efficiency %	97—105	50—95	90—104	94—114	84—100
Throwing power : Schlotter-Korpiun (0.8 amp./dm. ²)	1.20	1.75	1.29	1.73	1.19
Stability	Unstable	Stable	Unstable	Unstable	Stable
Quality of deposit	Bright	Semi-bright	Brighter	Bright	Bright

The nitrate and carbonate baths are stable whereas the other baths decompose after electrolysis. In the oxalate, citrate and tartrate baths, cathode efficiency values above 100% have also been obtained in a few cases. The nitrate and tartrate baths possess better throwing power. Other advantages of the nitrate bath are: low bath voltage, high conductivity and workability at higher temperatures; but the cathode efficiency is low and the deposits are not as bright. Higher c.d. can be used with the oxalate and carbonate baths. The deposits obtained from the citrate bath are brighter. The throwing power can be increased to a value of 3 by suitable additions. The throwing power per cent. was also calculated from the equation of Gardam^{4, 11} for the various baths with and without addition agents in the c.d. range where the cathode polarisation-log c.d. relationship was roughly linear. The throwing power range was: 9–13 (oxalate, 0.012 amp./cm.²), 21–29 (nitrate,

0.012 amp./cm.²), 40–50 (citrate, 0.004 amp./cm.²), 44–65 (tartrate, 0.008 amp./cm.²), 3–14 (carbonate, 0.024 amp./cm.²).

The rate of deposition of copper from these baths (with the best addition agent) was compared with that from the “low concentration” and “high efficiency” cyanide bath without brightener⁴ at a c.d. of 1.2 amp./dm.² (2.0 amp./dm.² for carbonate). It was in between the rates for the cyanide baths.

Temperature

Higher temperatures, 40–70° C., were not conducive to the proper working of the baths, resembling the mono- and di-ethanolamine baths in this respect. An exception to this was the nitrate-triethanolamine bath which could be operated satisfactorily by raising the temperature. With the optimum concentration bath it was possible to raise the limiting c.d. from 1.6 to 4.0 amp./dm.² at 70° C.

Addition Agents

In the oxalate, citrate and tartrate baths, a brown precipitate of cuprous oxide was noticed after electrolysis indicating decomposition. The unused bath did not decompose even after a long time. It was found that addition of small quantities (1.2 g./l.) of salts containing anions like nitrate, sulfate and chloride prevented the bath decomposition. Several addition agents were tried to effect an improvement in the bath performance and the results obtained with the beneficial additions are summarized below. In all cases, the additions have been made to the optimum concentration baths.

Ammonium, potassium and sodium nitrates (2–10 g./l.) increased the brightness of the deposits from the oxalate bath. The limiting c.d. was raised from 2.0 to 4.0 amp./dm.² by potassium and sodium nitrates and there was a decrease in the bath voltage and efficiency (up to 60%). They increased the conductivity, cathode polarization and throwing power.

In the nitrate bath, ammonia (24%, 10–75 ml./l.) and ammonium oxalate (5–15 g./l.) considerably increased the brightness of the deposits and increased the limiting c.d. from 1.6 to 3.2 and 3.6 amp./dm.² respectively. With 10 g./l. oxalate, the c.d. could be raised to 5.6 amp./dm.² at 70° C. Good quality deposits were also obtained with addition of 3–10 g./l. of ammonium chloride or sulfate. Ammonia decreased the copper ion concentration from 10⁻¹⁰ to 10⁻¹⁵ N. Ammonia, ammonium oxalate and chloride increased the conductivity of the bath but decreased the polarization.

Addition of excess amine to the citrate bath resulted in brighter deposits, up to an amine:salt ratio of 5. Ammonium sulfate (10 g./l.) gave very bright deposits, lowered the bath voltage, lowered the copper ion concentration from 10^{-12} to 10^{-14} , and increased the conductivity, cathode polarization and throwing power. Ammonium nitrate increased the c.d. range but reduced the cathode efficiency.

Ammonium sulfate (20 g./l.) was also beneficial in the tartrate bath; it increased the brightness, limiting c.d. (from 1.2 to 2.4 amp./dm.²), conductivity, cathode polarization and throwing power, and decreased the bath voltage as well as the metal ion concentration (from 10^{-11} to 10^{-13} N). The effect of ammonium nitrate was the same as in the citrate bath.

The brightness of the deposit was increased and the bath voltage decreased by the addition of rochelle salt (45 g./l.), potassium or sodium sulfate to the carbonate bath. Nitrates had the same effect as in the previous two baths. The metal ion concentration was decreased from 10^{-13} to 10^{-15} N. by rochelle salt. This salt as well as potassium sulfate (10 g./l.) increased the conductivity, cathode polarization and throwing power.

DISCUSSION

The triethanolamine baths give good quality deposits of copper on steel over a wide range of operating conditions. There is no immersion deposition due to the low copper ion concentration. The baths possess some advantages over those studied by previous workers. The triethanolamine-sodium oxalate-copper sulfate bath has been claimed by Brockman and Brewer⁶ to give good deposits. But the c.d. is very low (0.4 amp./dm.²) and immersion deposition takes place due to the high copper ion concentration (10^{-8} N). Levin⁷ has added ammonia to this bath to prevent immersion deposition (copper ion concentration: 10^{-11} N) and the c.d. range for bright deposits is 1.2–1.7 amp./dm.² Schweig⁸ has used the copper sulfate-rochelle salt-triethanolamine bath at 1.0 amp./dm.² On the other hand, the triethanolamine baths studied in the present work are comparatively simpler in composition and can be used over a wider c.d. range (up to 4.0 amp./dm.²). Addition agents have been used to improve the bath performance.

The tendency of the oxalate, citrate and tartrate baths to decomposition is probably due to the oxidation of the amine and also to the reducing nature of the anions. Cathode efficiency values over 100% in these baths are perhaps attributable to deposition of cuprous copper. The decrease in the efficiency on the addition of nitrate has also been observed in copper

deposition from mono- and di-ethanolamine baths.^{4, 5} Ammonium compounds and rochelle salt act as brighteners and also decrease the metal ion concentration possibly due to the formation of further complexes. The brighteners increase the cathode polarization, with the exception of the nitrate bath where there is a decrease. Taking all factors into consideration, it can be concluded that the performance of the triethanolamine bath is in general on the lines to be expected from a complex salt plating bath.

From these results and the previous work on copper plating from mono- and di-ethanolamine baths^{4, 5} it is possible to have an idea of the relative performance of the mono-, di- and tri-ethanolamine baths under optimum conditions and without addition agents. The mono-amine bath has a higher limiting c.d. and conductivity. The advantages of the tri-amine bath are: low bath voltage and possibility of working at higher temperatures (nitrate bath only); but some of the baths are comparatively unstable. There is not much difference between these baths in respect of quality of deposit, cathode efficiency (except tri-amine-nitrate bath), throwing power and improvement in bath performance by the use of addition agents.

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REFERENCES

1. Rama Char and Shivaraman .. *Curr. Sci.*, 1950, 19, 311.
2. Shivaraman and Rama Char .. *Proc. 37th Ind. Sci. Cong.*, 1950, Part 3, 179.
3. Sadagopachari, Shivaraman and Rama Char .. *Curr. Sci.*, 1951, 20, 154.
4. Rama Char and Shivaraman .. *J. Electrochem. Soc.*, 1953, 100, 227.
5. Shivaraman and Rama Char .. *J. Ind. Inst. Sci.*, 1953, 35A, No. 4, 293.
6. Brockman and Brewer .. *Trans. Electrochem. Soc.*, 1936, 69, 535.
7. Levin .. *J. Appl. Chem.*, U.S.S.R., 1941, 14, 74.
8. Schweig .. *Brit. Pat.*, 503,095, 1939.
9. Rama Char and Sadagopachari .. *J. Ind. Inst. Sci.*, 1953, 35A, No. 4, 298.
10. Schlotter and Korpiun .. *Trans. Electrochem. Soc.*, 1932, 62, 129.
11. Gardam .. *Trans. Faraday Soc.*, 1938, 34, 698.