STUDIES IN THE ELECTRODEPOSITION OF COBALT FROM FLUOBORATE BATH

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Received July 14, 1953

SUMMARY

The optimum conditions for the electrodeposition of cobalt were arrived at, from a study of the effect of different variables on the plating characteristics of cobalt fluoborate solutions.

The best plates were obtained from a still solution of the following composition:

Cobalt fluoborate	116–154 g./l.
Boric acid	15 g./l.

and under the following conditions:

Temperature	45–50° C.
pH	3·5
Cathodic Current Density ..	50–60 amps./sq.ft.

The bath is stable, non poisonous, easily controlled and maintained. The plates obtained are easily polished, fairly adherent and fine grained. A few gas spots were occasionally noticed in the plates but these could generally be eliminated by buffing.

Polarization values of the cathode were determined at current densities in the range 0–60 amps./sq.ft. with variation in speed of agitation, temperature and concentration of solution.

Specific conductivity, cathode current efficiency, and throwing power data were obtained from experiments, temperature, agitation and concentration being the variables in each case.

INTRODUCTION

Very little plating of pure cobalt is carried out at present. Watts mentions[1] 51 different solutions for the plating of cobalt in a comprehensive summary of the early literature, but the first detailed study of cobalt plating was done by Kalmus, Harper and Savell,[2] and two solutions especially were reported by them to be very satisfactory. Soderberg, Pinner and Baker[3] have excellently reviewed cobalt plating and given extensive references.

Bright nickel plating consists of the co-deposition of cobalt and nickel and this alloy is whiter,[4] harder and more resistant to corrosion than either cobalt or nickel plate.[5] Berger's[6] suggestion for the use of cobalt in mirrors and reflectors has been disagreed with by Blum and Hogaboom[7] who state it is less resistant to corrosion than nickel.

Cobalt and nickel are closely allied in both their physical and chemical properties. The cost of cobalt which is roughtly 4 to 5 times that of nickel is the main factor against the utilization of cobalt in place of nickel. Nickel plating solutions of the Watts type need careful control of pH. In addition elaborate filtration processes are necessary to keep the bath free of impurities and sludge. It has been observed that the maintenance and operation of cobalt fluoborate baths are simple, and also that impurities have only a slight adverse effect. For cobalt to compete with nickel therefore, its high cost must be offset by the ease and simplicity of operation and lower cost of equipment necessary to plate from fluoborate baths.

EXPERIMENTAL PROCEDURE

The effect of temperature, concentration of cobalt fluoborate solution, current density and agitation as variables were studied on:—

1. Type of plate obtained (addition agents also varied).
2. Cathode polarization.
3. Cathode current efficiency.
4. Throwing power using a Hull Cell (Effect of agitation not studied).

The influence of concentration and temperature were studied on:

5. Specific conductivity.
6. Hardness of cobalt deposit.

Details.—The experiments determining types of plate obtained under different conditions were carried out in a 150 c.c. beaker. The cathodes were always of brass strip and were approximately 3 inches × 1 inch. A constant cathodic area of 2 sq. inches was plated, the time of each test being generally 3 minutes. The anode was of high purity cobalt metal, 2·5 sq. inches external area, and the distance between the electrodes was invariably 1 inch. Standard ammeters, voltmeters, rheostats and rectifiers were employed to complete the plating circuit.

Plating solutions.—Fluoboric acid was prepared by stirring in small amounts of boric acid into 1 lb. of 48% hydrofluoric acid contained in a well cooled, waxed vessel. A slight excess of boric acid was added, left overnight and filtered. The solution was concentrated as desired.

Cobalt fluoborate solution was prepared by adding pure, powdered cobalt carbonate in small amounts at a time to well stirred, warm, fluoboric acid. The reaction was judged complete when no effervescence took place on further addition of cobalt carbonate. A slight excess was then added, the solution allowed to stand overnight and filtered. The desired concentration was obtained by dilution with distilled water. The Fischer electro-analyzer was used for the quantitative determination of cobalt concentration.

Electrodes.—The anode was of high purity cobalt metal and was only swilled vigorously in distilled water and dried between filter paper sheets, prior to commencement of any experiment.

The brass cathodes were polished successively by 2 F, F and O emery paper, swilled in running water, kept for ½ to 1 minute in a warm 5% solution of sodium carbonate, swilled again in water, dried between filter paper sheets, and immersed for 5 seconds in a bright dip of the composition:

Conc. H_2SO_4	..	25 c.c.
Con. HNO_3	..	10 c.c.
Conc. HCl	..	0·5 c.c.
Distilled Water	..	25 c.c.

The cathodes were immediately washed, dried between filter paper sheets and kept in a desiccator where they maintained their brightness and lustre indefinitely.

Temperature and agitation.—The temperature of the solution was maintained within ± 1° C. with the aid of a thermostat. Agitation was obtained by a strirrer attached to a fractional H.P. motor. The stirrer was a glass rod, ¼ inch diameter twisted into a spiral. Classification of agitation is as follows:—

Slow agitation	..	110 r.p.m.
Medium agitation	..	200 r.p.m.
Fast or vigorous agitation	..	250–270 r.p.m.

Specific conductivity measurement.—Kohlrausch's Alternating Current Bridge method was employed for the measurement of reisistance.

The cell constant of the cell used was determined by finding the resistance of a decinormal potassium chloride solution at a definite temperature. The specific conductance of the solution at that temperature was obtained from tables, and substitution in the formula

$$K = k_0 R_0$$

where K is the cell constant, k_0 the specific conductivity and R_0 the resistance.

Cathode current efficiency.—The cathode was weighed before and after the experiment in an analytical balance. An accurate stopwatch and ammeter were employed to note the time and deposition current respectively.

Data obtained in the different experiments were substituted in the expression:

$$\frac{\text{Weight of metal deposited}}{\text{Weight calculated from ampere-hours}} \times 100$$

to give the cathode current efficiency.

Cathode polarization.—The electromotive force of the cell formed by pressing the end of a capillary attached to a decinormal calomel electrode against the cathode of the cobalt fluoborate bath, was measured with the help of a Tinsley General Utility Potentiometer and Weston (Cadmium) Standard Cell. Polarization values of the cathode for different current densities were obtained by subtracting the static from the dynamic cathode potentials.

Hardness measurement.—Deposits, sufficiently thick to ensure elimination of the influence of the basis metal on hardness testing, were obtained by passing current for a sufficiently long time through the electrolytic cell. For good results, the thickness of the deposit should be at least 7 times the depth of the impression formed in the test. According to Macnaughtan and Hothersall,[8] *a thickness of 0·0044 inches of nickel is good* enough for accurate Brinell hardness measurement, using a 1 mm. ball and 10 kg. load. Assuming the cobalt deposit to have a hardness greater than this, current densities of 21·6 and 50·4 amps./sq. feet had to be passed for 4½ hours and 2 hours respectively before the thickness can be considered safe for testing.

The tests were performed on a Vicker's Hardness Testing Machine using a Pyramidal diamond point for penetration and a load of 5 kilograms.

EXPERIMENTAL RESULTS

TABLE I

Influence of current density, agitation and temperature on deposit

Current Density amps./sq. ft.	Agitation	Temperature °C.	Nature of Deposit
A. *Cobalt fluoborate concentration* 4 *N or* 466 *g./l.* ; *pH* 3·0			
25·2–194·4	Zero, slow, medium and fast	23–31	Plates obtained were smooth, adherent, fine-grained but spotted due to gas evolution. Easily polished.
36·0–158·4	Do.	45	Dark-grey, fine-grained and adherent plates. Agitation tends to give discoloured rough plates.
25·2–172·8	Do.	63	Dark-grey, fine-grained and adherent plates. Those obtained in still solution were comparatively smooth but others were non-uniformly coloured. They could be easily polished but had a few gas spots.
B. *Cobalt fluoborate concentration* 2 *N or* 233 *g./l.* ; *pH* 3·4			
28·8–108·0	Zero, slow, medium and fast	23	Agitation tends to give non-uniformly coloured, rough plates. Treeing in still solutions commenced at C.D.'s greater than 72 amps./sq. ft. The plates were fine-grained and adherent.
28·8–79·2	Do.	45	Plates deteriorate with agitation. Plates in still solution had few gas spots, were fine-grained, adherent and easily buffed to shining grey.
21·6–79·2	Do.	63	Still and slowly agitated solutions gave the best plates which were dark grey, fine-grained, adherent, easily polished with few gas spots. Microscopic examination of buffed plates at 113 diameter magnification showed uniform coatings.

TABLE I—(*Contd.*)

Current Density amps./sq. ft.	Agitation	Temperature ° C.	Nature of Deposit
			C. Cobalt fluoborate concentration 1 *N or* 116 *g./l.* ; *pH* 3·6
21·6–64·8	Zero, slow, medium and fast	24	Bright grey, fine-grained, adherent plates with a fair number of gas spots were obtained from still solutions. Plates from agitated solutions were generally non-uniformly coloured.
21·6–64·8	Do.	48	Current densities greater than 43·2 amps./sq. ft. gave smooth, fine-grained deposits from still and agitated solutions which were easily buffed to a shining grey.

Boric acid to saturation and β-naphthol were added. The only noticeable effect was to raise the current density at which burning took place.

Plating was also done on brass from mixed cobalt and nickel fluoborate solutions, nickel fluoborate being used as inorganic addition agent and added up to 20% by weight employing variation in concentration, temperature and current density. The best deposits were obtained from a 3 N solution of cobalt fluoborate with 20% by weight of nickel fluoborate. In all cases, gassing took place at the anode for current densities greater than 93·6 amps/sq. ft.

Limiting current density at 25° C.	223·2 amps./sq. ft.
Limiting current density at 45° C.	266 amps./sq. ft.

TABLE II

Influence of temperature on specific conductivity of 1 *N*, 2 *N and* 4 *N solutions of cobalt fluoborate*

1 N solution 116 g./l. pH 3·60		2 N solution 233 g./l. pH 3·4		4 N solution 466 g./l. pH 3·0	
Temperature ° C.	Specific Conductance (mhos)	Temperature ° C.	Specific Conductance (mhos)	Temperature ° C.	Specific Conductance (mhos)
25	0·05527	25	0·08190	25	0·090129
30	0·06148	30	0·09186	30	0·09877
40	0·07366	40	0·1083	40	0·1200
50	0·08485	50	0·124	50	0·1395

TABLE III

Influence of agitation, current density and temperature on cathode current efficiency of 1 N, 2 N and 4 N solutions

Cathode Current Density amps./sq. ft.	Cathode Current Efficiency				Normality of solution	g./l. of cobalt fluo-borate	pH
	Temp. of 25° C.		Temp. of 43° C.				
	With agitation	Without agitation	With agitation	Without agitation			
28·8	96·54	96·36	98·00	97·45	1 N	116	3·6
38·88	97·92	98·20	98·07	98·60			
50·40	98·62	98·52	99·09	99·27			
28·8	97·00	97·27	96·73	96·06	2 N	233	3·4
72·0	97·00	98·00	97·67	97·83			
129·6	98·25	97·85	97·80	98·87			
28·8	97·65	97·72	97·65	96·90	4 N	466	3·0
108·0	97·20	98·06	97·32	97·24			
216·0	99·36	98·95	98·63	99·50			

The Hull Cell was used for the estimation of throwing power instead of the more conventional Haring-Blum Cell, under different conditions of concentration, temperature and current density. Photographs were taken of the different plates and a visual evaluation of throwing power obtained.

175 c.c. of solutions were used in each experiment giving 1¼ inch depth of liquid.

Solutions used			Range of current in amperes at	
Normality	g./l.	pH	25° C.	43° C.
4	466	3·0	1·3–3·5	1·3–3·5
2	233	3·4	1·3–2·5	1·3–2·5
1	116	3·6	0·9–1·9	0·9–1·6

Hull Cell photographs show that cobalt fluoborate solutions have a fairly good throwing power which seems to increase with decrease in temperatures. In all experiments, that part of the cathode facing anode was fully covered or plated, but in certain cases (1 N solution at 43° C. and 4 N solution at 25° C. and 43° C.) a portion of the cathode face away from the anode was not plated. This effect was minimised with increase in current density for 1 N and 4 N solutions at 43° C., but increased with current density for 4 N solutions at room temperature.

TABLE IV

Influence of concentration, temperature and current density on the hardness of cobalt deposit

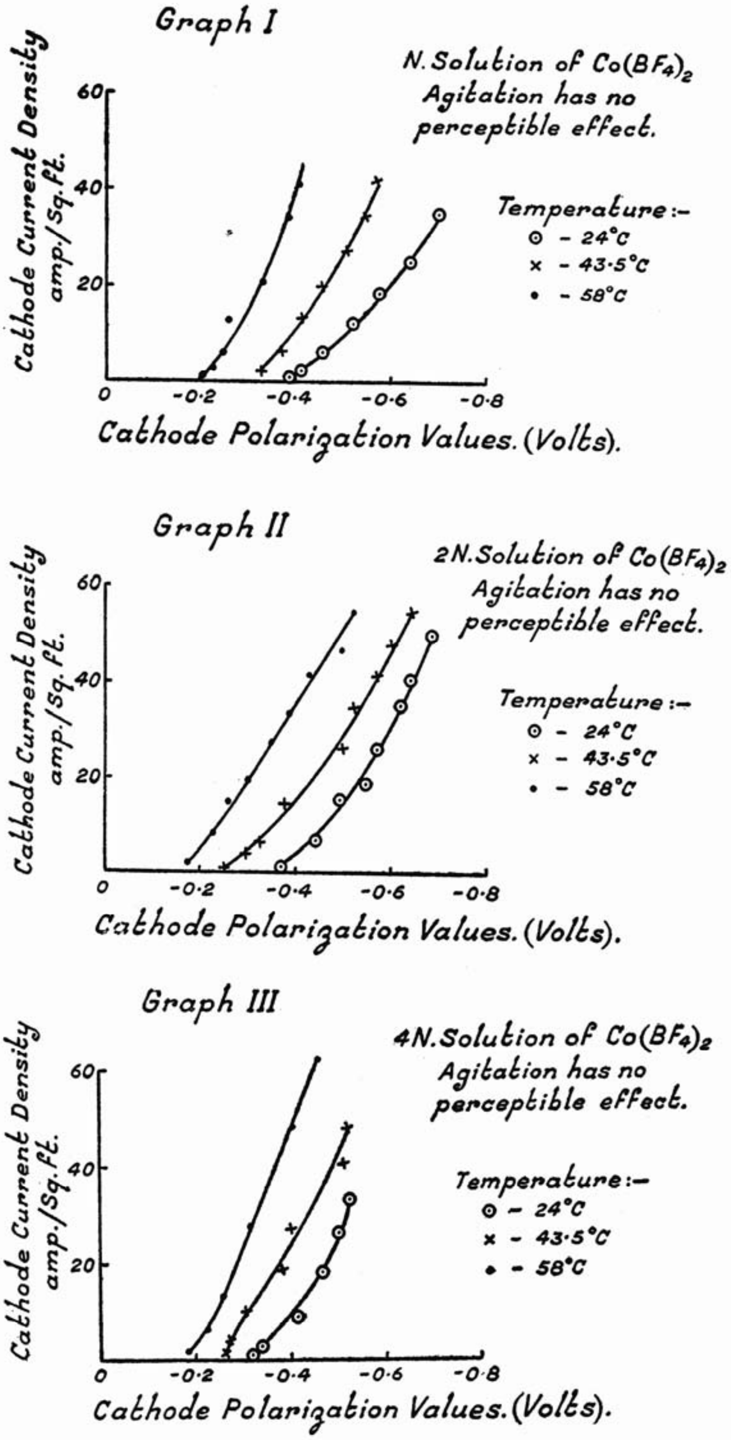
Normality of solution	g./l.	pH	Temperature 25° C. Cathode current density 21·6 amps./sq. ft. Time of deposition 5 hours—10 minutes Average V.P.H.N.	Temperature 45° C. Cathode current density 50·4 amps./sq. ft. Time of deposition 2 hours—30 minutes Average V.P.H.N.
4	466	3·00	443	180
2	233	3·4	329	384
1	116	3·6	330	350

TABLE V

Influence of very low current densities, agitation and temperature on cathode polarization

Concentration of solution 1 N or 116 g./l. of cobalt fluoborate; pH 3·6. Polarisation values in volts.

Cathode Current Density amps./sq. ft. $\times 10^{-3}$	Cathode polarization			Cathode polarization		
	Temperature: 23·5° C.			Temperature: 43·5° C.		
	Still solution	Slow agitation	Vigorous agitation	Still solution	Slow agitation	Vigorous agitation
40·78	—0·041	—0·019	—0·010	—0·003	—0·015	—0·014
47·52	—0·048	—0·027	—0·022	—0·010	—0·022	—0·020
59·04	—0·099	—0·038	—0·016	..	..	..
72·00	—0·232	—0·086	—0·024	—0·032	—0·030	—0·028
106·20	..	..	..	—0·068	—0·064	—0·040
108·00	..	..	..	—0·175	—0·159	—0·117
177·12	— 0·301	—0·287	—0·273	..	..	..
216·00	..	..	..	—0·236	—0·227	—0·228
360·00	—0·336	—0·342	—0·340	..	..	..



Graphs I, II & III show influence of **C.D.** agitation, temperature and concentration on cathode polarization.

Quality of deposit.—The plates darken in colour with increase in temperature. Increase in concentration raises the limiting current density and widens the range of current density for satisfactory plating. Agitation does not seem to serve much purpose.

The best plates are obtained from a still solution of the composition:

Cobalt fluoborate	..	116–54 g./l.
Boric acid	..	15 g./l.

and under the following conditions

pH	..	3·5
Temperature	..	45–50° C.
Cathodic Current Density		50–60 amps./sq. feet.

The deposits are dark, fine-grained, adherent, with few gas spots and easily buffed to a shining grey.

Mixed cobalt and nickel fluoborate solutions obtained by adding the nickel salt up to 20% by weight of cobalt fluoborate have the optimum composition:

Cobalt fluoborate	..	390–430 g./l.
Nickel fluoborate	..	80 g./l.
Boric acid	..	30–40 g./l.

Condition of deposition are as follows:

pH	..	3 –3·2
Temperature	..	25–50° C.
Cathode Current Density		100–50 amps./sq. feet.

The plates are hard, fine-grained and adherent with very few gas spots. When buffed they are whiter than cobalt plate.

Cathode current efficiency.—The cathode current efficiency was greater than 96% in all cases. As the concentration of the bath only increased very slowly during plating, the anodic current efficiency is of the same order. This, coupled with absence of anodic sludge or other disturbing factors, makes the bath easy to control and maintian.

Specific conductivity is seen to increase both with temperature and concentration.

Hardness of cobalt electrodeposits.—At room temperature, plates from 4 N solution are much harder than plates from 2 N and 1 N solutions, the latter hardness numbers being practically the same. Increase in temperature considerably lowers the hardness of plates from 4 N solution, but does not seem to affect those from 2 N and 1 N solutions.

Cathode polarization.—At cathode current densities greater than 0·5 amps./sq. ft., agitation has very little effect on cathode polarization which increases with decrease in concentration and temperature.

At lower current densities of the order 0·05–0·2 amps./sq. ft. agitation decreases polarization, and this condition is roughly intensified by temperature and concentration.

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