

Stefan's Law and those found experimentally by applying Newton's Law of cooling, agree. The term 'radiation correction' as used in connection with such experiments in calorimetry, therefore, seems basically wrong and misleading; instead 'cooling correction' should be the proper term used. It is further seen by comparing the cases (i) and (iv) with (ii) and (iii), that the rate of loss of heat is much more in the former case than in the latter. It is therefore advisable to keep the cooling surface dull instead of polishing² it for quicker cooling. It is also apparent that taking the convection loss to be the same at a particular temperature (though it is different at different temperatures) in all the cases, the loss by radiation depends on the nature of the cooling as well as the absorbing surfaces. It is therefore desirable to define the specific conditions under which the Newton's Law of cooling experiment be performed.

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P.U. Physics Dept.,
Govt. College,
Hoshiarpur (Punjab),
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OM PRAKASH.
SHADI LAL.
BALDEV SINGH.

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ELECTRO-DEPOSITION OF METALS AND ALLOYS FROM CYANIDE-FREE BATHS

Part II. Copper from Ethanolamine Solutions

In a previous communication from this laboratory,¹ it has been shown that the complex silver iodide bath gives electro-deposits of silver comparable to those from the silver cyanide bath. The present investigation deals with a similar attempt to obtain a suitable substitute for the commercial cyanide bath for the electro-deposition of copper, in view of its poisonous nature and instability.

Copper has been electro-deposited on steel from baths containing copper salt-ethanolamine complexes: (1) Copper oxalate-monoethanolamine, (2) copper oxalate-diethanolamine, and (3) copper oxalate, nitrate, citrate, tartrate, carbonate-triethanolamine. These baths are simpler than those attempted before.^{2,3,4,5} As in the cyanide bath, immersion deposition is prevented by complex formation which reduces the effective copper (cupric) ion concentration. The latter has been determined by the E.M.F. method and is found to be of the order

1×10^{-33} to 10^{-35} N. A detailed study has been made of the effect of variation in (a) concentration of copper, (b) concentration of ethanolamine and (c) c.d., on the electro-deposition. The bath is comparable to the cyanide bath in respect of cathode efficiency, c.d. range, rate of deposition and brightness, adherence and general quality of the deposit. The cathode efficiency is nearly 100 per cent., except in the copper nitrate-triethanolamine bath, which gives lower values.

Rochelle salt, as a constituent of the copper oxalate-monoethanolamine bath, improves anode corrosion, increases the c.d. range, conductivity, cathode polarisation and throwing power, and yields better quality deposits by eliminating treeing and increasing the brightness. The optimum conditions for the various baths are given in the following table:

TABLE I
Bath Voltage 1.2 to 5.5 Volts

Copper salt (g./L)	Ethanolamine (c.c./L)	pH	Temperature °C.	Bright c.d. range (amp./dm ²)
(a) Oxalate 60 + Rochelle salt 60 g./L. (mono-)	60	9.5	24	2.4 - 4.8
(b) Oxalate 45 + Rochelle salt 45 g./L.	(di-) 68	9.0	24	1.2 - 1.6
(c) " 60	(tri-) 150	8.1	24	0.68 - 2.0
(d) Nitrate 45	(tri-) 135	8.3	24	0.64 - 1.6
(e) Nitrate 45	(tri-) 135	8.3	40	1.2 - 3.6
(f) Citrate 30	(tri-) 150	9.3	24	0.4 - 1.12
(g) Tartrate 45	(tri-) 135	8.6	24	0.24 - 0.8
(g) Carbonate 45 + Ammonia (24%) 50 c.c./L.	(tri-) 135	9.5	24	1.2 - 2.0

Higher temperatures are not conducive to proper working, except in the copper nitrate-triethanolamine bath. The effect of addition agents has been studied. A substantial improvement in the performance of the bath and the quality of the deposit has been noticed with some addition agents. The pH, conductivity and cathode polarisation have been measured. The throwing power, as calculated from c.d.-cathode potential curves is not as good as that of the cyanide bath.

The copper salt-ethanolamine baths have some important advantages over the cyanide bath, in respect of higher cathode efficiency, ability for good working at room temperature, brightness of deposits and improved performance with certain addition agents. In some