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UNIVERSITY OF LOUISVILLE

THE ELECTRO-DEPOSITION OF THE BINARY SYSTEM

COPPER - CADMIUM

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

Allen Stratton Smith

1931

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I-INTRODUCTION

HISTORICAL

It is known that under certain conditions it is possible to deposit electrochemically two or more metals simultaneously from their mutual solution. The only alloy which is extensively deposited commercially is brass (1), although bronzes (2) and lead-tin (3) alloys have been electrodeposited, the latter on a small commercial scale by the U. S. Navy Department. Mention is also made in the literature of electrodeposited alloys of nickel-magnesium (4), iron-zinc (5), zinc-nickel (6), silver-gold (7), silver-cadmium (8), nickel-copper (9), nickel-iron (10), tin-cadmium (11), and cobalt-nickel (12).

Alloy deposition is subject to numerous undefined variables, and although certain general principles are known their application demands considerable research which has not been forthcoming, resulting in empirical bases for commercial alloy deposition. The first paper of this series on alloy deposition, prepared for the expressed purpose of placing the electrodeposition of the present commercial alloys on a scientific basis; and for the development of new, commercially useful alloys by a study of theoretical principles and their intelligent application, will appear shortly in the Journal of the American Electrochemical Society (13).

Numbers in parentheses refer to bibliography at end of volume.

THEORETICAL

Alloys of copper containing small amounts of cadmium, up to 1.2 percent, have been used in the form of wire for electrical transmission. Such alloys have an electrical conductivity greater than any other alloy of equivalent tensile strength, and may be mechanically worked. The tensile strength of hard drawn copper-cadmium wire, .081 inch in diameter, containing 1.1 percent cadmium is 100,000 pounds per square inch, while the conductivity of the annealed wire is 91 percent.

The physical properties and micro-constituents of copper-cadmium alloys prepared from the pure metals have been determined. The tables prepared by N. A. Pushin (14) show the presence of the three phases: Cd_2Cu , solid solutions of Cd in Cd_2Cu and of Cd_2Cu in Cu. From a study of the constitution of cadmium-copper alloys, C. Jenkins and D. Hansen (15) state that four intermediate constituents appear to exist: Cu_2Cd , Cu_4Cd_3 , Cu_2Cd_3 , and CuCd_3 . The existence has also been established of a metastable condition in which the α constituent is suppressed and a metastable eutectic included.

Up to 60 atomic percent copper the alloys are white; with 68 atomic percent copper they are bright yellow; with 80 atomic percent copper, rose colored; and with 90 atomic percent copper, red (copper color). The hardness with the concentration of copper, reaching a maximum at 33

atomic percent copper. Further addition of copper makes them brittle. Between 40 and 50 atomic percent copper the brittleness is such that they can be broken by hand. With 68 atomic percent they again become very hard and remain so up to 80 atomic percent copper when the hardness again decreases, gradually approaching that of pure copper.

Since copper-cadmium alloys for use in electrical transmission contain only small amounts of cadmium, metallurgical methods of preparation would be more economical. Alloys containing a high percentage of cadmium would be commercially useful for corrosion resisting coatings. Pure cadmium deposits take well on all metals, are highly resistant to atmospheric corrosion, and take a high polish. They are of a color approaching silver, but retain their polish without tarnishing longer than silver, or silver alloys. They are superior to tin as rust resisting agents for iron and steel, and form a highly efficient protective coating for aluminum.

A consideration of corrosion resisting alloys leads to the conclusion that to increase the resistance to corrosion of any base metal there should be alloyed with it another metal which is more resistant to corrosion and which a solid solution with the metal whose resistance to corrosion it is desired to enhance. In considering a copper-cadmium alloy, copper fulfills these conditions being nobler than cadmium, and forming solid solutions (16).

An alloy of two metals is commonly heterogeneous

in that it consists of an aggregate of crystals of two or more different kinds, containing the constituent metals in different proportions. In some cases the whole alloy consists of only one species of crystal, i.e. a single phase. In the former case, where there are two or more phases, the equilibrium potential of the alloy is determined essentially by the basest phase present. The chemical behavior of an alloy is indicated by its equilibrium potential. Thus it will replace from solution a metal which has a more positive equilibrium potential against that solution. Similarly, it will tend to replace hydrogen from an acid if its potential is baser than that of hydrogen against that acid. In each case it is the basest phase which will go into solution.

Fig. 1 (17) shows potential-composition curves for three types of alloys. In all cases A represents the baser metal and B the more noble. Curve I represents two metals which are insoluble in the solid state and form an inter-metallic compound A_2B_3 . Curve II corresponds to an alloy which does not form a complete series of solid solutions. Curve III is an example of two metals which are mutually soluble in the solid state in all proportions. The system copper-cadmium is an example of Curve II forming solid solutions of Cu in Cu_2Cd and Cu_2Cd in Cu, as well as several intermediate constituents.

Fig. 1
Potential-Composition Curves

Table I

Intermediate Constituents of The System Cu-Cd

Compound	Weight Percent		Atomic Percent	
	Cu	Cd	Cu	Cd
Cu_2Cd	53.2	46.8	66.6	33.4
Cu_4Cd_3	43.0	57.0	57.1	42.9
Cu_2Cd_3	27.4	72.6	40.0	60.0
Cu Cd_3	15.9	84.1	25.0	75.0
Cu Cd_2^*	22.1	77.9	33.3	66.7

*Not certain

Reference to Table I and Fig. 2 will show that an alloy containing approximately 53 percent copper and 47 percent cadmium will give a binary compound having a large proportion of the intermediate compound Cu_2Cd which forms a solid solution with Cu. It is the purpose of this thesis, then, to electrochemically deposit a copper-cadmium alloy containing approximately 55 percent copper. The above deductions are based entirely on the assumption that the electrodeposited alloy has a microstructure analogous to that of the binary system prepared from the pure metals, which is not definitely known.

Simultaneous deposition of two metals is, in general, only possible when the single potentials of the two metals lie very close together, unless either the deposition of the baser metal is considerably depolarized or the concentration of the ions is varied by regulation of current

Fig. 2
Copper-Cadmium Constitution Diagram

density, formation of complex ions or addition of the ion.

Metals below hydrogen in the electromotive series can be deposited from acid solutions with a high cathode efficiency because the single potential of the metal in a solution normal with respect to metal and hydrogen ions is higher than that of hydrogen. The deposition of hydrogen will therefore require a greater potential than would be necessary to deposit the metal, and hence will deposit with a high efficiency. This is shown by the Nernst formula which explains the origin of electromotive force on the basis of osmotic and solution pressure relations.

$$E = \frac{RT}{nF} \log_e \frac{P_s}{P_o}$$

Where

E = single electrode potential

R = gas constant expressed in volts, coulombs

F = electrochemical equivalent

n = valence of the metal ions

P_s = electrolytic solution pressure

P_o = osmotic pressure

T = absolute temperature of solution

Since osmotic pressure is proportional to the effective concentration, $P_o = KC$.

$$E = \frac{RT}{nF} \log_e \frac{P_s}{KC}$$

Since P_s/K is a constant at any given temperature, the single potential is

$$E = E_0 + \frac{RT}{nF} \log_e C$$

Where

E_0 = electrolytic potential

C = concentration in gram ions per liter

For two metals to be simultaneously deposited, their cathode potentials must be equal or lie very close together. The single potential of the two metals do not lie close together as may be seen in Table II (18).

Table II

Single Potentials of Metals Toward Solutions
with Normal Metal Ion Concentration

Metal	Volts*
Cadmium	- 0.40
Hydrogen	0.00
Copper	0.34

*Based on normal hydrogen electrode as zero.

If, however, the concentration of metal ions is decreased, e.g. by dilution, or the concentration of hydrogen ions is decreased, e.g. by addition of an acid, the potential of the metal may decrease while that of hydrogen increases and the two approach each other. When the potentials become equal, simultaneous deposition of the metal and hydrogen becomes possible. If the single potential were the only factor governing deposition, definite results could be predicted but current density (Fig. 3) (19), polarization,

Fig. 3

Current Density-Potential Curves
For Copper and Cadmium
in KCN Solution

overvoltage and temperature have also been shown to be important factors.

The potentials of copper and cadmium lie relatively far apart so that it is impossible to deposit them simultaneously from a solution in which their ionic concentrations are high. A low concentration of their ions may be obtained by extreme dilution and by the use of complex ion solutions. The complex cyanides of copper and zinc are used in brass plating, and those of copper and cadmium should be applicable in the proposed copper-cadmium alloy deposition. Reference to the ionic equations (20) shows the sources of the ions and Table III (21) indicates the relative amounts of each which will be present.

Table III

Instability Constants for the Complex Cyanides of Cu and Cd

Compound	Instability Constant	Conc. of metal ion in .1 M. sol.
$K_2(Cu(CN)_3)^*$	$\frac{(Cu^+) \times (CN^-)^3}{(Cd(CN)_4^{--})} = 0.5 \times 10^{-27}$	3.7×10^{-8}
$K_2(Cd(CN)_4)$	$\frac{(Cd^{++}) \times (CN^-)^4}{(Cd(CN)_4^{--})} = 1.4 \times 10^{-17}$	8.0×10^{-5}

*The correct formula for the copper complex is $KCu(CN)_2$ as determined by hydrogen ion measurements (22). It is assumed, however, that ^{like}the compound $K_2Cu(CN)_3$, it is more stable than the cadmium complex.

The fact that the addition of cyanide reduces the concentration of copper ions more rapidly than that of cadmium ions is the basis for the supposition that copper and cadmium can be simultaneously deposited since, as the concentration of copper ions decreases, its potential is reduced and approaches that of cadmium. Fig. 4 shows the effect of KCN on discharge potential (23). Copper and cadmium may be separated in a solution containing less than .25 mole of free KCN per liter and more than .275 mole. In the first solution the discharge potential of copper is less than that of cadmium and therefore would be preferen-

Fig. 4
Effect of KCN on Discharge
Potential

tially deposited before copper since its discharge potential is lower than that of copper.

Fig. 5 (17) shows graphically the effect of the addition of KCN. The potentials of both cadmium and copper are reduced, i.e. made more negative, by addition of KCN but that of copper is reduced more rapidly than that of cadmium so that the potential of the former gradually approaches, equals and becomes less than the latter. At the point where the potentials of copper and cadmium become equal simultaneous deposition is possible.

Depolarization of the deposition of the baser metal, i.e. cadmium, may also cause the equilibrium potentials of the two metals to become equal or nearly equal, so that simultaneous deposition may be effected. It is intended to study the conditions by which a simultaneous deposition of copper and cadmium may be obtained in the desired proportions.

Fig 5
Effect of KCN Addition on
the Potentials of Copper and
Cadmium

Cu +.34

0

Cd -.40

II - EXPERIMENTAL

Preliminary
Apparatus and Procedure

In order to determine from what type of bath a deposit containing copper and cadmium could be obtained, stock solutions of the complex copper cyanides and the complex cadmium cyanide were made up and these were used to prepare baths of different metal ion concentrations and different copper-cadmium ion ratios.

Table IV
Stock Solutions

Solution	Salt Used	Concentration	Total KCN	% Excess	Metal ion Content
$\text{KCu}(\text{CN})_2$	CuCN	40.2 g./l.	66.0 g./l.	158	28.5 g./l.
$\text{K}_2\text{Cd}(\text{CN})_4$	$\text{Cd}(\text{CN})_2$	46.5	76.9	169	31.8

Four cells were used connected in parallel with carbon anodes and nickel cathodes. Nickel was used as it had a low overvoltage and was but slightly soluble in concentrated nitric acid, in which the deposit was dissolved for analysis, since sufficient platinum for use as cathodes was not available. A current density of 0.3 ampere per square decimeter was maintained at the cathode.

A qualitative analysis only was performed for copper in the deposit. The cathodes were washed and dissolved in 50 c.c. of concentrated nitric acid. The solutions were evaporated to a volume of 5-10 c.c., diluted

with 25 c.c. of distilled water, neutralized with dilute ammonium hydroxide and made acidic with acetic acid. 5 c.c. of the solutions were tested with potassium ferrocyanide, one drop being added, allowed to stand for 2-3 minutes, then 3 c.c. more added. A pink to red coloration indicated the presence of copper. The intensity of color in both the ammonia and potassium ferrocyanide solutions was compared and the relative amounts of copper present in each deposit was thus judged. A summary of the data obtained in the preliminary work follows.

Preliminary Results with
Several Metal Ion Ratios and an Addition Agent

Solution No.		1	2	3	4
Metal ion ratio	Cu	90	70	50	30
	Cd	10	30	50	70
Total metal ion content		28.75	29.40	30.10	30.7
Copper analysis		Present	None	None	None

Same solutions as above; 12 g./l. added to each one of NaHSO_3 .

Solution No.		5	6	7	8
Copper Analysis		Present	None	None	None

Same solutions as above; 12 g./l. of NaHSO_3 additional added to each one.

Solution No.		9	10	11	12
Copper analysis		None	Present	None	None
Solution No.		13	14	15	16
Metal Ion Ratio	Cu	60	60	60	60
	Cd	40	40	40	40
Total Metal Ion Content		29.8	29.8	29.8	20 g./l.
NaHSO_3 added, g./l.		0.0	12	24	8
Copper Analysis		Trace	None	None	Present
Solution No.		17	18	19	20
Metal Ion Ratio	Cu	60	60	60	60
	Cd	40	40	40	40
Total Metal Ion Content		25	25	20	20 g./l.
NaHSO_3 added, g./l.		0	10	0	8
Copper Analysis		None	Trace	Trace	Present

It is evident from the preliminary results that a low metal ion concentration and the presence of NaHSO_3 (which reduces the amount of free KCN, see explanation under "Effect of NaHSO_3 Addition", page 30) are to be desired. A bath for the experimental work was therefore selected containing copper and cadmium in the ratio of 60:40 and a total metal ion concentration of 20 grams per liter.

Experimental Work - Final

Apparatus and Procedure

The cell used was a crystallizing dish. Cast anodes of copper and cadmium were employed, and a cathode consisting of a small platinum crucible one and three-eighths inches in height, three-fourths inch in diameter at the bottom and one and one-eighth inches at the top. A Leeds and Northrup potentiometer hookup was used for potential measurements with a saturated calomel reference electrode by three salt agar-agar bridges to the neighborhood of each electrode. The current density at the cathode and anode was kept equal and the current density at each anode was one-half of that at the cathode which was 0.3 ampere per square decimeter. A wiring diagram of the instruments and apparatus is shown in Fig. 7.

The composition of the four solutions used in the different runs is given in Table V.

Table V.

Composition of Plating Solutions

Solution No.	I	II	III	IV
CuCN g./l.	16.93	16.93	16.93	21.17
Cd(CN) ₂ g./l.	11.70	11.70	11.70	7.31
KCN g./l.	43.20	44.90	49.20	48.34
Percent excess KCN	100.00	105.00	127.00	128.00
Cu/Cd Ratio	60:40	60:40	60:40	60:20
Total Metal Ion Content, g./l.	20.0	20.0	20.0	20.0

WIRING DIAGRAM OF THE APPARATUS

1. Student Type Potentiometer
2. Resistance Box
3. Weston Standard Cell
4. Galvanometer
5. Protecting Resistance

6. Plating Bath
7. Milliammeter
8. Ammeter
9. Copper Coulombmeters
10. Voltmeter

Fig. 7

Each run was approximately two hours in length. Ten minute readings were taken of the current at the electrodes and in the line, and the potential of the electrodes in the solution with the current flowing. Single potentials of the electrodes were also measured before and after each run without the current flowing. Copper coulometers were used in each electrode circuit to check the total quantity of current passed.

The electrodes and coulometer cathodes were removed from the cells after the runs, washed with water, alcohol and ether, dried in a dessicator and weighed. The deposit on the platinum cathode was dissolved in 1:2 Nitric acid and the copper was determined by the method in Scott's "Technical Analysis", page 193. Cadmium was taken by difference. Calculations were made to determine anode and cathode efficiencies. Data sheets are given together with curves showing the variation of electrode potentials with time, single potential with copper content of the deposit, and the efficiencies with copper content. Further experiments were made to determine the effect of sodium bisulphite. In the following pages, the observed results are discussed and presented in tabular and graphical form. Agitation was not used since it was known from previous work to be of no value (15).

Table VI
Experimental Data

Run No.	Efficiencies			Percent Cu in Deposit	Total KCN g./l.	Potential with Current			Character of Deposit
	Anodes		Cathode			Anodes		Cathode	
	Cu	Cd				Cu	Cd		
4	52.9	115.9	76.4	30.5	47.2	2.6225	0.8580	2.0870	Gray
5	101.9	117.6	77.5	25.98	53.2	0.4625	0.9650	2.0375	Streaked
6	53.7	110.02	71.9	13.02	53.2	4.4760	0.8780	2.1635	Smooth
7	10.15	116.7	33.0	3.69	53.2	1.2125	0.9000	1.4445	Gray
8	62.6	111.8	63.5	21.92	53.2	4.4865	0.9440	2.1255	Blistered
9	61.2	119.8	79.4	23.69	59.2	4.4230	0.8825	1.7100	Gray
10	77.4	104.2	67.2	19.86	54.2	0.2825	0.2425	2.2240	Rough
11	55.7	113.8	97.2	29.05	49.2	5.0615	0.6515	1.0000	Gray
12	110.0	117.4	65.2	6.30	68.3	0.5440	0.9430	2.3455	Streaked
13	88.5	109.4	70.8	9.92	58.3	4.2280	0.8480	2.2375	Gray
14	41.3	78.7	89.0	33.40	48.3	0.9935	2.3000	2.5200	Smooth
15	75.4	116.7	125.8	58.4	48.3	3.8075	0.4850	1.8730	Gray
Current Density- 0.3 Amp./sq. dm. Temperature- 22-24°C.									

Fig. 8
Potential-Time Curves

Fig. 9
Electrode Efficiencies

Table VII
Single Potential of Alloy Deposits

Run No.	E.M.F.	E.M.F. of Reference Electrode	Single Pot.	Percent Cu
5	1.1310	.5260	.6050	25.98
6	1.1240	.5264	.5976	13.02
7	1.0865	.5264	.5261	3.69
8	1.0930	.5266	.5664	21.92
9	1.1235	.5263	.5972	23.69
10	1.1160	.5266	.5894	19.86
11	1.0830	.5268	.5562	29.05
12	1.1820	.5264	.6556	6.30
13	1.1250	.5263	.5987	9.92
14	1.0575	.5262	.5313	33.40
15	0.9740	.5264	.4476	58.40

E.M.F. of Saturated Calomel electrode at 25°
equals 0.5266 volt.

Temperature coefficient: 0.0002 v./°C.

Fig. 10
Single Potential of Alloy Deposits

Effect of Potassium Cyanide

Theory

The effect of KCN on the metal ion concentration of the plating bath was first studied. An increase of the cyanide ion, CN^- , should decrease the secondary ionization of the complex cyanide salts, as shown by the equations on Page 11, and thus decrease the concentration of the metal ions. The ionization constants for the secondary ionization of the complex copper salt is less than that for the complex cadmium salt which supports the fact that the concentration of copper ions is decreased more rapidly by the addition of the cyanide ion than that of the cadmium ions.

KCN should, therefore, reduce the copper content of the deposit. The experimental results agree closely with the theoreticall facts as shown by the results given in Table VIII. Runs A and B were made using a bath of metal ratio of Cu:Cd of 60:40 while in the other runs a bath containing Cu and Cd in the ratio of 60:20 was used.

Table VIII
Effect of Potassium Cyanide

Run No.	Efficiencies			Percent Copper	Total KCN	Potential with Current		
	Cu	Cd	Cathode			Cu	Cd	Cathode
A	52.6	115.9	76.4	30.54	47.2	2.6225	0.8580	2.0870
B	101.9	117.6	77.5	25.98	53.2	0.4625	0.9650	2.0375
C	55.7	113.8	97.2	29.05	48.3	-5.0615	0.6560	1.0000
D	88.5	109.4	70.8	9.92	58.3	-4.2280	0.8480	2.2375
E	110.0	117.4	65.2	6.30	68.3	0.5440	0.9430	2.3455

Discussion

Figs. 11 and 12 show graphically the various effects of the addition of KCN. The curves, while not being complete, show the trend of the effect. Increasing the amount of free cyanide increases the potential of the anodes and the cathode. Increased polarization of the cathode is accounted for by the fact that the equilibrium of the ionization of the complex salts (see page 11) is shifted toward the left resulting in a decrease in metal ions. In order to deposit the copper and cadmium a greater potential at the cathode is necessary then. The percentage of copper in the deposit decreases as the amount of KCN is increased which is to be expected from the increased cathode polarization. Anode efficiencies increase while the cathode efficiency decreases as the result of the suppression of metal ions and the resulting increase in cathode potential causing deposition of larger quantities of hydrogen.

Fig. 11
Effect of KCN

1. Eff. Cd Anode
2. " Cu "
3. " Cathode "
4. Percent Copper in Deposit

Fig. 12
Effect of KCN

1. Potential Cathode
2. " Cd Anode
3. " Cu "
4. Percent Copper in Deposit

Effect of Sodium Bisulphite Addition

Theory

A study of the various ionization equations of the copper and cadmium complexes, page 11, show that acid and alkaline substances should have a pronounced effect on the concentration of metal ions and thus would influence the composition of the deposit. It is evident that an addition of an alkaline substance would force the reactions to the left, decreasing the metal ion concentration and increasing the amount of undissociated complex salt. Acid substances, on the other hand, would force the reactions to the right by reacting with the potassium hydroxide and forming the slightly dissociated hydrocyanic acid and water. The concentration of metal ions would be decreased from the greater dissociation of the complex salts. The stability of the copper and cadmium complex salts are dissimilar (see page 12), that of copper being greater. The dissociation of the cadmium complex salt thus proceeds more rapidly than that of the copper and the ratio of cadmium to copper ions becomes greater. The potential of copper approaches that of cadmium as its ionic concentration decreases and it may even become more electro-negative than the cadmium. The ratio of the percent of copper to the percent of cadmium deposited is increased as the potential of copper becomes equal to and becomes lower than that of cadmium as seen in Fig. 5

Experimental Results

The addition of sodium bisulphite was found to increase the copper content of the deposit. Table IX shows the results obtained in a bath containing copper and cadmium in the ratio of 60:20.

Table IX

Effect of Sodium Bisulphite Addition

Efficiencies			Percent Cu	NaHSO ₃ g./l.	Potential with Current		
Cu	Cd	Cath.			Cu	Cd	Cath.
55.7	113.8	97.2	29.05	0.0	-5.0615	0.6560	1.0000
61.2	115.0	79.4	33.40	12.5	-4.4230	0.5231	1.7100
75.4	116.7	125.8	58.40	20.0	-3.8075	0.4850	1.8730

Figs. 13 and 14 show the effect of sodium bisulphite on the efficiencies and potentials of the cathode and the anodes.

Discussion

Sodium bisulphite is but a slightly acid substance and its acid properties should not be great enough to cause an increase in the forward reaction to a very great degree. The reaction would proceed to completion if one of the products were removed from the reaction. Von Pechman and Manck (24) have shown that an addition product of the formula

Fig. 13
Effect of NaHSO_3

1. Efficiency of Cathode
 2. " " Cd Anode
 3. " " Cu " "
 4. Percent Copper in Deposit

Fig. 14
Effect of NaHSO_3

1. Potential Cathode
2. Percent Copper in Deposit
3. Potential Ed Anode
4. " Cu "

is formed when hydrocyanic acid reacts with sodium bisulphite. If this reaction is correct, the explanation of its effect in increasing the percent of copper in the deposit is readily understood.

Effect of Current Density

All the runs were made using a current density at the cathode of .3 ampere per square decimeter. The effect of increasing the current density was briefly studied and the results, as shown in Table X, show that an increase materially decreases the copper content of the deposit.

Table X

Effect of Current Density

Efficiencies			Percent Cu	Current Density	Potential with Current		
Cu	Cd	Cath.			Cu	Cd	Cath.
101.9	117.6	77.5	25.9	66.7	0.4625	0.9650	2.0375
53.7	110.0	71.9	13.0	95.4	4.4760	0.8780	2.1635

It may be seen in Figs. 15 and 16 that the cathode potential increases with the current density. This would cause the deposition of hydrogen and the baser metal, cadmium, to take place in larger quantities, resulting in decreased cathode efficiency and a lower percentage of copper in the deposit. The curves show this to be true. At the higher current density the deposit is blistered and heavily streaked at the sides.

Fig 15
Effect of Current Density

1. Efficiency Cd Anode
 2. " Cathode
 3. " Cu Anode
 4. Percent Cu in Deposit

Fig 16
Effect of Current Density

1. Potential Cathode
2. " Cd Anode
3. " Cu
4. Percent Cu in Deposit

Effect of Temperature

The temperature at which the runs were made was kept between 22 and 24°. An increase of temperature, it was thought, would increase the percentage of copper in the deposit since there would be a more rapid diffusion of metal ions towards the cathode. In investigations on the effect of temperature in brass plating solutions (1) shows this to be true. The results given in the following table and in Figs. 17 and 18 show that this is not the case in the simultaneous deposition of copper and cadmium.

Table XI

Effect of Temperature

Efficiencies			Percent Cu	Temp. °C.	Potential with Current		
Cu	Cd	Cath.			Cu	Cd	Cath.
101.9	117.6	77.5	25.9	22	0.4625	0.9650	2.0375
10.2	116.7	33.0	3.7	68	1.2125	0.9000	1.4445

The efficiency of the cathode and anode rapidly decrease with increased temperature which may be explained by the increased chemical solubility of the metals and alloy in the plating solution at higher temperature. The potential of the cathode decreases, but the percentage of copper in the deposit also falls off rapidly.

Fig 17
Effect of Temperature

1. Efficiency Cd Anode
 2. " Cathode
 3. " Cu Anode
 4. Percent Cu in Deposit

Fig. 16
Effect of Temperature

1. Potential Cathode
 2. " Cu Anode
 3. " Cd
 4. Percent Cu in Deposit

Effect of Dilution

The effect of a decrease in metal ion content, i.e. dilution, was briefly studied. Table XII and Figs. 19 and 20 show that the percent of copper in the deposit decreases as well as the electrode efficiencies.

Table XII

Effect of Dilution

Efficiencies			Percent Cu	Metal Content	Potential with Current		
Cu	Cd	Cath.			Cu	Cd	Cath.
101.9	117.6	77.5	25.9	20 g./l.	0.4625	0.9650	2.0375
62.6	118.8	63.5	21.9	15	4.4865	0.9040	2.1255

Fig. 19
Effect of Metal Content

Total Metal Content - g./l.

- 1. Efficiency Cd Anode
- 2. " Cathode
- 3. " Cu Anode
- 4. Percent Cu in Deposit

Fig. 20
Effect of Metal Content

1. Potential Cathode
 2. " Cd Anode
 3. " Cu "
 4. Percent Cu in Deposit

Summary

1. It has been shown that it is possible to electrodeposit a copper-cadmium alloy containing 58.4 percent copper, which should make the alloy more resistant to corrosion than either of the pure metals.

2. A plating bath containing Cu and Cd in the ratio of 60:20 and a total metal ion content of 20 grams per liter with NaHSO_3 as an addition agent is recommended for the deposition of the alloy of 58.4 percent copper and 41.6 percent cadmium. The minimum amount of excess KCN should be used.

3. The effect of variations in temperature, current density, dilution, excess KCN, and amount of NaHSO_3 on the copper content of the deposit has been studied.

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Born February 10, 1906 at Ogleable, Illinois.

Attended grammar school in Freeport, Ill., Los Angeles, California, and Minneapolis, Minn.

Was graduated from Central High School, Minneapolis, in December 1922.

Attended the University of Minnesota, January 1923 to June 1926, receiving the B.S. degree in Chemical Engineering.

From September 1926 to June 1927, was Assistant in Chemistry at the University of Louisville.

Left the U. of L. to become Research Chemical Engineer at the Atmospheric Nitrogen Corporation, Syracuse, N. Y.

Was transferred from Syracuse to the Hopewell, Virginia plant for construction work, later assuming the duties of Supervisor of Instruments.

Resigned position at Hopewell to become Associate Physical Chemist at the U. S. Bureau of Mines, Amarillo, Texas in June 1931.

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