THE ELECTRODEPOSITION OF TERNARY ALLOYS OF CADMIUM, COPPER AND TIN

By

ROBERT C. OLSEN

A THESIS

Submitted to the Faculty of
Michigan State College of Agriculture and Applied Science
in Partial Fulfillment of the requirements for
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Doctor of Philosophy

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PRINTED IN U.S.A.
Lithoprinted by Edwards Brothers, Inc., Lithoprinters and Publishers
Ann Arbor, Michigan, 1936

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The three metals, cadmium, copper and tin, have been electrolytically deposited singly and in pairs from solutions of their salts. The purpose of this investigation is to determine whether the three metals can be deposited simultaneously from an aqueous solution of the complex cyanides of cadmium and copper and sodium stannate, and to study the effects of metal ratio, temperature, current density and free cyanide content on the composition of the metal deposited.

THEORETICAL

The simultaneous electrodeposition of metals should take place when the single electrode potentials are nearly the same. Deposition will take place under these conditions if no other factors except the single electrode potentials are involved. The normal electrode potentials of the metals under consideration are:

Copper	+.344 volts
Cadmium	-.401 volts
Tin	-.136 volts
Hydrogen	.000 volts

Substituting these values in the Nernst electrode potential equation we find that copper alone should be deposited from a solution normal with respect to the several ions; hydrogen would be discharged preferentially to cadmium and tin and in such a solution simultaneous deposition seems impossible.

The Nerst electrode potential equation,

$$E = E^{o} - \frac{RT}{nF} \ln \frac{1}{C}$$

wherein E is the single electrode potential, E^{o} is the normal electrode potential, R is the gas constant, T is the absolute temperature, n is the valence of the ion, F is Faraday's constant and C is the concentration of the metal ion, shows that the single electrode potential may be changed by altering the ion concentration. Dilution and complex ion formation are the means of establishing a suitable metal ion ratio. The decrease in metal ion concentration upon dilution results in a corresponding decrease in conductivity and lower energy efficiency and results in gassing at the cathode and a low current efficiency.

Complex ion formation is preferable to dilution in bringing about the same conditions of ionic concentration; it has similar disadvantages as to decreased efficiencies, but to a very much less extent. Measuring the electrode potentials of copper and cadmium in their complex cyanides and tin in sodium stannate, we have:

Cu, CuCN (.1M) + KCN(.2M)	$Cu^{+} + e \rightarrow Cu$	E = -.61 volts
Cd, $CdCN_2$(.1M) + KCN(.2M)	$Cd^{++} + 2e \rightarrow Cd$	E = -.71 volts
Sn, Na_2SnO_3(.1M)	$Sn^{++++} + 4e \rightarrow Sn$	E = -.79 volts

The deposition potentials of copper and cadmium become more electronegative with increase in free cyanide, with increase in current density and with decrease in temperature; the potential of tin remains nearly constant with increase in free cyanide, becomes more electronegative with increase in temperature and with increase in current density.

Theoretical considerations show a possibility of the deposition of the three metals simultaneously from an aqueous solution of the complex cyanides of copper and cadmium and sodium stannate.

LITERATURE OF TERNARY ALLOY ELECTRODEPOSITION

Few references to the deposition of ternary alloys from aqueous solutions are recorded in the literature. Glasstone, (1) in his work on the electrolytic polarization of the iron group metals, nickel, cobalt and iron, studied the deposition potentials of the three metals, singly, in pairs and the three together. He drew the conclusions that the deposition potential (1) varies directly with the metal concentration ratios, (2) varies directly with the temperature and (3) is independent of the hydrogen ion concentration. He used the sulfates of the metals, buffered with sodium acetate, boric acid or acetic-acetate mixture.

Wernlund (2) patented a process of deposition of cadmium-zinc alloys from a solution of zinc cyanide, cadmium hydroxide, sodium cyanide and sodium hydroxide. The patent specified the addition of mercury to the electrolyte, making it a ternary system.

The Electrochemical Rubber and Manufacturing Company (3) has patented the deposition of an alloy of copper, zinc and antimony from an electrolyte of antimonyl trichloride and the complex cyanides of copper and zinc. They found that the antimony content of the deposit can be controlled by (1) varying the composition of the solution, (2) varying the anode composition and (3) varying the voltage.

Fields (4) reported the deposition of an alloy of copper, nickel and zinc from cyanides of the metals. Yamazaki (5) obtained a bronze consisting of copper, zinc and tin by electrolyzing a solution of their cyanides.

Stout and Faust, (6) working on the electrodeposition of iron, copper and nickel alloys from cyanide solutions state: (1) the deposition of copper is favored over that of nickel and iron, especially at low current densities, (2) very high concentration of iron is required in solution to obtain even small iron content in deposits, (3) the metal content of the deposit does not depend directly on the percent of that metal in the solution, but upon its concentration relative to each of the other metals, (4) the percent of copper and nickel in the deposit is relatively greater than that in the bath, (5) increase in current density favors the deposition of nickel and iron at the expense of the copper, (6) increase in copper to nickel ratio in the bath causes an increase in the copper to nickel ratio in the plates, (7) the ratio of copper to nickel in the plate is unaffected by the amount of iron in the bath, (8) it is necessary to use very low concentrations of free cyanide to obtain the ternary alloys.

Ernst and Mann, (7) investigating the ternary alloys of copper, cadmium and zinc from cyanide baths concluded: (1) the copper in the deposit increases as the potassium cyanide decreases or the sodium bisulfite increases, increases as the cadmium in the solution and deposit decreases, and increases as the zinc in the solution and deposit increases, (2) the cadmium in the deposit increases as the potassium cyanide increases or the sodium bisulfite decreases, increases as the copper in the solution and deposit decreases and increases as the zinc in the solution and deposit decreases, (3) the zinc in the deposit increases as the potassium cyanide decreases or the sodium bisulfite increases, increases as the copper in the solution and deposit increases and decreases as the cadmium in the solution and deposit increases, (4) the effect of free cyanide is the most important factor in cyanide deposition, (5) increasing the current density increases the percentage of cadmium and zinc and decreases the percentage of copper in the deposit, (6) with increasing temperature the percentage of cadmium increases, while the percentage of copper decreases and the percentage of zinc remains fairly constant.

Faust and Montillon (8) deposited alloys of copper, nickel and zinc from a solution of their cyanides. They found the following: (1) zinc is more readily deposited than nickel and both metals are more readily deposited than nickel, (2) the percent of copper in the deposit is relatively greater than the percent of copper in the bath, (3) the percent of nickel in the deposit is relatively much less than the percent of nickel in the bath, (4) the percent of zinc in the deposit is nearly the same as that of the bath, (5) increase in current density favors the deposition of zinc and nickel over copper, and zinc deposits more readily than nickel with increase in current density, (6) increase in temperature causes an increase in percent of copper in the deposit, (7) increase in temperature causes a relatively greater decrease in the percent of zinc in the deposit than the percent of nickel, (8) at about 50°C. there ia a rearrangement of the factors controlling deposition which causes a reversal in the slope of curves plotted for percent of copper and percent of zinc versus the percent of these metals in the bath.

Stout and Goldstein (9) deposited alloys of cadmium, zinc and antimony from a solution of antimonyl tartrate and the complex cyanides of cadmium and zinc. Their conclusions were: (1) deposition of zinc and antimony are favored over the deposition of cadmium, (2) a comparatively large cadmium concentration in the bath is required to produce an appreciable amount of cadmium in the deposit, (3) the effect of an increase in concentration of one metal in the bath is to increase the content of that metal in the deposit, (4) an increase in current density at 20°C. produces an increase in antimony content of the deposit when the cadmium and zinc concentrations are low and a decrease in the antimony when the cadmium and zinc contents are high, (5) an increase in current density at 20°C. causes a slight decrease in the zinc content of the deposit, (6) the effect of temperature on the composition of the deposit is almost identical with the effect of current density.

Stout and Agruss (10) deposited ternary alloys of cadmium, tin and zinc from a bath consisting of complex cyanides of cadmium and zinc and sodium stannate. They concluded from their study: (1) deposition of cadmium is favored over the other two metals, (2) a comparatively large amount of tin is necessary in the bath to produce an appreciable amount of tin in the plate, (3) an increase in the cadmium and tin concentrations in the bath produces an increase in their compositions in the deposit, (4) at low current densities increase of zinc in the bath decreases the metal content of the plate, but at higher current densities zinc behaves as the other two metals, (5) at a current density of two amperes per square decimeter the tin and zinc contents of the deposit increase while the cadmium decreases with increasing temperature and (6) at half an ampere per square decimeter the zinc content of the deposit increases with increasing temperature while the content of tin and cadmium does not change.

EXPERIMENTAL

All chemicals used in this investigation were of C.P. quality. The individual baths were made up by mixing measured volumes of the following stock solutions:

(1)	CuCn	44.8 g/L,
	NaOH	10.0 g/L,
	Na_2CO_3	13.2 g/L,
(2)	CdO	16.0 g/L,
	$CdCO_3$	21.6 g/L,
(3)	Na_2SnO_3	26.6 g/L,
	NaOH	10.0 g/L,
	Na_2CO_3	13.2 g/L.

Sufficient sodium cyanide was incorporated in each of the stock solutions to give the desired amount of free cyanide after complete solution. Three sets of stock solutions were made up of .50, .75 and 1.00 normal in free cyanide. All stock solutions and the resulting individual baths were .5 normal in metal content, .25 normal in NaOH and .25 normal in carbonate.

The individual baths were made up of the following volumes of the stock solutions and the resulting ratios of equivalents of metal:

Bath	cc. Stock Sn Soln	cc. Stock Cd Soln	cc. Stock Cu Soln	Metal ratio
A	600	600	600	1 : 1 : 1
B	900	450	450	2 : 1 : 1
C	1275	255	255	5 : 1 : 1
D	1500	150	150	10 : 1 : 1
E	450	450	900	1 : 1 : 2
F	255	255	1275	1 : 1 : 5
G	150	150	1500	1 : 1 : 10
H	450	900	450	1 : 2 : 1
I	255	1275	255	1 : 5 : 1
J	150	1500	150	1 : 10 : 1

The electrolytic cell consisted of a rectangular glass jar 9 cm. by 15 cm. by 15 cm. deep. Four cells, wired in series were placed in a water bath maintained at a constant temperature within an error of .5° C. The baths were agitated by air-driven glass stirrers. Sheet steel anodes were placed seven centimeters from each side of the chromium-plated cathodes. The anode and cathode areas were the same, one square decimeter. Current was supplied by a motor generator. The surrent was measured with an ammeter graduated to one-tenth of an ampere. Voltage was measured with a high resistance voltmeter.

After electrolysis the cathode was transferred to a beaker; the plate was removed under water by wiping with a rubber-tipped glass rod; the metal was filtered through a previously weighed Gooch crucible, washed with water and alcohol, dried and weighed.

To determine the effect of temperature on composition of deposit, baths C and F, with a free cyanide content of .75 normal were electrolyzed at a current density of two amperes per square decimeter at temperatures of 20°, 40°, 60° and 80°C. All other runs were carried out at a temperature of 60 ± .5°C. The major part of the investigation was to determine the effect of metal ratio at current densities of 0.5, 2.0 and 4.0 amperes per square decimeter in baths of .50, .75 and 1.00 normal in free cyanide.

Only the stock solutions were analyzed. The free cyanide content was determined by titration to turbidity with silver nitrate. The carbonate was precipitated with barium chloride and titrated with standard acid. The metal content was determined by electrolysis in a Braun cabinet after the cyanide had been destroyed, tin from oxalate solution, copper from sulfate and cadmium from cyanide solution.

Analysis of deposits consisted of sulfide separations and electrolytic determinations by methods adopted by the American Society of Testing Materials. A sample was dissolved in mixed hydrochloric and nitric acids, evaporated to dryness on a water bath, digested with sodium hydroxide, oxidized by hydrogen peroxide, ammonium oxalate and oxalic acid added and the copper and cadmium precipitated as sulfide. The filtrate was electrolyzed for tin. The residue was dissolved in nitric acid, made alkaline with sodium hydroxide, sodium cyanide added and the cadmium precipitated as sulfide. The filtrate was boiled with sulfuric acid, neutralized with sodium hydroxide, nitric acid added and copper electrolyzed. The residue was dissolved in hydrochloric acid, made alkaline with sodium hydroxide, the precipitate just dissolved with sodium cyanide and the cadmium electrolyzed. In cases of very small amounts of tin, the alloy was dissolved in nitric acid, evaporated to dryness, baked, taken up with hot water and the metastannic acid filtered, ignited and weighed.

DATA AND RESULTS

The data taken is recorded in the following eight tables. Tables I and II state the conditions under which deposition was carried out to determine the effect of temperature on the composition of deposit. Tables III, IV and V give the conditions governing the investigation of the effect of metal ratio in the bath, current density and normality of free cyanide on the composition of plate and Tables VI, VII and VIII the results of analysis and a comparison between normality of metal in the bath and the percentage of metal in the deposit.

Table I

Effect of Temperature

Bath	Temp	Amps	Time	Volts	Weight
C	20	2.0	10	3.4	.231
C	40	2.0	10	3.0	.452
C	60	2.0	10	2.7	.522
C	80	2.0	10	2.3	.565
F	20	2.0	10	3.3	.281
F	40	2.0	10	3.2	.465
F	60	2.0	10	2.7	.497
F	80	2.0	10	2.4	.657

Table II

Effect of Temperature

Bath	Temp	Composition of Bath				Plate Analysis		
		N CN	N Sn	N Cd	N Cu	% Sn	% Cd	% Cu
C	20	0.75	.356	.071	.071	1.9	98.1	0.0
C	40	0.75	.356	.071	.071	3.0	95.8	1.3
C	60	0.75	.356	.071	.071	14.4	81.4	4.3
C	80	0.75	.356	.071	.071	23.0	64.4	12.6
F	20	0.75	.071	.071	.356	0.4	98.3	1.3
F	40	0.75	.071	.071	.356	0.7	92.7	6.6
F	60	0.75	.071	.071	.356	1.7	84.0	14.3
F	80	0.75	.071	.071	.356	2.0	75.5	22.5

Table III

Effect of Metal Ratio of Bath
on Plate Composition
0.5 amp/ sq. dm.

Bath	Free CN	Ratio Sn/Cd	Ratio Sn/Cu	Ratio Cu/Cd	Volts	Time	Weight Plate
A	1.00	1	1	1	1.8	60	1.173
A	0.75	1	1	1	1.8	60	1.092
A	0.50	1	1	1	1.8	60	1.001
B	1.00	2	2	1	1.9	60	0.968
B	0.75	2	2	1	1.9	60	1.051
B	0.50	2	2	1	1.9	60	1.005
C	1.00	5	5	1	2.0	60	1.042
C	0.75	10	5	1	2.2	60	0.984
C	0.50	5	5	1	2.2	60	0.943
D	1.00	10	10	1	2.2	60	0.885
D	0.75	10	10	1	2.2	60	0.848
D	0.50	10	10	1	2.1	60	0.840
E	1.00	1	.5	2	1.9	60	1.099
E	0.75	1	.5	2	2.1	60	1.121
E	0.50	1	.5	2	1.9	87	1.511
F	1.00	1	.2	5	1.9	60	1.110
F	0.75	1	.2	5	1.9	60	1.121
F	0.50	1	.2	5	2.1	87	1.490
G	1.00	1	.1	10	2.0	60	1.041
G	0.75	1	.1	10	2.1	60	1.077
G	0.50	1	.1	10	2.0	87	1.351
H	1.00	.5	1	.5	1.9	60	0.980
H	0.75	.5	1	.5	1.9	60	1.024
H	0.50	.5	1	.5	1.8	87	1.462
I	1.00	.2	1	.2	1.9	60	1.051
I	0.75	.2	1	.2	1.9	60	1.057
I	0.50	.2	1	.2	1.9	60	1.003
J	1.00	.1	1	.1	1.8	60	1.042
J	0.75	.1	1	.1	2.0	60	1.043
J	0.50	.1	1	.1	1.7	60	0.948

Table IV

Effect of Metal Ratio of Bath on Plate Composition

2.0 amps/sq.dm. Temp 60° C.

Bath	Free CN	Ratio Sn/Cd	Ratio Sn/Cu	Ratio Cu/Cd	Volts	Time	Weight Plate
A	1.00	1	1	1	2.2	20	1.169
A	0.75	1	1	1	2.4	20	1.188
A	0.50	1	1	1	2.4	21	1.403
B	1.00	2	2	1	2.3	20	1.230
B	0.75	2	2	1	2.4	20	1.253
B	0.50	2	2	1	2.4	21	1.387
C	1.00	5	5	1	2.8	20	0.845
C	0.75	5	5	1	2.9	20	0.891
C	0.50	5	5	1	2.9	21	1.017
D	1.00	10	10	1	2.8	20	0.621
D	0.75	10	10	1	2.8	20	0.818
D	0.50	10	10	1	2.8	21	0.760
E	1.00	1	.5	2	2.7	20	1.157
E	0.75	1	.5	2	2.7	21	1.118
E	0.50	1	.5	2	2.5	20	1.166
F	1.00	1	.2	5	2.8	20	0.777
F	0.75	1	.2	5	2.7	21	1.004
F	0.50	1	.2	5	2.5	20	1.214
G	1.00	1	.1	10	2.8	20	0.676
G	0.75	1	.1	10	2.7	21	0.826
G	0.50	1	.1	10	2.6	20	0.931
H	1.00	.5	1	.5	2.4	20	1.255
H	0.75	.5	1	.5	2.3	21	1.387
H	0.50	.5	1	.5	2.2	20	1.377
I	1.00	.2	1	.2	2.2	20	1.315
I	0.75	.2	1	.2	2.2	20	1.163
I	0.50	.2	1	.2	2.4	20	1.386
J	1.00	.1	1	.1	2.1	20	1.309
J	0.75	.1	1	.1	2.2	20	1.245
J	0.50	.1	1	.1	2.3	20	1.367

Table V

Effect of Metal Ratio of Bath on Plate Composition

4.0 amps/sq.dm. Temp 60° C.

Bath	Free CN	Ratio Sn/Cd	Ratio Sn/Cu	Ratio Cu/Cd	Volts	Time	Weight Plate
A	1.00	1	1	1	2.8	10	1.174
A	0.75	1	1	1	2.6	10	1.166
A	0.50	1	1	1	2.9	10	1.313
B	1.00	2	2	1	2.9	10	1.154
B	0.75	2	2	1	2.9	10	1.141
B	0.50	2	2	1	3.1	10	1.124
C	1.00	5	5	1	3.2	10	0.793
C	0.75	5	5	1	3.3	10	0.813
C	0.50	5	5	1	3.4	10	0.860
D	1.00	10	10	1	3.3	10	0.442
D	0.75	10	10	1	3.3	10	0.521
D	0.50	10	10	1	3.4	10	0.571
E	1.00	1	.5	2	3.2	10	0.997
E	0.75	1	.5	2	3.1	10	1.064
E	0.50	1	.5	2	3.0	10	1.105
F	1.00	1	.2	5	3.2	10	0.730
F	0.75	1	.2	5	3.3	10	0.812
F	0.50	1	.2	5	3.1	10	1.125
G	1.00	1	.1	10	3.2	10	0.526
G	0.75	1	.1	10	3.2	10	0.669
G	0.50	1	.1	10	3.1	10	1.019
H	1.00	.5	1	.5	2.6	10	1.215
H	0.75	.5	1	.5	2.8	10	1.361
H	0.50	.5	1	.5	3.0	10	1.301
I	1.00	.2	1	.2	2.6	10	1.350
I	0.75	.2	1	.2	2.7	10	1.357
I	0.50	.2	1	.2	2.8	10	1.301
J	1.00	.1	1	.1	2.6	10	1.349
J	0.75	.1	1	.1	2.8	10	1.379
J	0.50	.1	1	.1	2.6	10	1.264

Table VI

Effect of Metal Ratio of Bath on Plate Composition

0.5 amp/sq. dm. Temp 60° C.

Bath	Composition of Bath				Plate Analysis		
	N CN	N Sn	N Cd	N Cu	% Sn	% Cd	% Cu
A	1.00	.166	.156	.166	0.0	100.0	0.0
A	1.75	.166	.156	.166	0.0	100.0	0.0
A	0.50	.166	.156	.166	0.4	99.3	0.3
B	1.00	.249	.116	.165	0.0	100.0	0.0
B	0.75	.249	.116	.125	0.3	99.7	0.0
B	0.50	.249	.116	.125	0.8	99.2	0.0
C	1.00	.355	.065	.071	1.4	98.6	0.0
C	0.75	.354	.066	.071	7.1	92.9	0.0
C	0.50	.355	.064	.071	0.3	99.7	0.0
D	1.00	.418	.039	.042	8.9	91.1	0.0
D	0.75	.416	.038	.042	17.3	82.4	0.3
D	0.50	.419	.037	.042	17.9	81.7	0.4
E	1.00	.125	.117	.250	0.0	100.0	0.0
E	0.75	.125	.117	.250	0.0	100.0	0.0
E	0.50	.125	.116	.249	0.8	98.0	1.2
F	1.00	.071	.066	.355	0.0	100.0	0.0
F	0.75	.071	.063	.355	0.0	100.0	0.0
F	0.50	.071	.063	.354	1.1	80.7	18.2
G	1.00	.042	.038	.419	0.9	88.2	10.9
G	0.75	.042	.037	.419	0.8	88.6	10.5
G	0.50	.042	.037	.415	0.8	56.8	42.4
H	1.00	.125	.241	.125	0.0	100.0	0.0
H	0.75	.125	.240	.125	0.0	100.0	0.0
H	0.50	.125	.241	.125	0.0	100.0	0.0
I	1.00	.071	.345	.071	0.0	100.0	0.0
I	0.75	.071	.346	.071	0.0	100.0	0.0
I	0.50	.071	.345	.071	0.0	100.0	0.0
J	1.00	.042	.408	.042	0.0	100.0	0.0
J	0.75	.042	.409	.042	0.0	100.0	0.0
J	0.50	.042	.409	.042	0.0	100.0	0.0

Table VII

Effect of Metal Ratio of Bath on Plate Composition

2.0 amps/sq.dm. Temp 60° C.

Bath	Composition of Bath				Plate Analysis		
	N CN	N Sn	N Cd	N Cu	% Sn	% Cd	% Cu
A	1.00	.166	.146	.166	2.0	98.0	0.0
A	0.75	.166	.146	.166	4.5	94.0	1.5
A	0.50	.166	.146	.166	0.8	99.2	0.0
B	1.00	.249	.106	.125	3.6	96.4	0.0
B	0.75	.249	.106	.125	4.2	95.2	0.6
B	0.50	.249	.106	.125	2.2	97.8	0.0
C	1.00	.355	.055	.071	14.1	83.6	2.3
C	0.75	.353	.056	.071	16.8	78.9	4.3
C	0.50	.355	.055	.071	13.5	82.4	4.1
D	1.00	.417	.032	.042	18.0	80.7	1.5
D	0.75	.413	.031	.042	29.0	68.6	2.4
D	0.50	.416	.032	.042	24.2	70.7	5.1
E	1.00	.125	.106	.250	4.5	90.4	5.1
E	0.75	.125	.106	.249	2.7	95.6	1.7
E	0.50	.125	.101	.249	2.3	92.4	5.3
F	1.00	.071	.055	.355	2.5	73.5	24.0
F	0.75	.071	.054	.355	1.8	83.9	14.3
F	0.50	.071	.055	.351	1.4	65.9	32.7
G	1.00	.042	.029	.418	1.9	75.3	22.8
G	0.75	.042	.028	.418	2.3	64.5	33.2
G	0.50	.042	.030	.409	2.0	38.2	61.8
H	1.00	.125	.231	.125	0.0	100.0	0.0
H	0.75	.125	.230	.125	0.0	100.0	0.0
H	0.50	.125	.226	.125	0.0	100.0	0.0
I	1.00	.071	.334	.071	0.0	100.0	0.0
I	0.75	.071	.335	.071	0.0	100.0	0.0
I	0.50	.071	.335	.071	0.0	100.0	0.0
J	1.00	.042	.398	.042	0.0	100.0	0.0
J	0.75	.042	.398	.042	0.0	100.0	0.0
J	0.50	.042	.390	.042	0.0	100.0	0.0

Table VIII

Effect of Metal Ratio of Bath on Plate Composition

4.0 amps/sq.dm. Temp 60° C.

Bath	Composition of Bath				Plate Analysis		
	N.CN	N.Sn	N.Cd	N.Cu	% Sn	% Cd	% Cu
A	1.00	.166	.166	.166	1.9	97.7	0.4
A	0.75	.166	.166	.166	2.1	97.4	0.5
A	0.50	.166	.166	.166	2.0	97.4	0.6
B	1.00	.250	.125	.125	3.3	96.6	0.1
B	0.75	.250	.125	.125	3.9	95.9	0.2
B	0.50	.250	.125	.125	3.4	96.2	0.4
C	1.00	.356	.071	.071	10.9	87.3	1.8
C	0.75	.356	.071	.071	11.4	85.7	2.9
C	0.50	.356	.071	.071	10.8	86.7	2.5
D	1.00	.420	.042	.042	22.9	75.5	1.6
D	0.75	.420	.042	.042	14.2	83.5	2.3
D	0.50	.420	.042	.042	12.8	84.8	2.4
E	1.00	.125	.125	.250	3.6	92.8	3.6
E	0.75	.125	.125	.250	3.5	92.7	3.8
E	0.50	.125	.125	.250	1.6	93.6	4.8
F	1.00	.071	.071	.356	2.1	77.1	20.8
F	0.75	.071	.071	.356	2.2	83.2	14.6
F	0.50	.071	.071	.356	1.0	75.0	24.0
G	1.00	.042	.042	.420	0.0	74.3	25.7
G	0.75	.042	.042	.420	0.0	72.6	27.4
G	0.50	.042	.042	.420	0.0	47.2	52.8
H	1.00	.125	.250	.125	1.4	98.6	0.0
H	0.75	.125	.250	.125	1.1	99.0	0.0
H	0.50	.125	.250	.125	1.0	98.8	0.2
I	1.00	.071	.356	.071	0.0	100.0	0.0
I	0.75	.071	.356	.071	0.6	99.4	0.0
I	0.50	.071	.356	.071	0.6	99.5	0.0
J	1.00	.042	.420	.042	0.0	100.0	0.0
J	0.75	.042	.420	.042	0.3	99.7	0.0
J	0.50	.042	.420	.042	0.0	100.0	0.0

EFFECT OF TEMPERATURE ON % METALS IN DEPOSIT

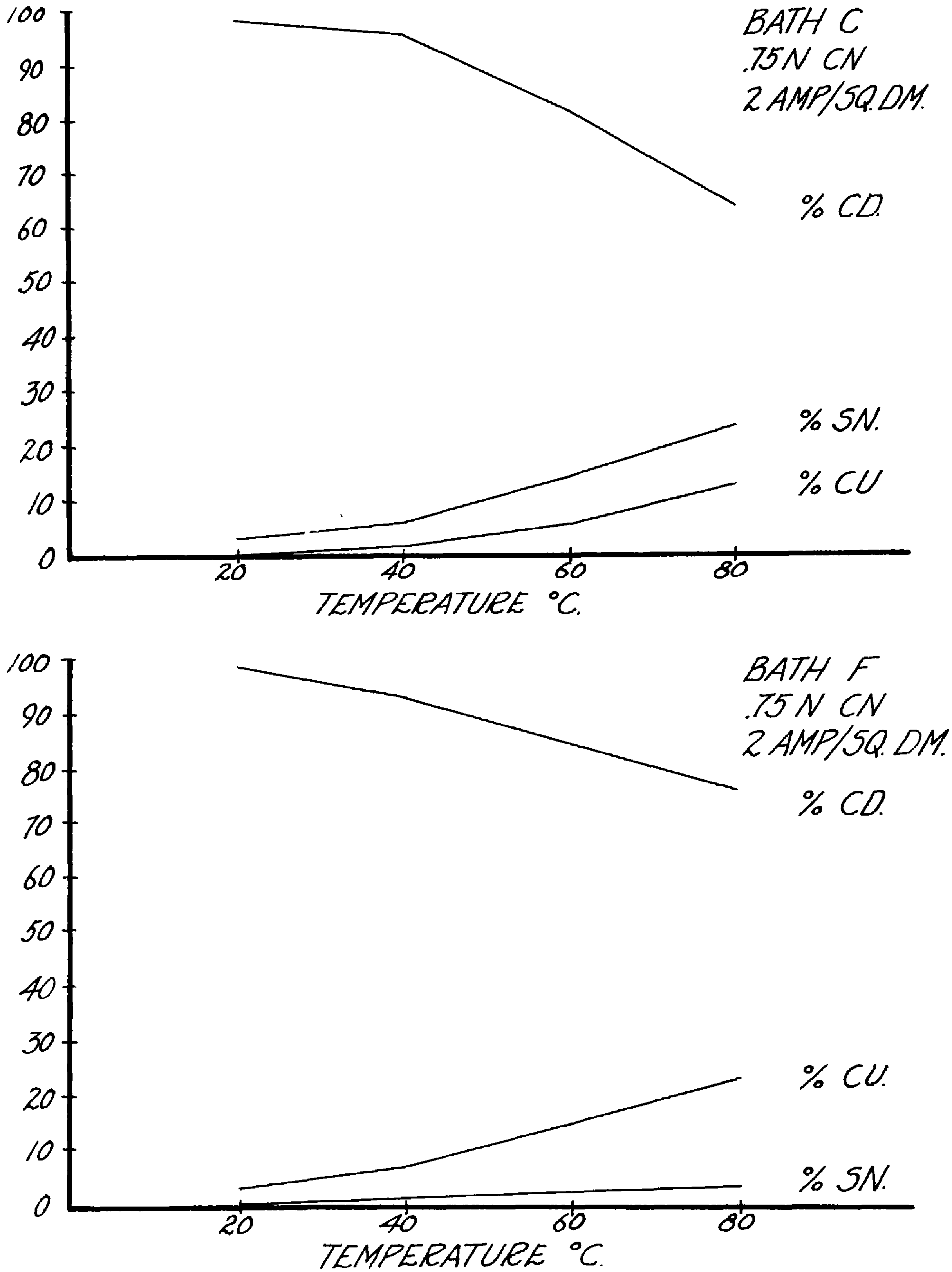

FIG. 1

EFFECT OF METAL RATIO IN BATH ON % TIN IN DEPOSIT

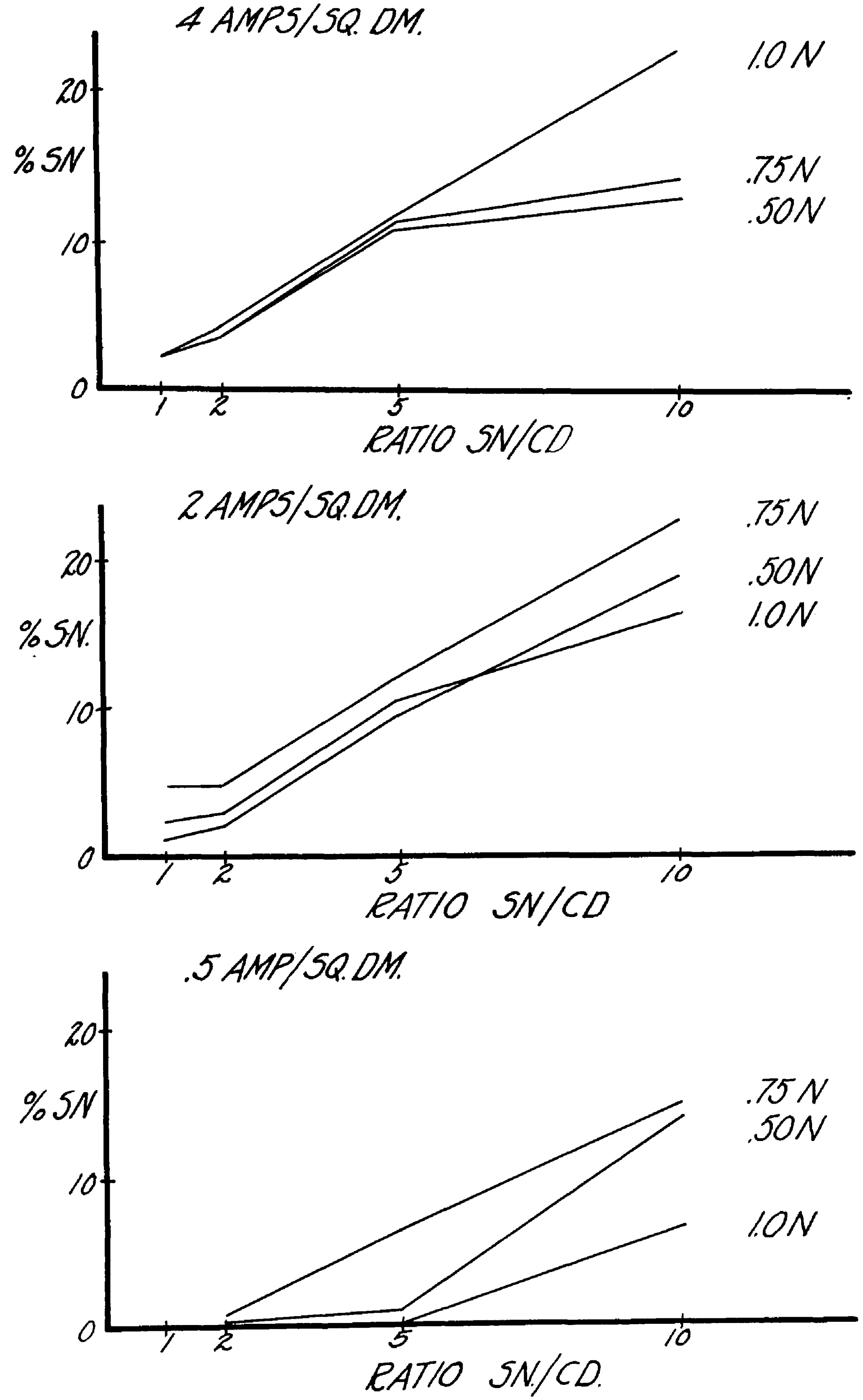

FIG. 2

EFFECT OF METAL RATIO IN BATH ON % COPPER IN DEPOSIT

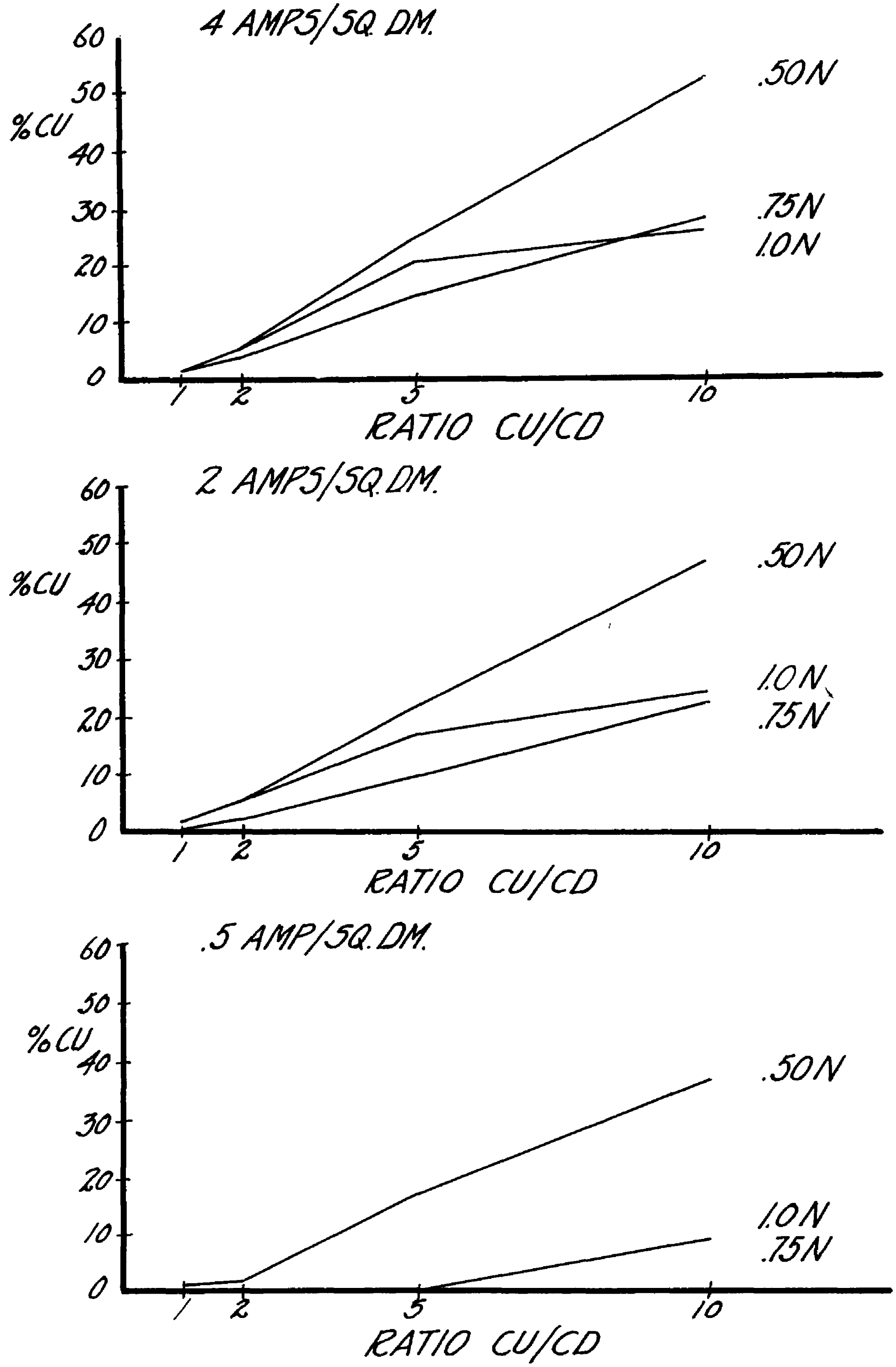

FIG. 3

EFFECT OF METAL RATIO IN BATH ON % CADMIUM IN DEPOSIT

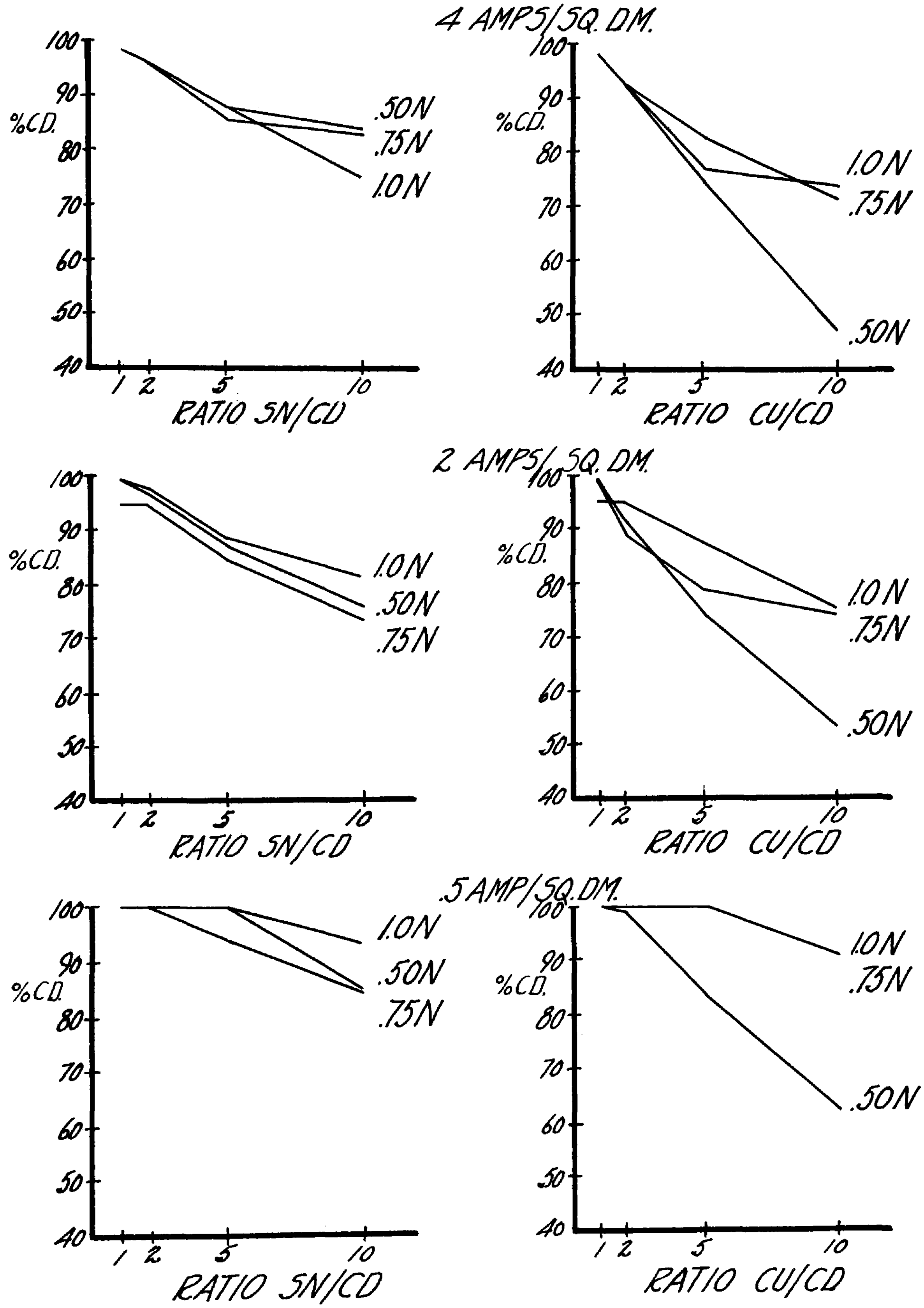

FIG. 4

EFFECT OF CYANIDE CONTENT ON % TIN IN DEPOSIT

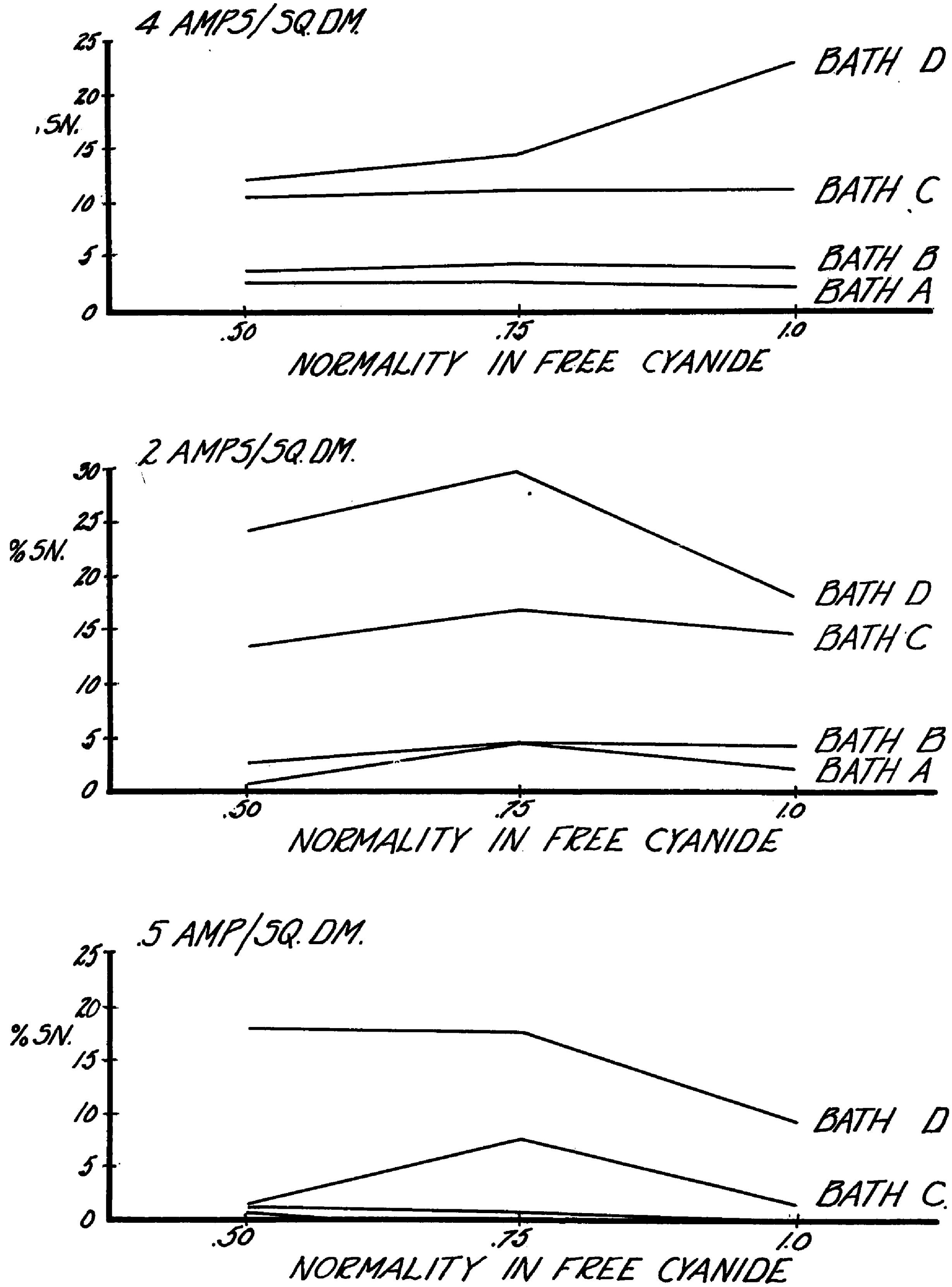

FIG. 5

EFFECT OF CYANIDE CONTENT ON % COPPER IN DEPOSIT

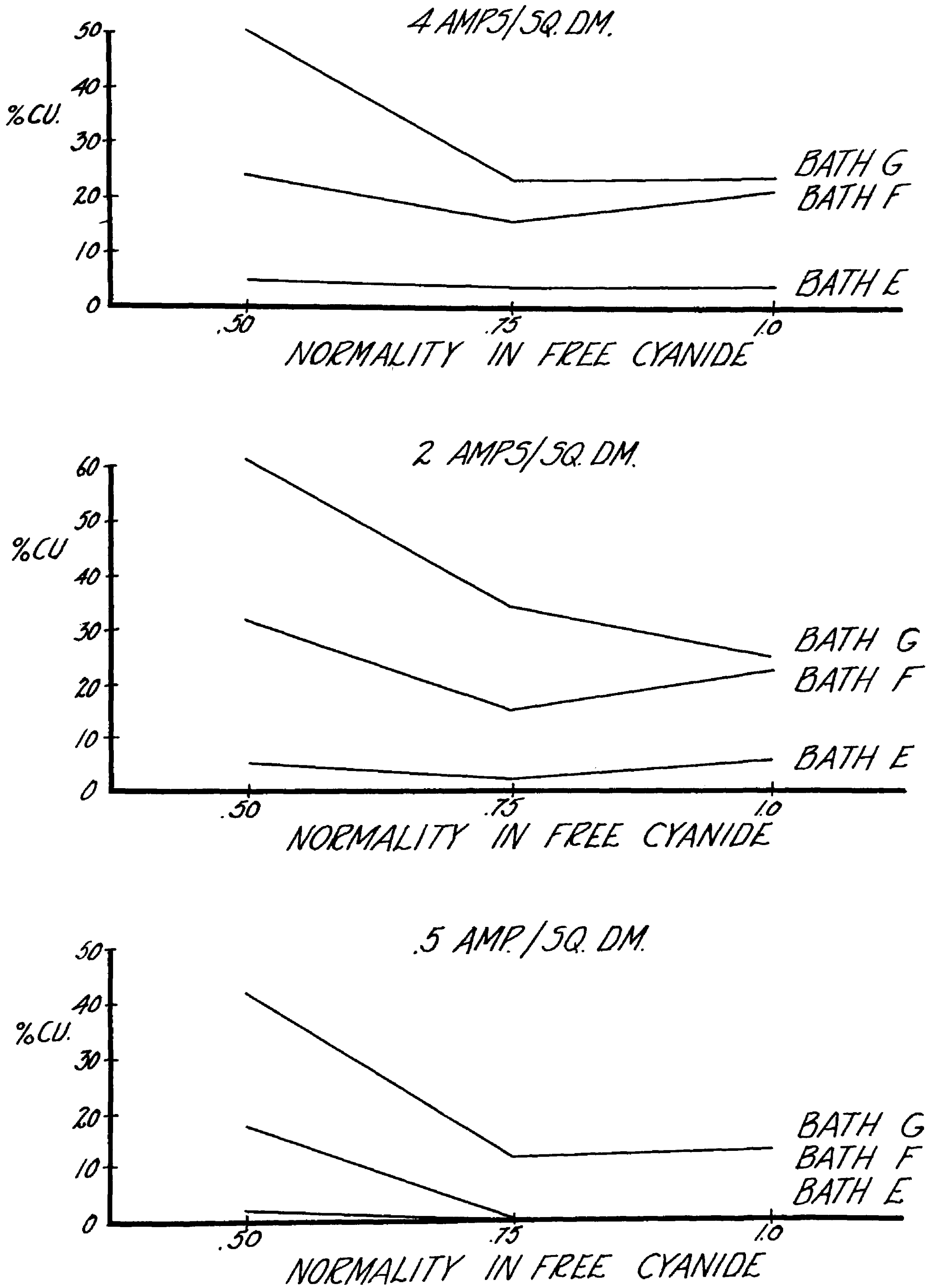

FIG. 6

EFFECT OF CYANIDE CONTENT ON % CADMIUM IN DEPOSIT

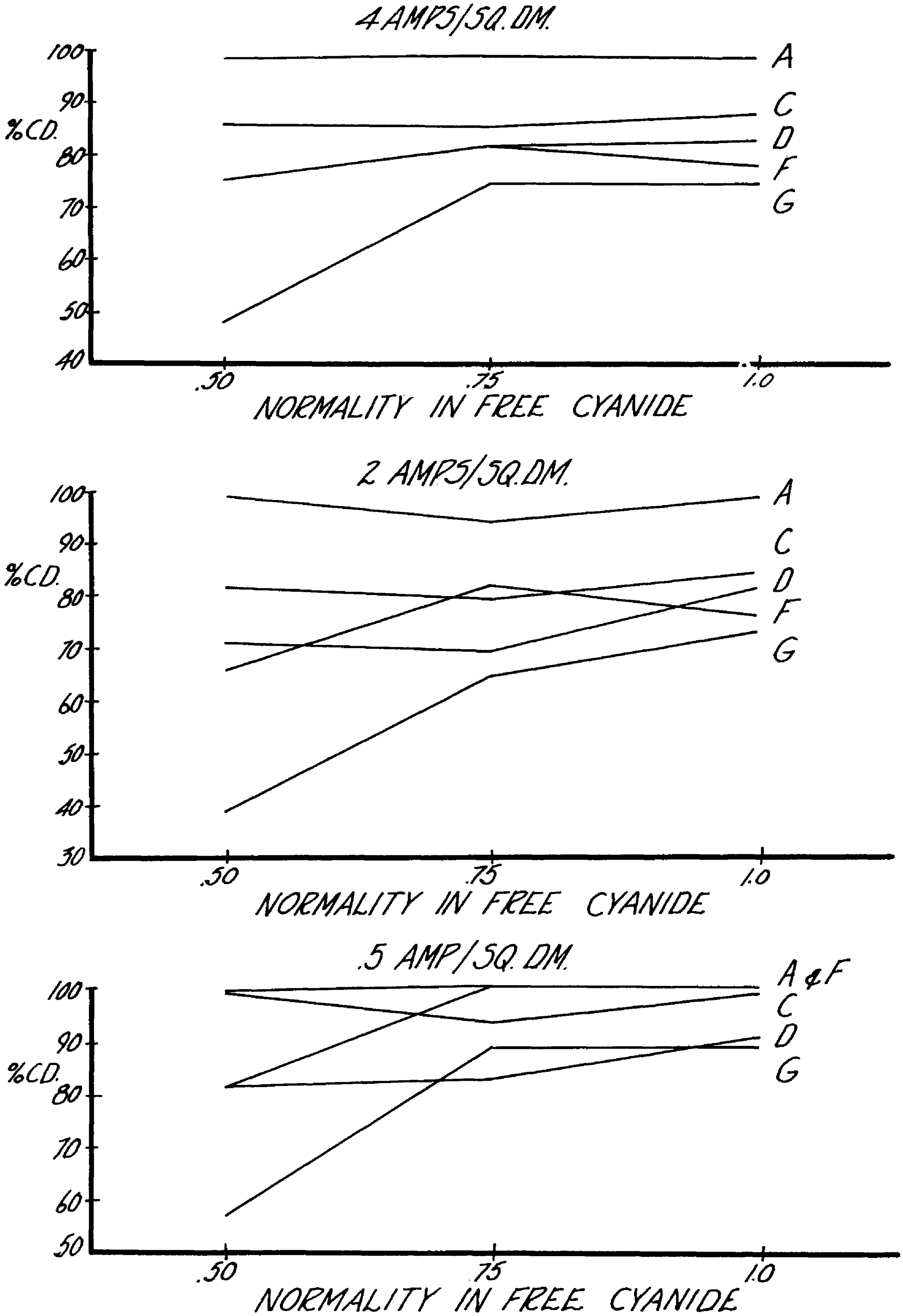

FIG. 7

EFFECT OF CURRENT DENSITY ON % TIN IN DEPOSIT

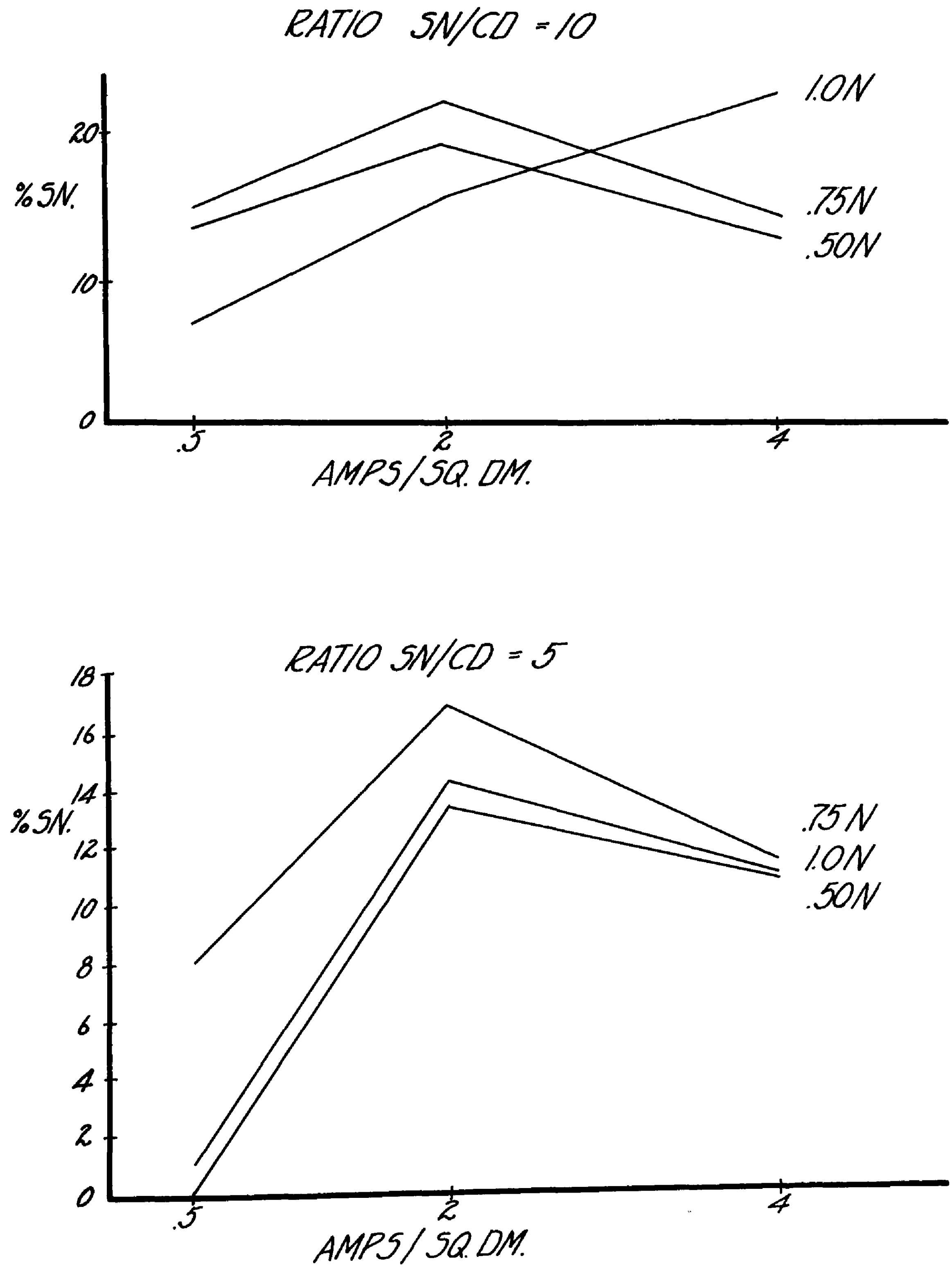

FIG. 8

EFFECT OF CURRENT DENSITY ON % COPPER IN DEPOSIT

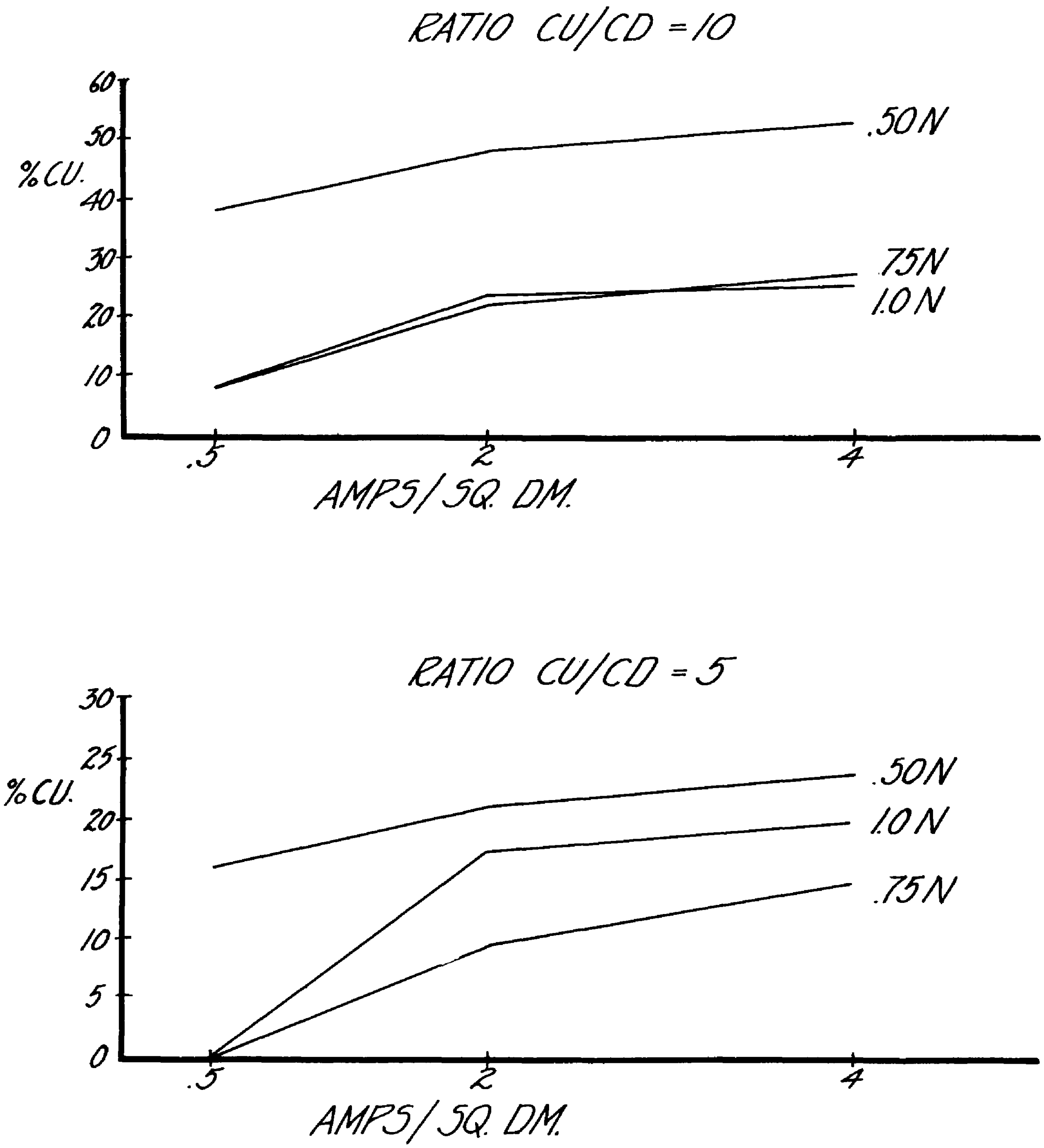

FIG. 9

EFFECT OF CURRENT DENSITY ON % CADMIUM IN DEPOSIT

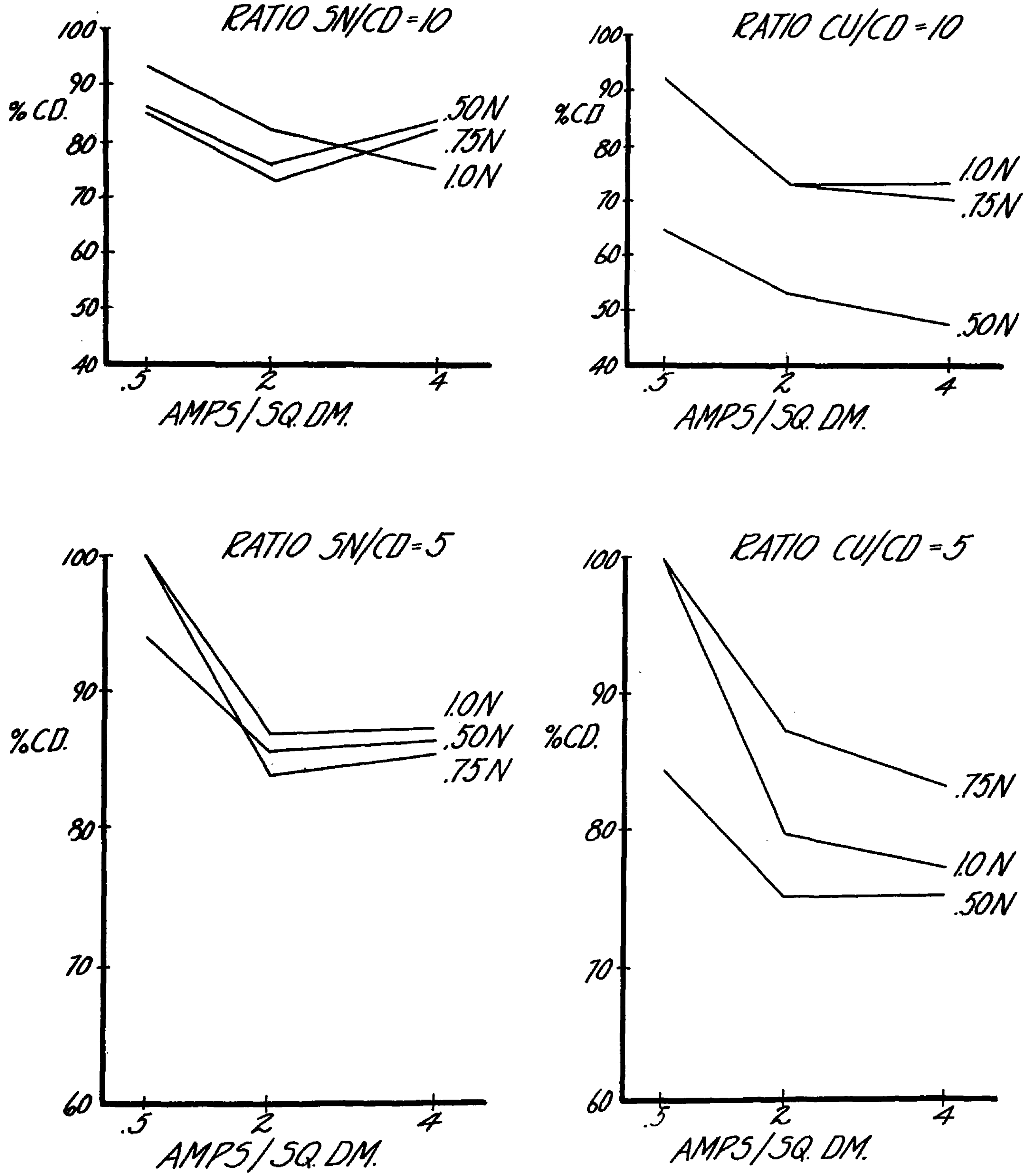

FIG. 10

The effect of temperature on the percent of the component metals in the deposit is shown graphically in Fig. 1. As the temperature increases the percent of cadmium decreases and the percents of copper and tin increase. The percent of copper increases faster than tin with increasing temperature. Theoretically, an increase in temperature should aid the deposition of the more noble metal. This was found to be the case.

Cadmium deposition is favored over that of copper and tin under the conditions of this investigation and copper is slightly favored over tin. It is necessary that there be a comparatively large tin or copper content in the bath to produce an appreciable amount of tin or copper in the deposit. When the tin content of the bath is maintained constant there is a higher percent of tin in the deposit when the copper content is greater than cadmium than when the cadmium predominates. In the same way there is more copper in the deposit from a high tin bath. The effect of metal ratio is shown in Figures 2, 3 and 4, drawn from data of Tables VI, VII and VIII. They show that all three metals behave in the usual way, an increase in the content of one metal causes an increase in the percent of that metal in the deposit. It is shown however, that when cadmium constitutes more than one-fourth of the metal content of the bath, there is very little tin or copper in the deposit. The copper content of the deposit increases more rapidly with increasing copper to cadmium ratio in the bath than does the tin content with increasing tin to cadmium ratio in the bath. This is especially true at low free cyanide concentrations and high current densities.

The effect of free cyanide on the composition of deposit is shown in Figures 5, 6 and 7, where the baths remain constant in metal ratio and the electrolysis is carried on at constant current density. At high current density baths low in tin content show little effect of cyanide; with high tin content of bath, the percent of tin in the deposit increases with increasing cyanide content. At two amperes per square decimeter the percent of tin increases with increasing cyanide up to .75 normal in free cyanide and then decreases with further increase in cyanide. At low current density, the percent of tin decreases with increasing cyanide content.

Baths high in copper content show a decrease in copper content with increasing cyanide throughout the range studied. With a copper to cadmium ratio less than five to one copper decreases with increasing cyanide up to .75 normal free cyanide, then increases with increasing cyanide. In general, the percent of cadmium increases with increasing cyanide, though changes in slope of curves and small changes in direction occur at a normality of .75 in free cyanide. We can predict that at very low cyanide concentration that copper deposition would be favored over cadmium.

The curves in Figures 8, 9 and 10 represent the situation in which the metal ratio is held constant and show the effect of current density on the percentage of metals in the deposit. The percent of tin increases with increasing current density up to two amperes per square decimeter and decreases with further increase in current density. Copper increases with increasing current density, though the amount of increase is less marked when more than two amperes are used per square decimeter. The cadmium content of the deposit decreases with increasing current density; the rate of decrease is less when amperages greater than two amperes per square decimeter are employed; this is more marked in baths of high cadmium and high tin content. Where the ratio of cadmium to tin is one to ten there is a reversal and the percent of cadmium increases as the current density is increased past two amperes per square decimeter.

SUMMARY

This investigation shows that ternary alloys of copper, cadmium and tin can be electrodeposited from aqueous solutions of sodium stannate, complex cyanides of cadmium and copper, excess sodium cyanide, sodium carbonate and sodium hydroxide.

Cadmium content of plate, favored over the deposition of copper and tin, can be increased by increasing the cadmium content of the bath, increasing the free cyanide content of the bath and decreasing the current density and temperature.

The copper content of the alloys can be increased by increasing the copper content of the bath, increasing the current density, decreasing the concentration of free cyanide and increasing the temperature.

The tin content of the alloys can be increased by increasing the tin content of the bath, increasing the current density up to two amperes per square decimeter, increasing the free cyanide up to .75 normal and increasing the temperature.

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