ELECTROLYTIC CO-DEPOSITION OF METALS

By

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INTRODUCTION

Certain alloys are known to have higher corrosion resistant properties than those of the individual metals. It is well known that under certain conditions it is possible to deposit two metals simultaneously from a solution containing both ions. During the last several years a large amount of investigation has been carried out in the field of alloy deposition, and a great deal of new knowledge has been accmmulated.

From the literature, study of co-deposited metals by the aid of x-rays show that alloys, compounds and solid solutions, are actually formed and not a simple mixture. Although certain general principles of alloy deposition are fairly well established, their application involves a knowledge of so many, at present, undefined variables that the question remains, can the deposition of an alloy be predicted from the data for the separate metals.

In electroplating many factors enter in which affect the characteristics of the deposits; current density, concentration, agitation, temperature, conductivity, metal ion concentration, hydrogen ion concentration, addition agents, and structure of the base metal. Plating of alloys, however, is an exceedingly complex problem, and numerous difficulties are encountered which may not be present at all, or to a much less degree, in the plating of the elements alone.

When two or more different cations deposit together, one of them may be preferred over the other, for such causes as a differences in potentials, or in degree of hydration, mobility, valence or metal ratio. The fundamental problem of alloy deposition is to find that composition of solution in which the potentials of the metals are equal, or at least, nearly so.

Variables which one would expect to affect the composition of a deposit, and also the structure of the deposit are: Ratio of the metals in the bath, temperature, current density, total metal concentration, addition of a common ion or complex ion, agitation, overvoltage, polarization, and valence. It also sometime happens that one metal affects the deposition of the other to an unforseen extent. In operating conditions, a number of these factors may tend to conteract each other, the actual deposit obtained being the net result of all the factors.

The purpose of this work has been to supplement this present knowledge, dealing with the behavior of solutions under varying conditions, studying the factors which affect the structure of the deposited metals, and their effects upon the composition of the co-deposited metals. With a review of the present knowledge of the subject, it is designed to point the way to a more complete correlation of the accumulated data on alloy deposition to evolve some working hypothesis to fit the facts.

THEORY UNDERLYING CO-DEPOSITION

When a metal is in contact with a solution containing ions of that metal there is a certain tendency for the metal to go into the solution to form positively charged ions of the metal , the electrode being left with a negative charge. On the other hand this "solution pressure" is opposed by a certain "osmotic pressure" which tends to deposit metal on the electrode from the solution. This difference between solution and osmotic pressures, or electrode potentials may be represented by the Nernst equation,

$$E = \frac{RT}{nF} \log_e \frac{p}{P} ,$$

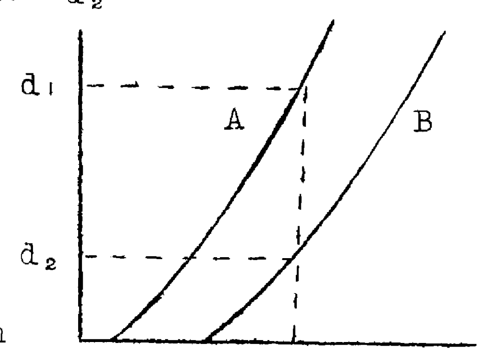
where E= electrode potential in volts, R= gas constant, T= absolute temperature, n= valence of the metal ions, F= Faraday's constant, p = "osmotic pressure" of the metal ions, P="solution pressure of metal. From this it is seen qualitatively that the potential of an electrode depends upon the concentration of its ions in solution.

Theoretically, metals commence to deposit at their reversible potentials, but as the passing of current takes place their cathode potentials become more negative due to concentration polarization and hydrogen overvoltage. Agitation and temperature tend to reduce these effects.

When a group of metallic salts are present in solution, the metal will plate out in the largest proportion which has; (1) Lowest electrode potential(most positive), (2) Greatest concentration, and (3) Highest ionic mobility. Upon passing a current deposition will occur when the cathode potential just exceeds the potential of the most positive metal. Alloy deposition will occur if ; (1) Electrode potentials are close together and polarization is small, (2) If the difference in overvoltage brings the deposition potentials closer together than are their reversible potentials,(3) If the concentration of the ions of the more noble metal is reduced.

The following figure gives the current density-cathode potential curves for two metals,A and B. Theoretically, the amounts of each metal which will be deposited will be proportional to the current density corresponding to the intersection of the vertical line and the current density-electrode potential curves of the metals at a given current density. Metal A would deposit at a rate proportional to d_1 and B proportional to d_2. Then the fraction $\frac{d_1}{d_1 + d_2}$ will be the part of the current utilized in depositing A.

The enormous variation in the electrode potential of a metal which can be effected by altering the relative concentration of metal and cyanide often changes the potentials of metals which are widely separated in an acid solution , bringing them closely enough that co-deposition occurs. Increase of temperature conteracts polarization and decreases hydrogen overvoltage,and electrode potentials approach their true values.



Cathode Potentials when co-deposition is possible

With complex cyanides, Deposition commences at the reversible potential, but considerable polarization results, due to; (1) Deposition of the metal ions faster than the complex metal ions dissociate to form simple ions, (2) The marked increase in cathode potential may be due to even a small change in ratio of metal to free cyanide, (3) Cathode potential may reach the point at which hydrogen evolution can begin. When hydrogen is evolved overvoltage enters in and affects the relative amounts of metal and hydrogen deposited.

In an electrolyte containing a common ion, the degree of dissociation depends solely upon the concentration of the common ion, and in turn, the potentials depend upon metal ion concentration. In a solution containing several metals, in the form of the same salt, the relative ion concentrations are governed by the common ion, each metal affecting the concentration of the other.

In alloy deposition the variable factors which affect the composition of the deposit also affects it structure. X-ray studies have shown that the principle difference in appearance and physical properties are caused by difference in size or shape of each metal crystal. This is, in turn, dependent upon the relative rates of crystal growth, and of crystal nuclei formation. A rapid formation of nuclei favors production of finer grained, bright and smooth plate. In solutions whose salts are highly dissociated, rapid growth of crystals takes place during deposition. Favorable conditions for the production of fine grained deposits are obtained when only few metal ions are present, but with a high metal concentration which will furnish a fresh supply of ions almost as fast as they are removed from the solution.

At low current densities, the result is toward the growth of crystals, while at higher current densities, in general, the rate of nuclei formation increases, resulting in finer grained deposits.

Temperature has several effects, some of which oppose one another. Increase of temperature (1) Favors diffusion and convection, tending to give a uniform, fine deposit, (2) Increases conductivity, due to increased ionic mobilities, (3) Increases rate of crystal growth, tending towards the formation of coarse deposits, (4) Decreases polarization and overvoltage and favors crystal growth.

Addition agents are commonly used for producing smooth or bright deposits, by (1) Reducing metal ion concentration due to the common ion added, or (2) By hindering the growth of crystals mechanically. Any foreign substance which is adsorbed or included in the deposit, as with colloidal addition agents, will hinder the growth of crystals and assist in the formation of finer grained deposits. A similar effect is produced if two metals are deposited simultaneously. In general, such alloys have a finer structure than either of the components deposited separately under similar conditions, each metal acting as an addition agent, preventing the growth of the crystals of the other.

SURVEY OF THE LITERATURE

Blum and Haring(Trans.Amer.Electrochem.Soc.,40, 287-306(1921), plated lead-tin alloy from a fluoborate solution and concluded that; (1) Lead and tin have nearly equal potentials in fluoborate solutions,(2) Composition of the deposits obtained under otherwise similar conditions depends upon the metal ratio in the solutions, (3) Increasing current density in the baths of low tin content increases the tin in the deposit, (4) Increasing amounts of glue in the solution have the same effect as current density,(5)Deposits of lead-tin alloy have a finer crystalline structure than lead or tin deposited under same conditions, (6) In the presence of glue the deposits are still finer grained.

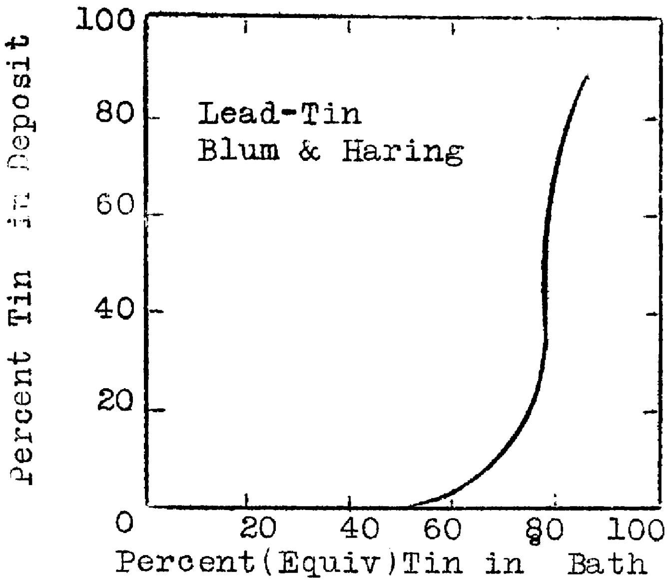
Efremor (Ann. Inst. Polytechn. Oural, 6, 111-50 (1927) claims plating of copper-cadmium alloy from cyanide solutions. He states that (1) Free cyanide content of the bath must be below .3 normal, (2) A 1 to 1 ratio of copper-cadmium in the bath gives an alloy of 62 to 72 percent Cadmium, (3) Temperature has but little influence on the deposit.

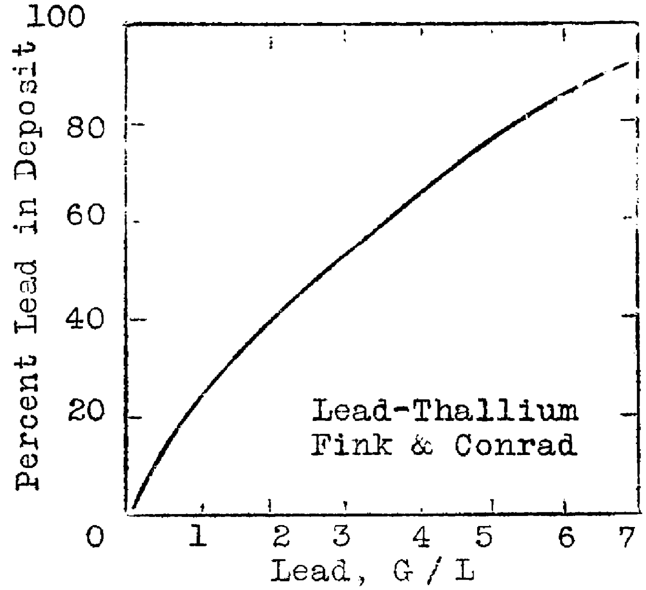
Ferguson and Sturdevant(Trans. Amer. Electrochem. Soc.,38,167-201(1920) in depositing brass from the cyanide solutions find that (1) An increase in the ratio of copper to zinc in the solution increases copper in the deposit, (2) Increase of temperature decreases cathode polarization and consequently increases the percent of copper in the deposit, (3) Increase of current density produces a gradual decrease in percent of copper in the deposit,(4)Alkaline substances decrease the percent of copper in the deposit,(5) Increase of free cyanide decreases the rate of copper deposition and favors a high zinc content deposit.

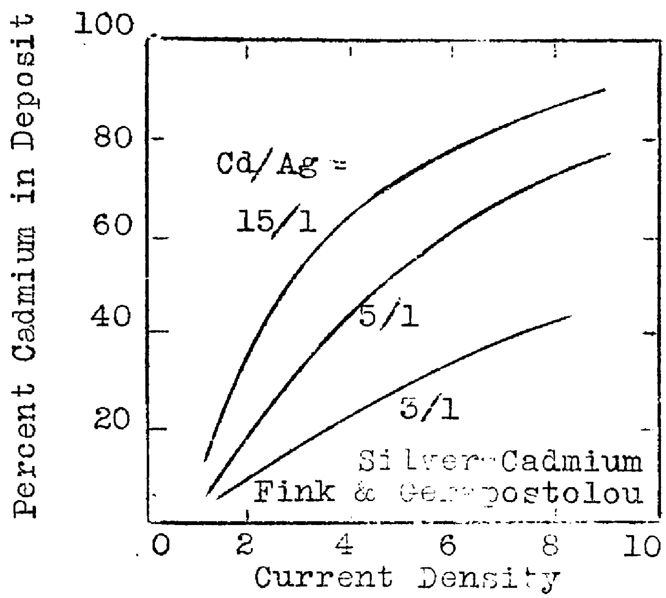
Fink and Conrad(Trans. Amer. Electrochem. Soc.,58,437-63(1930) in the deposition of lead-thallium alloy from a perchlorate bath found that (1) A high ratio of thallium to lead in the bath is necessary to co-deposit the two metals, (2) Ratio of thallium to lead in the deposit decreases as current density increases.

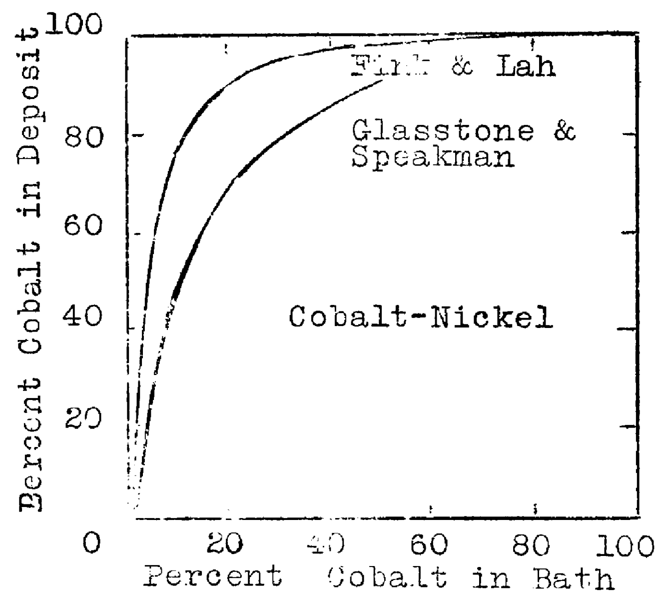
Fink and Gerapostolou (Metal Ind. (N.Y.) 28,519-21 (1930), depositing silver-cadmium alloy, give the following conclusions; (1) Increase in mol ratio of cadmium to silver in the bath increases mol ratio in deposit, (2) Increase of current density increases cadmium to silver ratio in the deposit, more marked with low silver baths, (3) Increasing the temperature decreases cadmium percent and makes the deposit more brittle, (4) Increase of free cyanide decreases the efficiency, (5) Microstructure of deposits reveals a heterogeneous mixture of at least two constituents, one of a silver rich solid solution, and the other of a cadmium rich solid solution.

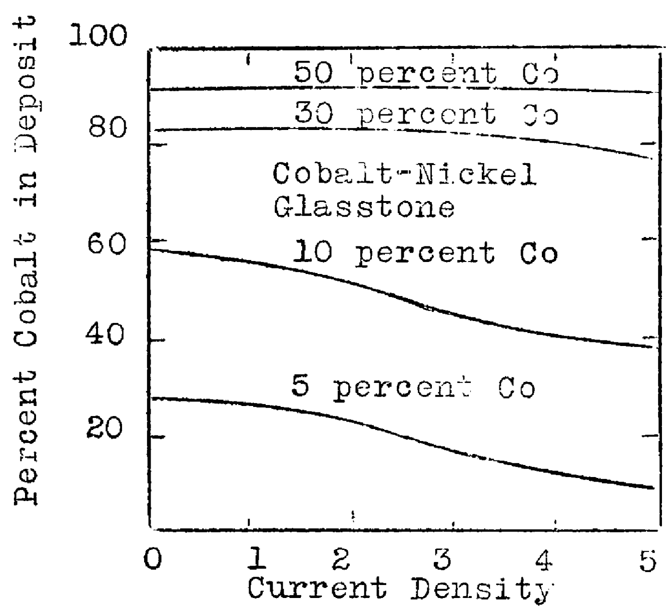
Fink and Lah (Trans. Amer. Electrochem. Soc., 58,373-85 (1930) found in depositing nickel-cobalt alloys from the sulfate-chloride bath, (1) As cobalt in the bath increases in small quantities, the

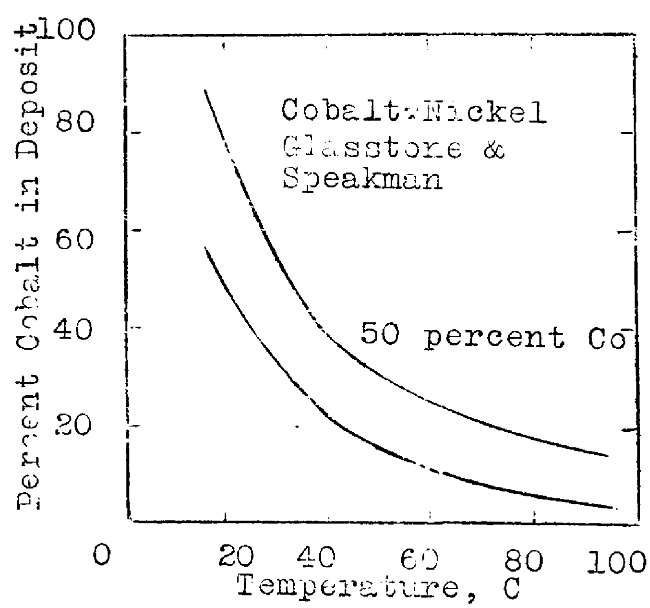

Lead-Tin
Blum & Haring
Percent Tin in Deposit
Percent (Equiv) Tin in Bath
0
20
40
60
80
100

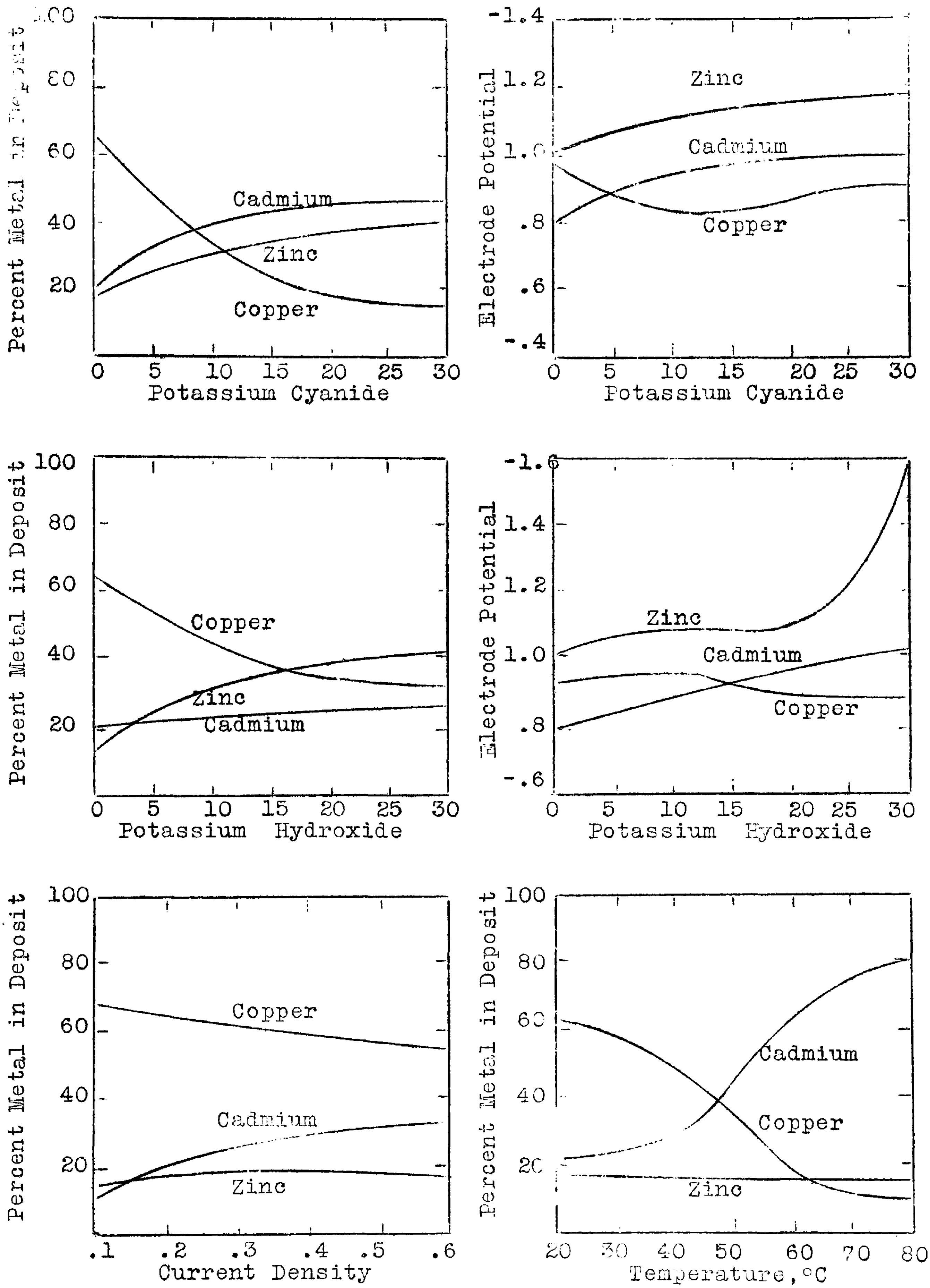

Lead-Thallium
Fink & Conrad
Percent Lead in Deposit
Lead, G / L
0
1
2
3
4
5
6
7
20
40
60
80
100


Cd/Ag =
15/1
5/1
3/1
Fink &
Percent Cadmium in Deposit
Current Density
0
2
4
6
8
10
20
40
60
80
100


& Lah
Glasstone & Speakman
Cobalt-Nickel
Percent Cobalt in Deposit
Percent Cobalt in Bath
0
20
60
80
100
40


50 percent Co
30 percent Co
Cobalt-Nickel
Glasstone
10 percent Co
5 percent Co
Percent Cobalt in Deposit
Current Density
0
1
2
3
4
5
20
40
60
80
100


Speakman
50 percent Co
Percent Cobalt in Deposit
Temperature, C
0
20
40
80
100
60



Copper-Cadmøum-Zinc Alloys
Ernst & Mann

percentage of cobalt in the deposit increases rapidly, (2) As the total metal concentration increases, at a constant metal ratio, the cobalt content of the deposit increases, (3) Increase of temperature decreases the cobalt content of the deposit,(4) Increasing current density increases cobalt content of the deposit,(5) Increasing pH increases the cobalt content of the deposit.

In the electrodeposition of Chromium-Iron alloy, Fuseya and Sasaki (Trans. Amer. Electrochem. Soc.,59,445-60 (1931), concluded that at higher current density, and lower temperature or acidity of the bath, the higher the chromium content of the deposit. Temperature has the same effect as acidity. Increase of iron sulfate in the bath increases the iron content of the deposit.

Glasstone and Symes (Trans. Faraday Soc.,23,213-26 (1927), 24, 370-8 (1928), in co-depositing nickel and iron from the sulfate-oxalate bath found that: (1) An increase of nickel to iron ratio in the bath increases nickel to iron ratio in the deposit, (2) An increase of the oxalate concentration of the bath increases the nickel content of the deposit,(3) Increasing temperature increases the nickel to iron ratio of the deposit, (4) Increasing current density increases the content of iron in the deposit, (5) Relative tendencies for iron and nickel to deposit as an alloy is independent of hydrogen ion concentration of the bath.

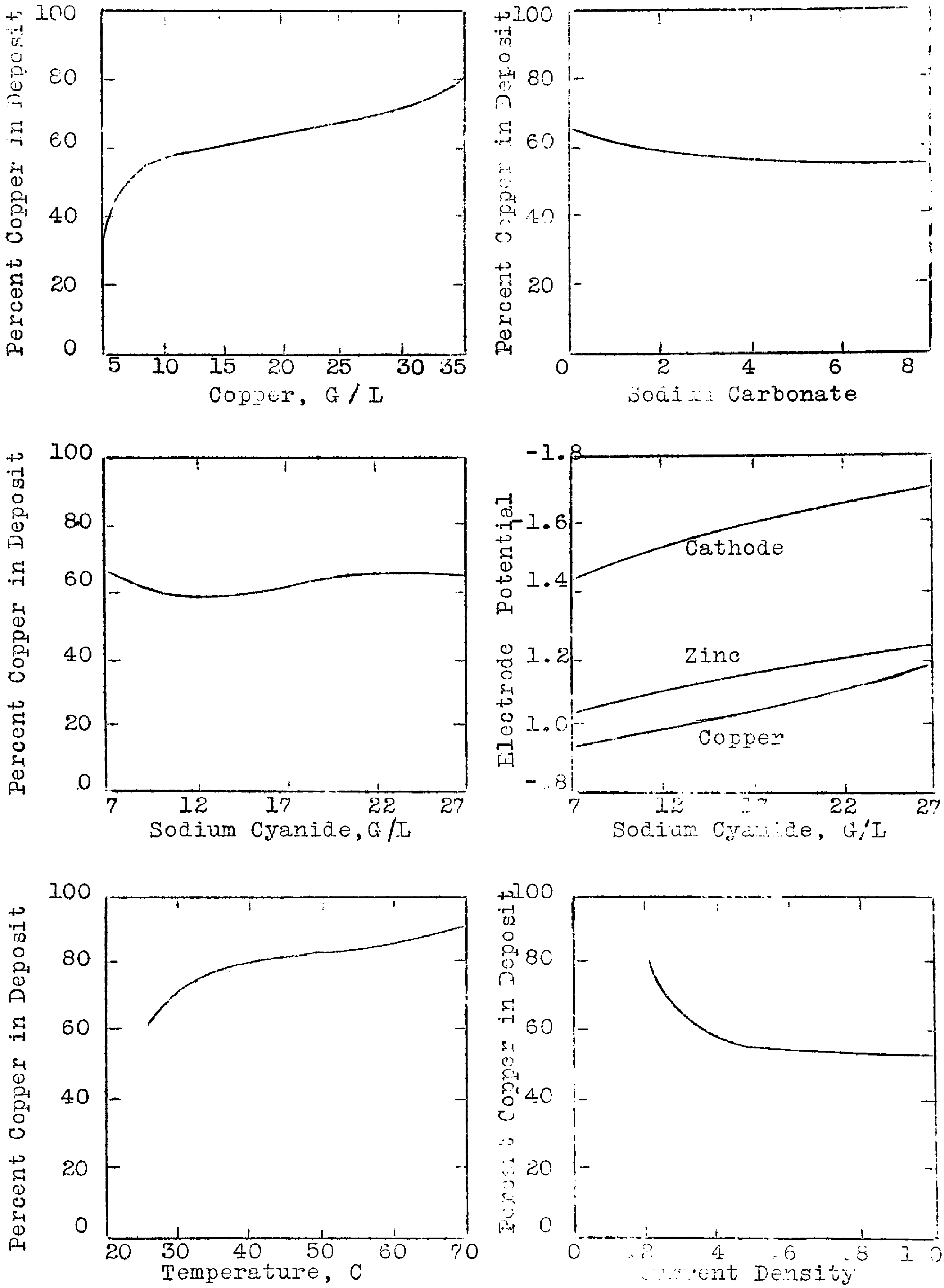
In plating Cobalt-Nickel-alloys, Glasstone and Speakman(Trans. Faraday Soc.,26,565-74 (1930); 27,29-35 (1931), give the following information, (1) As the temperature increases, the deposition potential of nickel becomes less negative, and the proportion of nickel in the plate increases with increasing temperature, (2) As current density increases, the cathode potential of cobalt becomes more negative and the proportion of cobalt in the deposit increases rapidly toward a maximum value, (3) Alloys always contained relatively more cobalt than present in the bath.

With iron-cobalt, iron-nickel, and cobalt-nickel deposition, Glasstone and Speakman (Trans. Faraday Soc. 28,733-40 (1932); 29, 426-8 (1933) concluded that (1)Increase of A in the bath increases A in the deposit, (2) Increase of temperature decreases A in the deposit,(3) Increase of current density increases A in the deposit, where A is the first metal mentioned in the above pairs.

Mathers and Sowder (Trans. Amer. Electrochem. Soc., 37, 525-8 (1920), plated a copper-tin alloy from the oxalates of copper and tin dissolved in ammomium oxalate, and also from potassium cyanide, potassium stannate, and potassium hydroxide.

Schoch(J. Amer. Chem. Soc.,29,314-21(1907) gives the following conclusions on his work with nickel-zinc alloys; (1) Proportion of zinc in the deposit increases with current density,(2)Proportion of zinc in the deposit increases with increasing zinc content of the bath.

While it is very difficult to deposit nickel or iron from cyanide baths, the work of Hineline and Cooley(Trans. Amer. Elect-



Copper-Zinc Alloys
Ferguson & Sturdevant

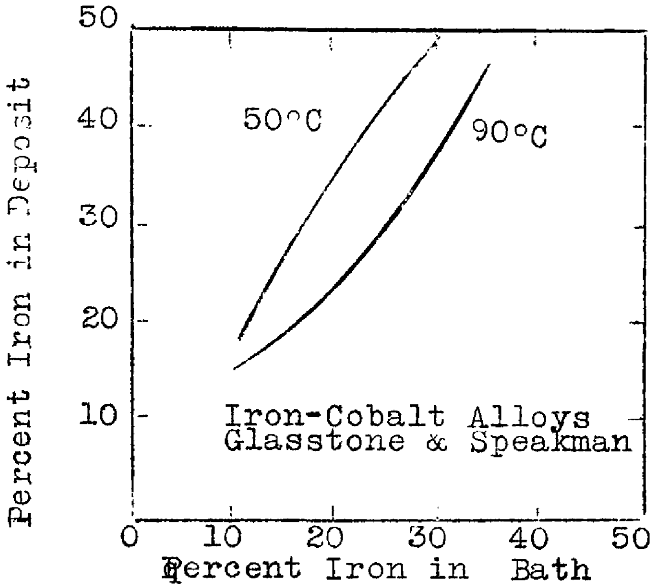
rochem. Soc.,48, 61-8(1925), and of Stout,Burch and Langsdorf(Ibid., 57,113-27 (1930) have shown it to be much easier to obtain their alloys. They conclude (1) The percent of copper in the deposit is always greater than that of the bath,(2) Ratio of copper to nickel on the plate increases linearly with the temperature, (3) Low current density favors deposition of high copper alloys,(4)Increase in free cyanide was found to lower the rate of deposition. Concentration of free cyanide should be low as possible. Stout shows that the relationship between copper-nickel ratio in the plate,Rp, and the copper-nickel ratio in the solution, Rs, may be of the hyperbolic type expressed by the general equation $b + x = a\frac{x}{y}$, where a and b are constants, and x(Rs) is the abcissae,and y(Rp) is the ordinate. From the curves, the copper to nickel ratio in the deposit increases linearly with temperature, $Rp = C + K T$.

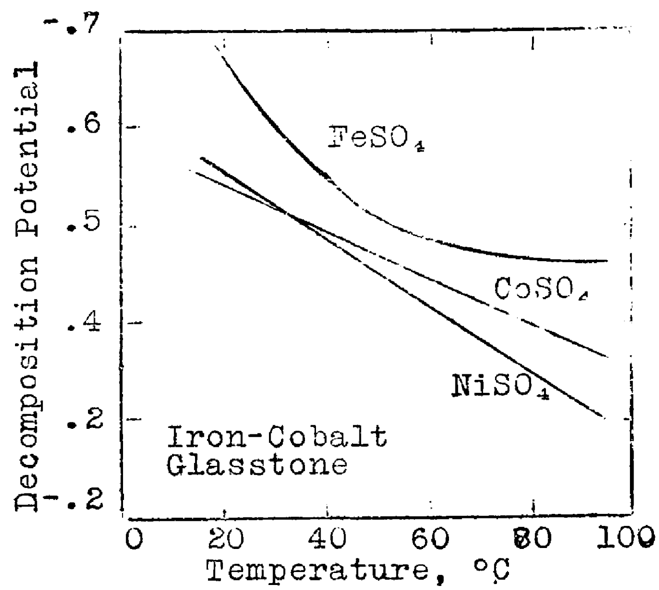
In their work on iron-nickel alloys, Stout and Carol (Trans. Amer. Electrochem. Soc., 58,357-72(1930), find (1) Iron content of the deposit tends to be higher than that present in the bath,(2) Percent nickel in the deposit increases with current density. Low temperatures minimize the changes in composition of the deposit with increasing current density. At high temperature the effect of changes in current density becomes more appreciable, (3)The nickel content of the deposit increases rapidly with an increase in temperature,(4) Even with high iron content, a large excess of cyanide will give iron free deposits, (5) Potassium tartrate proved to be the ideal addition agent.

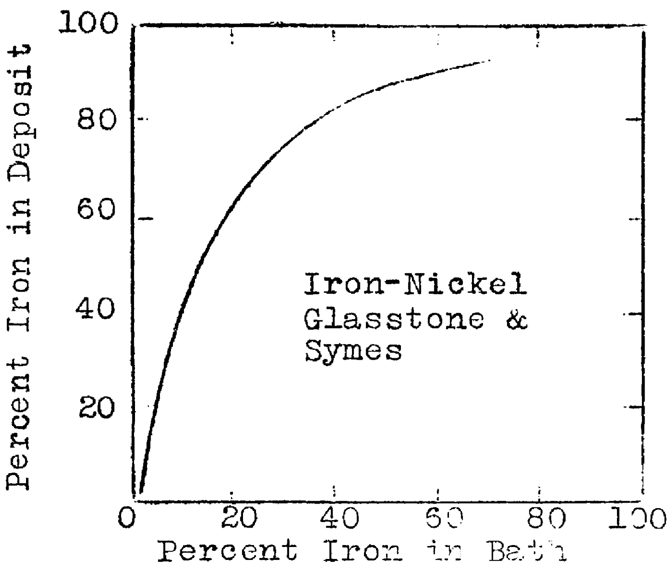
Very few references to the deposition of ternary alloys are in the literature. According to Ernst and Mann (Trans. Amer. Electrochem. Soc., 61, 363-95 (1932), in their investigation of copper-cadmium-zinc alloys, find (1) Copper has a depolarizing effect on the deposition of zinc,as has cadmium,and the alloy should deposit at a potential lower than the potential of the three metals, Zinc and cadmium are depolarized by copper. (2) The percent copper decreased, cadmium and zinc increased, and cathode efficiency decreased, as the amount of free cyanide increased, (3) With the addition of alkalie the percent of copper was decreased,while that of cadmium and zinc increades, resulting in coarse crystalline structure, (4) Percent of copper in the deposit increased with a decrease of temperature, while that of cadmium increases with increasing temperature,(5) Percent of copper and zinc decreases with increasing current density, (6) Percent of copper and zinc increases, and cadmium decreases, with dilution.

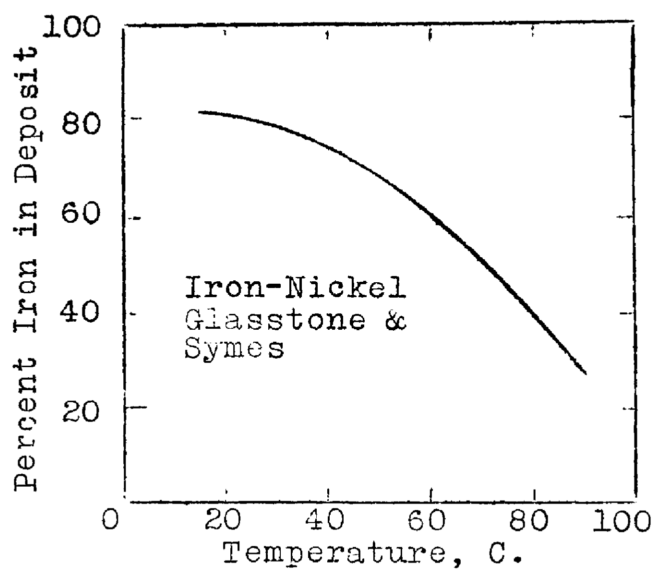
Glasstone (J. Chem. Soc., 129, 2897-902 (1926) in his work on polarization of the iron,nickel and cobalt group, studied deposition potentials and concluded; (1)They vary directly with the metal ratios, (2) Varies directly with temperature, (3) Is independent of hydrogen ion concentration.

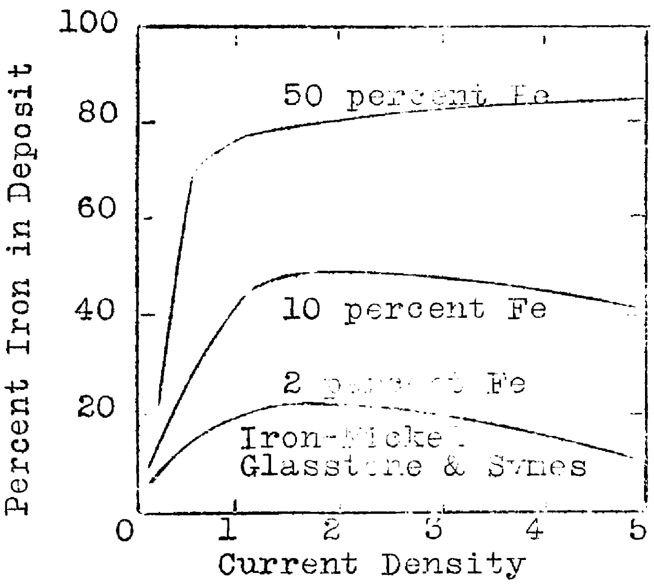
Later in his work with the deposition of alloys of zinc with cobalt, nickel and iron (J. Chem. Soc.,130,641-7 (1927),finds that (1) A decrease in temperature decreases the cobalt to zinc ratio, (2) The cathode potential at some point rises rapidly,and an alloy rich in zinc is deposited. The same phenomena has also been

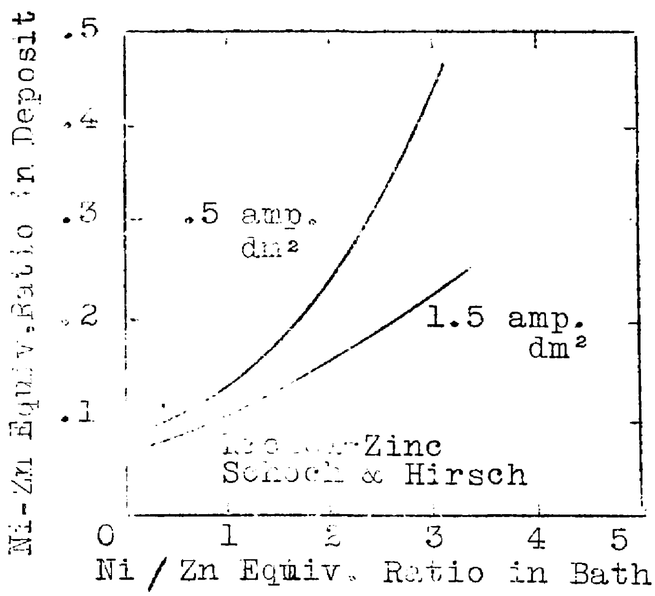

Percent Iron in Deposit
50°C
90°C
Iron-Cobalt Alloys
Glasstone & Speakman
Percent Iron in Bath

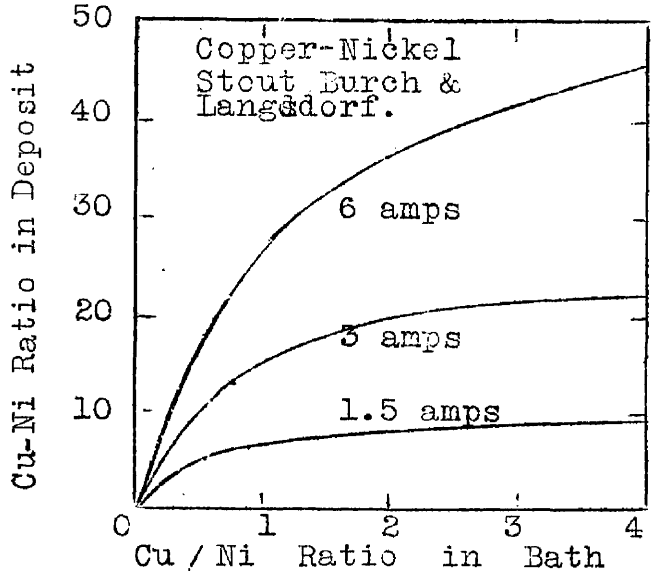

Decomposition Potential
FeSO4
CoSO4
NiSO4
Iron-Cobalt
Glasstone
Temperature, °C

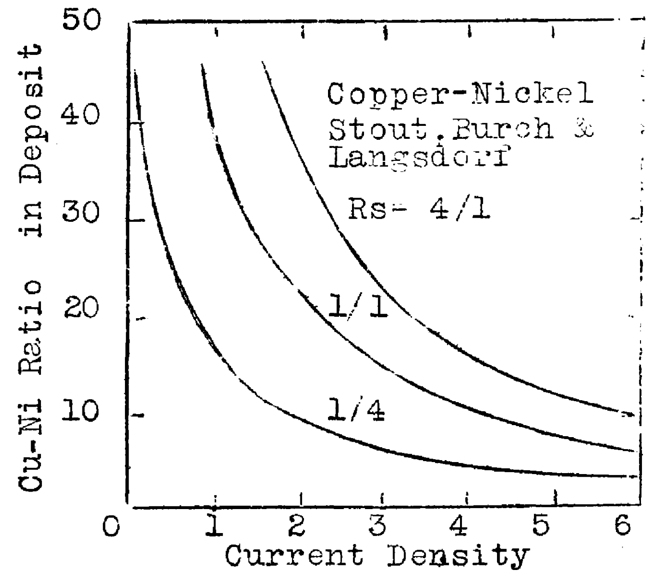

Percent Iron in Deposit
Iron-Nickel
Glasstone &
Symes
Percent Iron in Bath

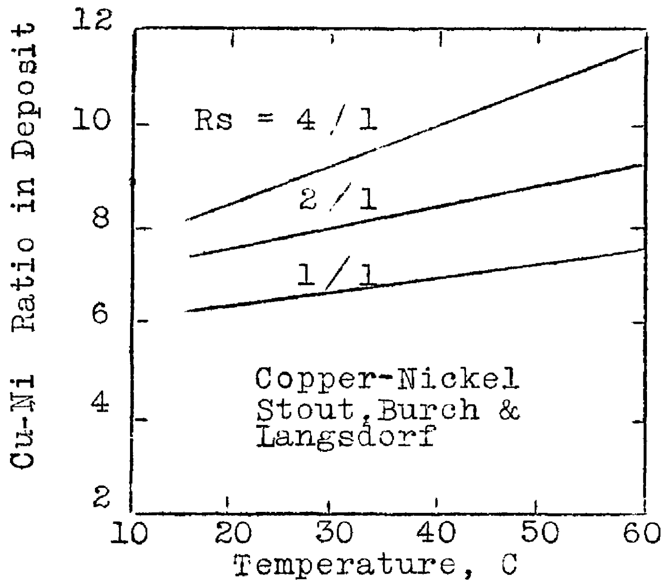

Percent Iron in Deposit
Iron-Nickel
Glasstone &
Symes
Temperature, C.

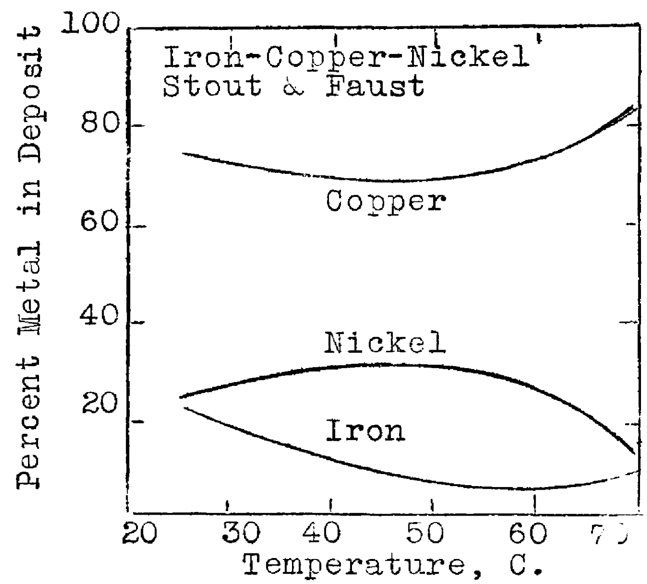

Percent Iron in Deposit
10 percent Fe
Current Density

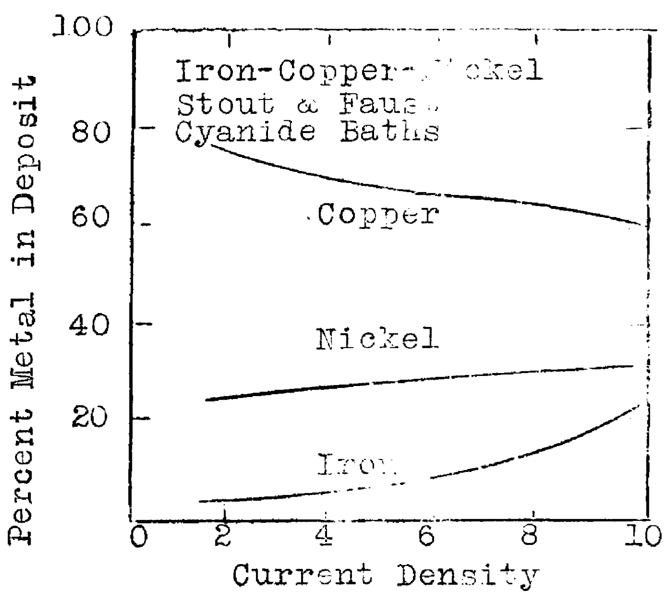

.5 amp.
1.5 amp.
dm²
Hirsch
Ni / Zn Equiv. Ratio in Bath

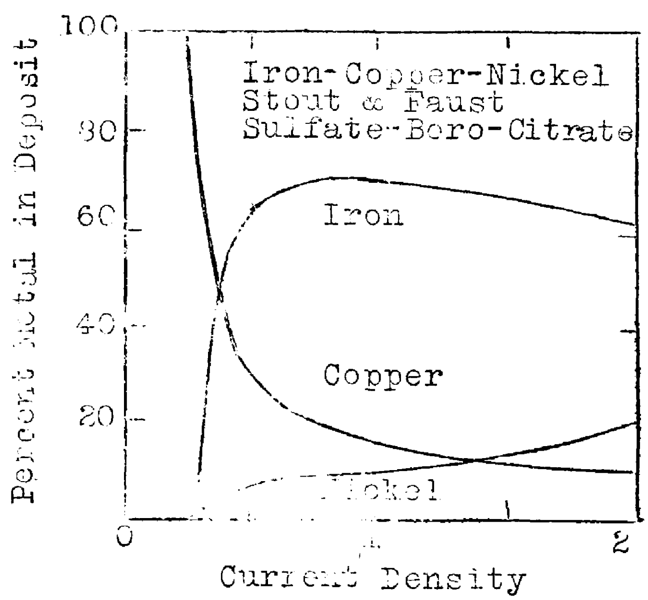

Copper-Nickel
Stout Burch &
Langsdorf.
6 amps
3 amps
1.5 amps
Cu-Ni Ratio in Deposit
Cu / Ni Ratio in Bath
0
1
2
3
4
10
20
30
40
50


Copper-Nickel
Stout, Burch &
Langsdorf
Rs= 4/1
1/1
1/4
Cu-Ni Ratio in Deposit
Current Density
0
1
2
3
4
5
6
10
20
30
40
50


Rs = 4 / 1
2 / 1
1 / 1
Copper-Nickel
Stout, Burch &
Langsdorf
Cu-Ni Ratio in Deposit
Temperature, C
10
20
30
40
50
60
2
4
6
8
10
12


Iron-Copper-Nickel
Stout & Faust
Copper
Nickel
Iron
Percent Metal in Deposit
Temperature, C.
20
30
40
50
60
40
60
80
100


Cyanide Baths
Copper
Nickel
Percent Metal in Deposit
Current Density
0
2
4
6
8
10
20
40
60
80
100


Iron-Copper-Nickel
Stout & Faust
Sulfate-Boro-Citrate
Iron
Copper
Current Density
0
2
20
60
80
100

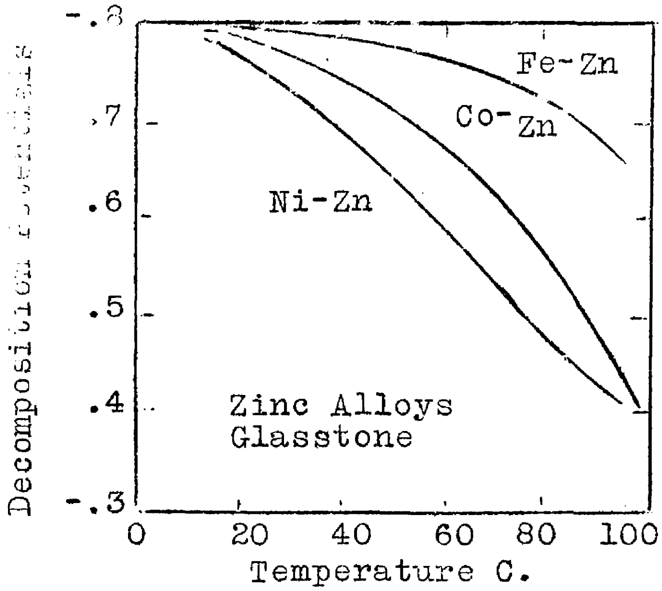
observed with cobalt and zinc, (3) The sudden increase of cathode potential is attributed to a decrease in the concentration of iron, nickel oer cobalt ions in the vicinity of the cathode, and with the result that an alloy richer in zinc ,and with a higher overvoltag e, is deposited. (4) The lower the temperature, the greater the proportion of zinc in the deposit.

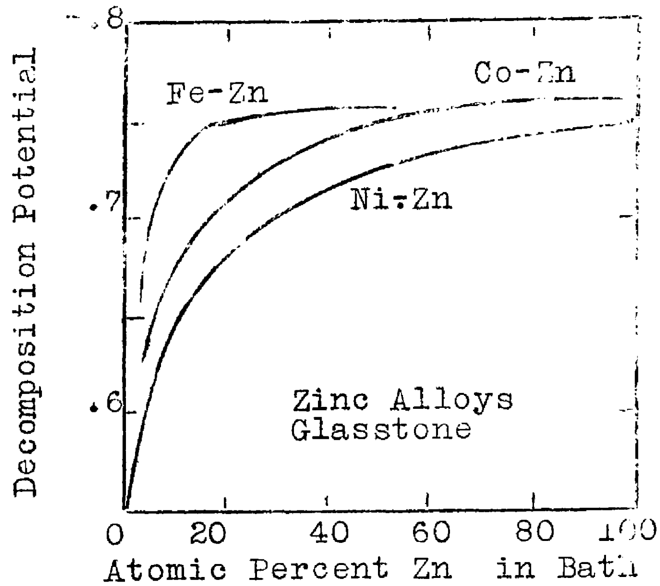
In the deposition of ternary alloys of iron-copper-nickel, Stout and Faust (Trans. Amer. Electrochem. Soc., 60, 271-96(1931); 61, 341-62 (1932) claim, (1) Ternary alloys of copper, nickel and iron can be deposited in cyanide baths in the presence of tartrates, the presence of tartrates being necessary for the deposition of the iron. (2) Deposition of copper is favored over nickel and iron. Increase of current density more equalizes the amounts of each metal depositing, (3) Increasing temperature has the opposite influences at low current densities than it has at high current densities, (4) High concentrations of iron are required in bath in order to permit even small amounts in the deposit, (5) Increase of current density favors the deposition of nickel and iron at the expence of the copper, (6) Effect of free cyanide is marked, as no ternary alloy was obtained with excess cyanide, (7) Copper to nickel ratio is not affected very much by tartrate, but is necessary for the iron to deposit. (8) Composition of the deposit depends upon the relative concentrations of each metal in the bath. The Percent copper in the deposit is relatively much greater than in the bath, the percent nickel in the deposit being slightly less than in the bath.

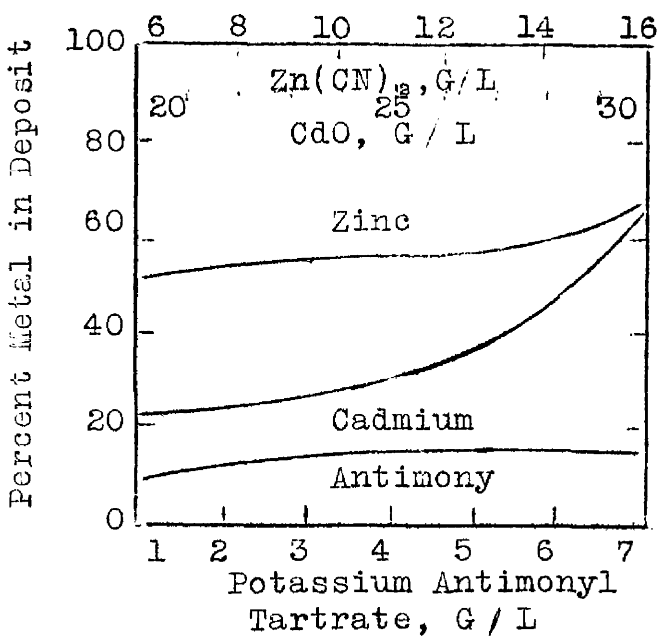
Stout and Goldstein(Trans. Amer. Electrochem. Soc.,63,preprint, 21 pp (1933) deposited cadmium-zinc-antimony alloys from the cyanide bath, with potassium antimonyl tartrate, concluding, (1) Deposition of zinc and antimony is favored over cadmium, (2) An increase of one metal in the bath tends to increase that metal content of the deposit, (3) An increase in current density causes an increase in antimony content of the deposit when the cadmium and zinc contents of the bath are low, and a decrease when they are high. An increase in current density causes a slight decrease in zinc content, and an increase in cadmium content of the deposit, (4) Temperature has the same effect as that of current density, (5) Increasing current density increases the cadmium content more than that of zinc, (6) Alkalie reduces the zinc content, but affects that of cadmium but little, (7) A comparatively large cadmium concentration in the bath is required to produce an appreciable amount in the deposit.

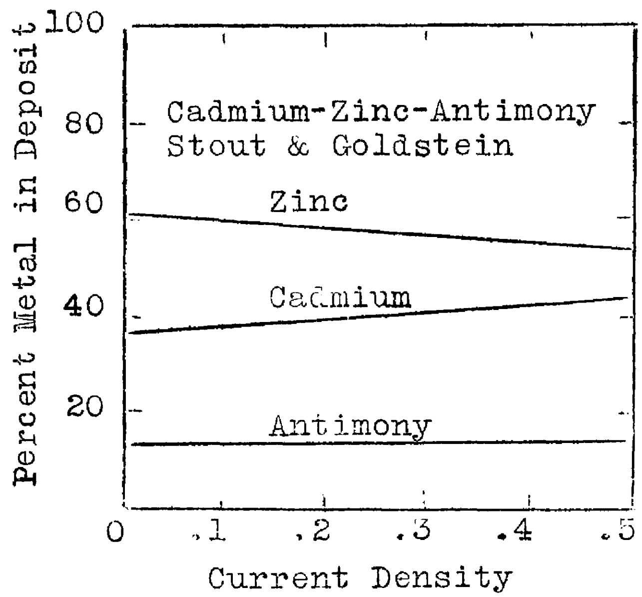
EXPERIMENTAL

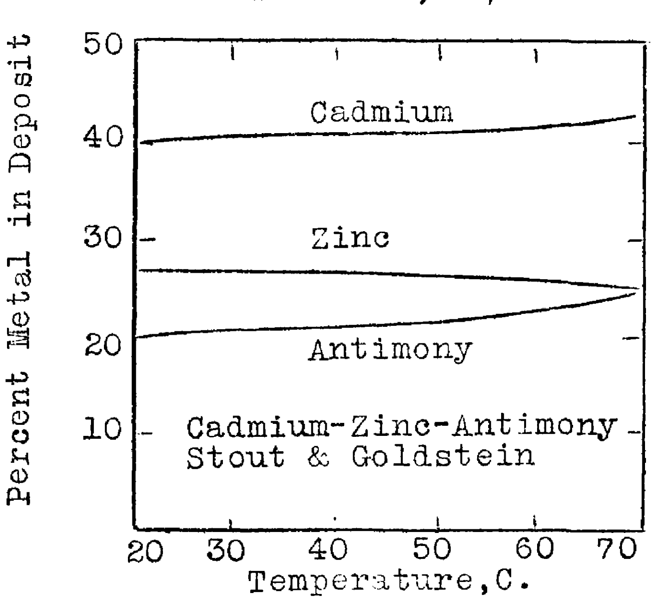
In studying the problem of alloy deposition, the affect of the following factors were determined experimentally,(1) Metal ratio , (2) Current density,(3) Temperature,(4) Addition agents, and (5) Total metal concentration, determining the resulting effect upon composition of deposit, and changes in electrode potentials. With a potentiometer set up, and a hydrogen reference electrode, both static equilibrium electrode potentials ,and the dynamic potential during the process of plating, were measured. The results obtained on five pairs of metals , Copper-Tin; Silver-Cadmium; Silver-Tin; Silver-Copper; and Cobalt-Nickel, are recorded as follows.

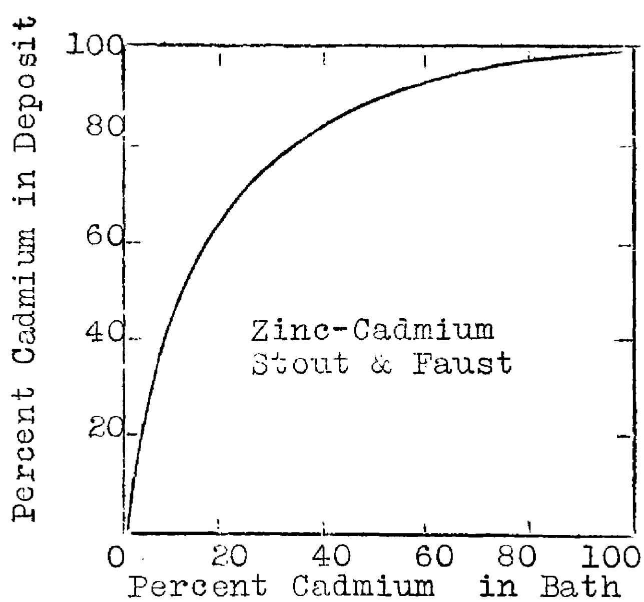

Decomposition Potentials
Fe-Zn
Co-Zn
Ni-Zn
Zinc Alloys
Glasstone
-.8
.7
.6
.5
.4
-.3
0
20
40
60
80
100
Temperature C.


Decomposition Potential
Fe-Zn
Co-Zn
Ni-Zn
Zinc Alloys
Glasstone
-.8
.7
.6
0
20
40
60
80
100
Atomic Percent Zn in Bath


Percent Metal in Deposit
6 8 10 12 14 16
Zn(CN)2, G/L
20 25 30
CdO, G / L
Zinc
Cadmium
Antimony
100
80
60
40
20
0
1 2 3 4 5 6 7
Potassium Antimonyl
Tartrate, G / L


Percent Metal in Deposit
Cadmium-Zinc-Antimony
Stout & Goldstein
Zinc
Cadmium
Antimony
100
80
60
40
20
0
.1
.2
.3
.4
.5
Current Density


Percent Metal in Deposit
Cadmium
Zinc
Antimony
Cadmium-Zinc-Antimony
Stout & Goldstein
50
40
30
20
10
20 30 40 50 60 70
Temperature, C.


Percent Cadmium in Deposit
Zinc-Cadmium
Stout & Faust
100
80
60
40
20
0
20
40
60
80
100
Percent Cadmium in Bath

COPPER-TIN ALLOYS

Effect of Metal Ratio

Composition of Bath, Molal Percent Cu	Composition of Deposit Percent Copper		Equilibrium Electrode Potential			
			Theo. Cyanide		NaCN 10 G/L	
	Theo. CN	NaCN 10 G L	Copper	Tin	Copper	Tin
0	0	0	----	-.774	-----	-.782
20	75.0	38.5	-.453	-.683	-----	-.730
33	87.8	70.5	-.443	-.638	-.848	-.753
50	93.5	83.2	-.455	-.610	-.710	-.738
66	96.2	89.6	-.467	-.660	-.675	-.742
100	100.0	100.0	-.505	----	-.635	----

Effect of Metal Ratio on Decomposition Potentials

Composition of Bath, Molal Percent Cu	Decomposition Potentials			
	Theoretical Cyanide		NaCN 10 G / L	
	Copper	Cathode	Copper	Cathode
0	-----	----	----	-.778
25	-.419	-.531	----	-.802
33	-.415	-.532	-.770	-----
50	-.420	-.546	-.680	-.808
75	-.4510	-.558	-.635	-.775
100	-.500	-.578	-.615	-.735

Effect of Total Metal Concentration

Total Metal Concentration Mols per Liter	Composition of Deposit, Cu	Electrode Potential NaCN 10 G /L		Decomposition Potentials	
		Copper	Tin	Copper Theo	Cathode CN
.1	40.0	-.742	-.622	-.550	-.782
.2	50.0	-.745	-.699	-.623	-.791
.4	69.2	-.745	-.752	-.675	-.800
.6	85.6	-.698	-.735	-.680	-.810

Composition of bath, 50 percent(molal) Copper.
Current Density, 0.2 amps. per square decimeter.

Effect of Alkalie

NaOH G / L	Composition of Deposit Percent Cu	Electrode Potential				Decomposition Potential		
		Cu in CuCN	Sn in Na_2SnO_3	Cu CuCN	Sn 50 %	Cu in CuCN	Sn in Na_2SnO_3	Cathode CUCN 50 %
0	85.6	-.505	-.775	-.699	-.735	-.499	-.579	-.810
5	77.2	-.475	-.835	-.764	-.841	----	----	-.880
10	63.7	-.462	-.855	-.775	-.862	-.450	-.590	-.902
15	49.3	----	----	-.778	-.874	----	----	-.922
20	----	-.448	-.870	----	----	-.440	-.580	----
30	----	-.435	-.885	----	----	-.440	-.571	----

Effect of Free Cyanide

NaCN G/L	Composition of Deposit Percent Cu	Decomposition Potentials		In 50 Percent Cu-Sn Bath		
		Cu in CuCN	Sn in Na_2SnO_3	Copper	Tin	Cathode
0	93.5	-.499	-.657	-.420	-.565	-.545
5	90.5	-.561	----	-.575	-.655	-.720
10	85.2	-.613	-.662	-.680	-.695	-.805
15	62.5	----	----	----	----	----
20	35.2	-.724	-.660	-.755	-.715	-.840
30	32.2	-.773	-.660	-.825	-.725	-.870

Current Density 0.2 amps per decimeter²

Effect of Free Cyanide on Electrode Potentials

NaCN G/L	Equilibrium Electrode Potentials							
	Cu in CuCN	Sn in Na_2SnO_3	33 % (Molal) Cu-Sn Copper	33 % (Molal) Cu-Sn Tin	50 % Cu-Sn Bath Copper	50 % Cu-Sn Bath Tin	66 % Cu-Sn Copper	66 % Cu-Sn Tin
0	-.504	-.779	-.445	-.638	-.458	-.610	-.542	-.667
5	-.570	----	-.692	-.737	-.623	-.680	-.662	-.723
10	-.635	-.780	-.847	-.765	-.698	-.735	-.712	-.742
20	-.739	-.775	-.888	-.785	-.793	-.783	-.756	-.760
30	-.895	-.778	-----	-.795	-.870	-.785	-.790	-.773

Effect of Temperature

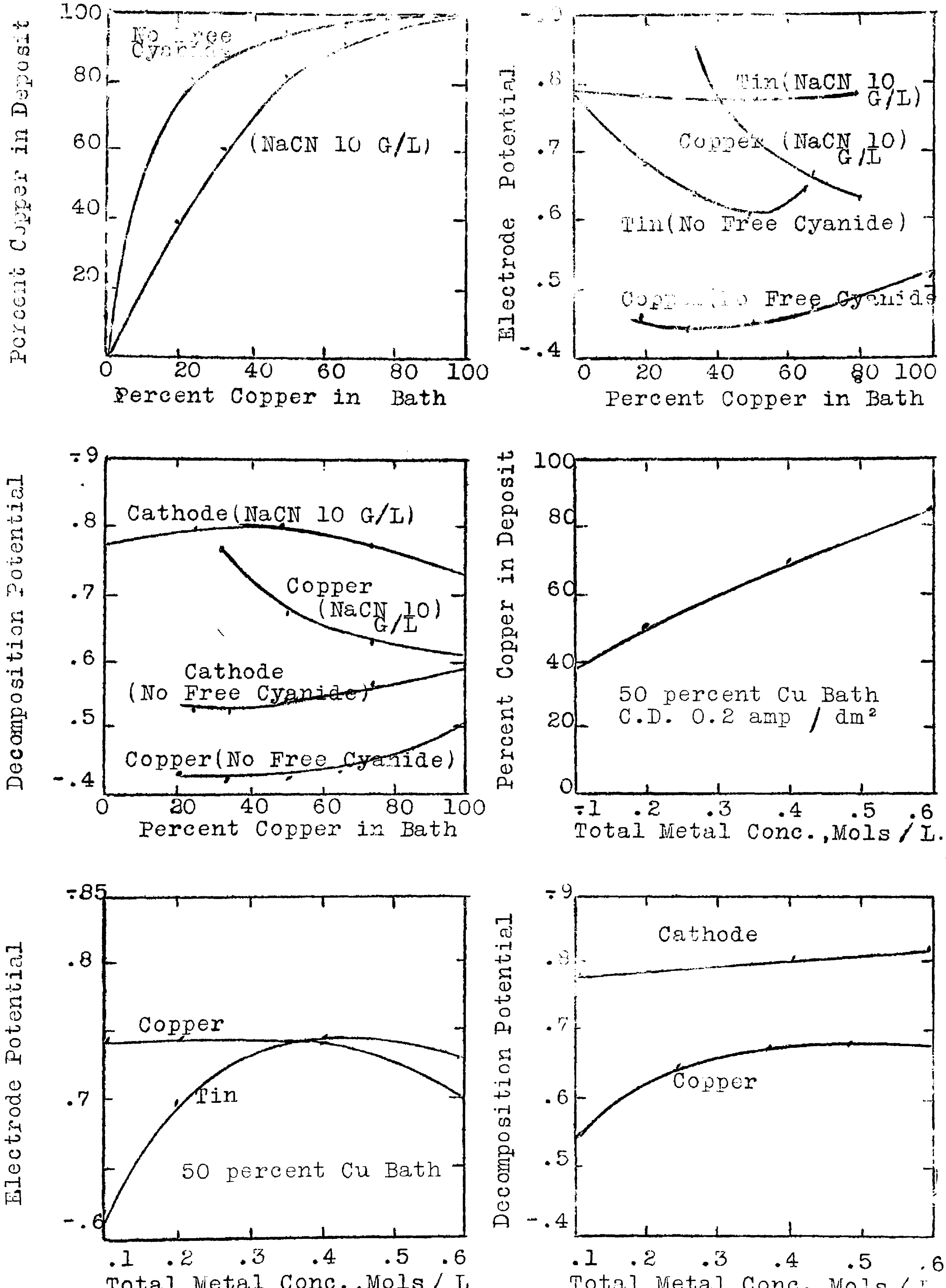
Temp. °C.	Composition of Deposit Percent Cu	Electrode Potentials				Decomposition Potential		
		Cu in CuCN	Sn in Na_2SnO_3	Alloy Bath Copper	Alloy Bath Tin	Cu in CuCN	Sn in Na_2SnO_3	Cathode in Alloy Bath
20	85.5	-.634	-.781	-.698	-.736	-.615	-.764	-.810
40	58.8	-.675	-.786	-.762	-.764	-.653	-.780	-.877
50	51.6	-.692	----	-.792	-.778	-.670	----	-.890
60	----	-.716	-.816	----	----	----	-.812	-----
70	64.5	-.739	-.848	-.822	-.794	-.725	-.828	-.780
80	76.2	----	----	---	----	----	----	----

Composition of Bath, 50 percent (molal) Cu-Sn
NaCN, 10 G L Current Density, 0.2 amps per Dm²

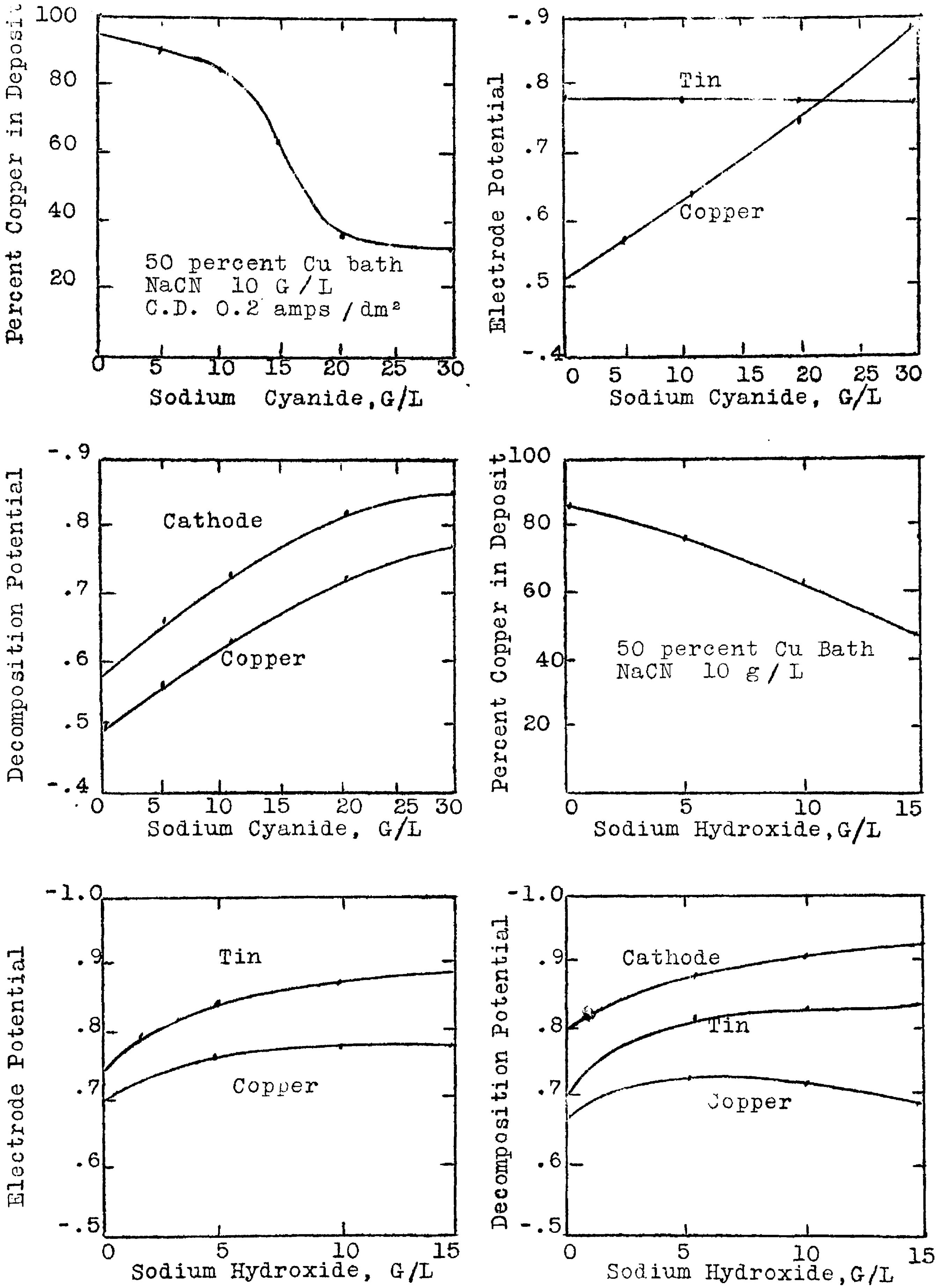
Effect of Current Density

Current Density Amp/Dm²	Composition of Deposit Percent Copper: Theo. CN	Composition of Deposit Percent Copper: NaCN 10 G/L	Current Density Amp./Dm²	Cathode Potential: Cu in CuCN	Cathode Potential: Sn in Na_2SnO_3
.05	98.0	710	0	-.085	-.206
.10	96.5	65.8	.0010	-.685	-.741
.20	93.5	56.0	.0025	-.753	-.840
.40	92.2	41.2	.0050	-.776	-.901
.50	90.6	36.2	.0100	-.792	-.988
			.0200	-.810	-1.069
			.0300	-.830	-1.115
			.0400	-.865	-1.145
			.0500	-.958	-1.170

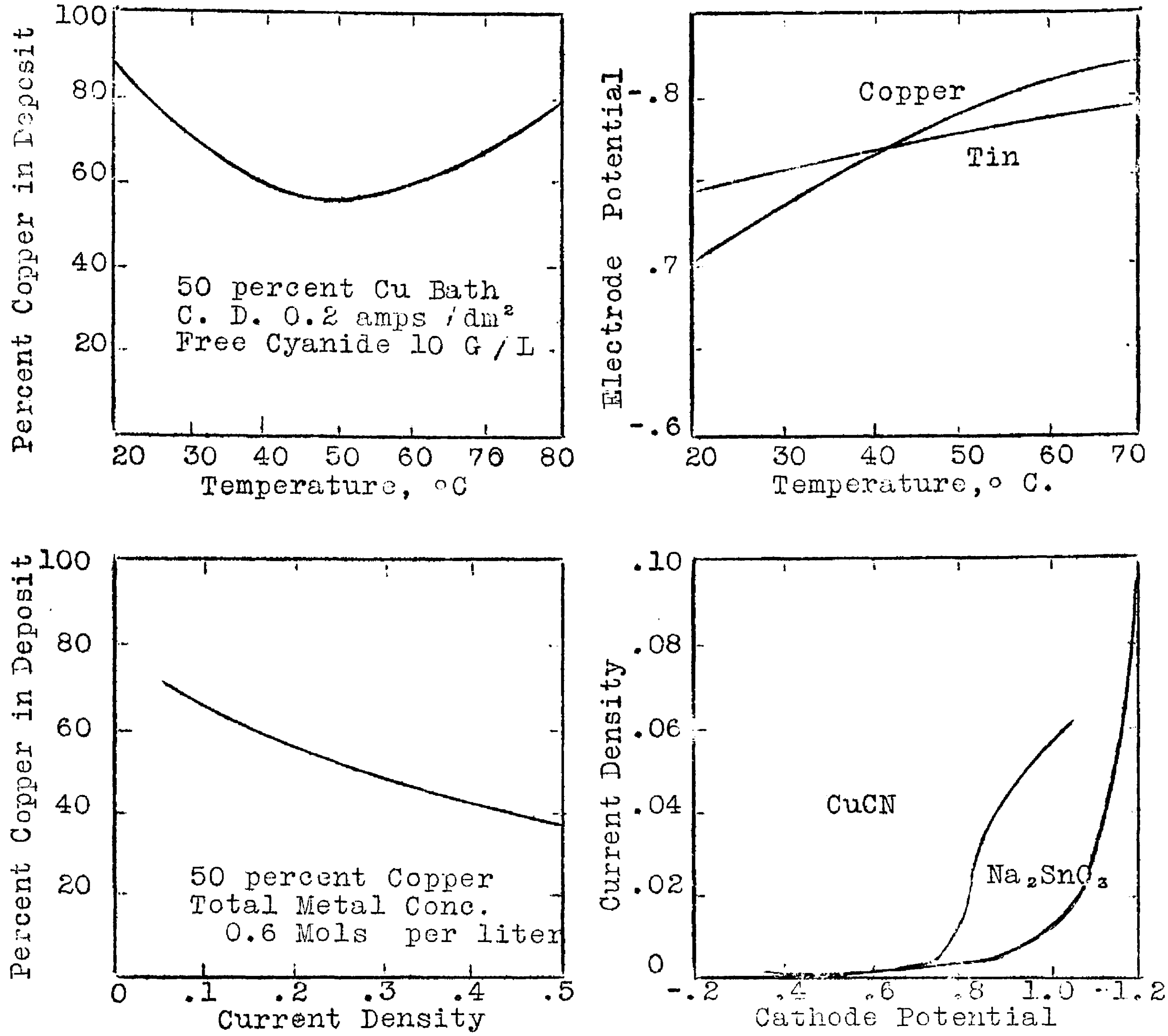
50 percent (molal) Cu-Sn Bath



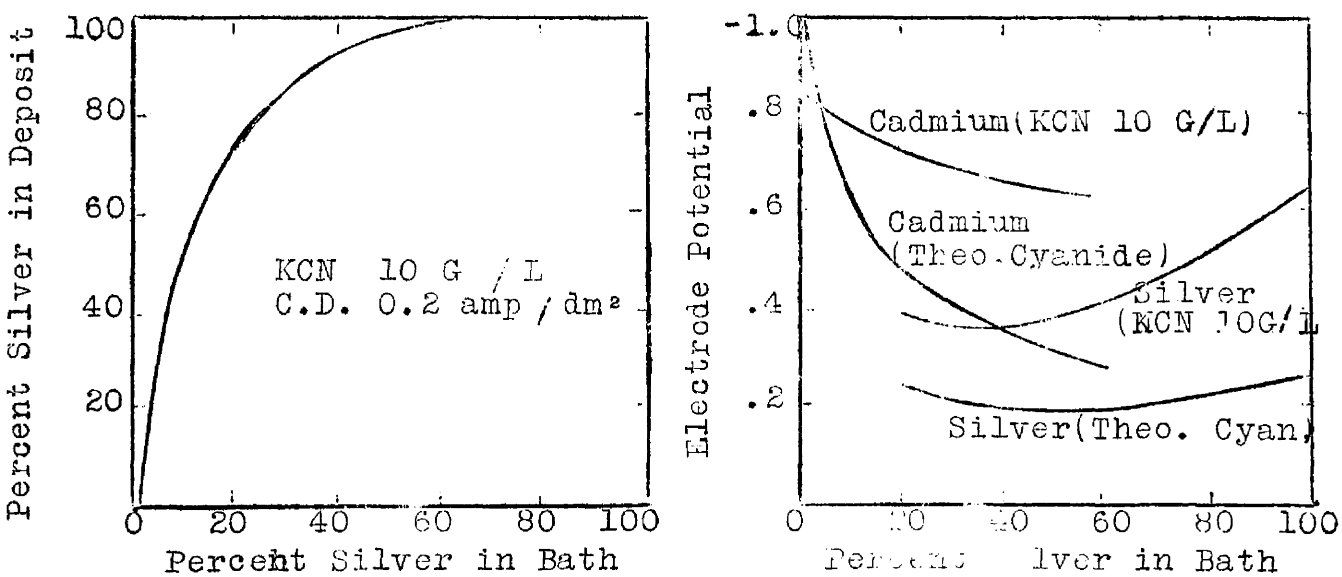
Copper-Tin Alloys



Copper-Tin Alloys



Copper-Tin Alloys



Silver-Cadmium Alloys

SILVER-CADMIUM ALLOYS

Effect of Metal Ratio

Composition of Bath Percent Ag	Composition of Deposit Percent Ag			Equilibrium Electrode Potential: Cadmium			Silver		
	Theo. Cyan.	KCN 10 G/L	KCN 30 G/L	Theo. Cyan.	KCN 10/G	KCN 30G	Theo. Cyan.	KCN 10G/L	KCN 30G/L
0	0	0	0	-1.032	-.814	-.865	---	---	----
10	78.8	55.0	40.7	---	---	---	---	---	----
20	88.2	77.0	68.5	-.441	-.710	-.846	-.216	-.375	-.490
40	96.5	94.1	91.4	-.325	-.657	-.848	-.187	-.341	-.466
50	100.0	100.0	100.0	---	---	---	---	---	---
60	---	---	---	-.268	-.645	-.854	-.182	-.404	-.487
100	---	---	---	---	---	---	-.212	-.635	-.676

25 percent Silver-Cadmium Bath; Current Density, 0.2 amp. / Dm².

Effect of Free Cyanide

KCN G/L	Composition of Deposit: 10 % Ag Bath	25 % Ag Bath	Electrode Potentials: Cyan. Bath Cd	Cyan. Bath Ag	Alloy Bath Cd	Alloy Bath Ag	Decomposition Potential: $K_2Cd(CN)_4$ Cd	$KAg(CN)_2$ Ag	10 % Ag Bath
0	78.8	91.5	-1.035	-.210	-.547	-.210	-.135	-1.050	-.325
5	----	----	-.748	-.540	-.738	-.343	-.130	-.282	-.132
10	55.2	82.2	-.800	-.618	-.788	-.395	-.126	-.056	-.096
20	49.3	79.6	-.843	-.680	-.815	-.448	-.115	-.050	-.065
30	44.5	77.5	-.860	-.728	-.839	-.483	-.109	-.043	-.060

Total Metal Concentration, 1 molal; Current Density, 0.2 amps/Dm²

Effect of Alkalie

KOH G/L	Composition of Deposit Percent Ag	Electrode Potential Cd	Electrode Potential Ag
0	78.8	-.644	-.423
5	64.5	-.675	-.299
10	58.2	-.690	-.266
20	51.0	-.680	-.263
30	44.0	-.672	-.278

10 % Ag Bath; KCN 10 G L.

Effect of Metal Concentration

Metal Conc. Mols/L	Composition of Deposit Percent Ag	Electrode Potential Cd	Electrode Potential Ag
.1	82.3	-.786	-.390
.2	91.7	-.719	-.357
.4	97.0	-.552	-.295
.5	97.1	-.485	-.265

25 % Ag Bath; KCN 10 G L.

Effect of Temperature

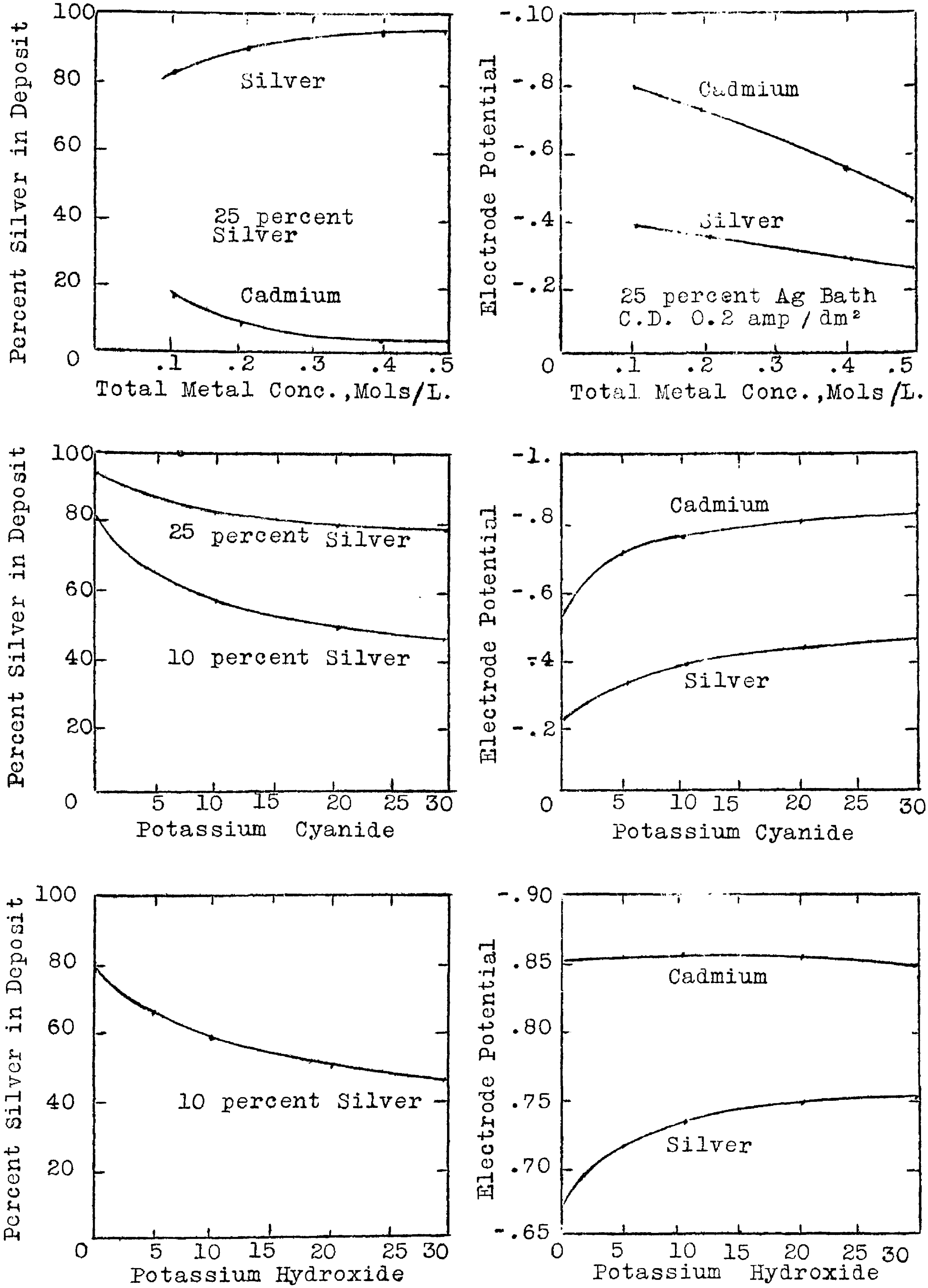
Temp. °C.	Composition of Deposit Percent Ag	Electrode Potential Cd	Electrode Potential Ag
20	78.0	-.786	-.393
40	88.6	-.705	-.383
50	90.2	-.685	-.387
70	95.2	-.722	-.388

25 % Ag Bath; KCN 10 G/L

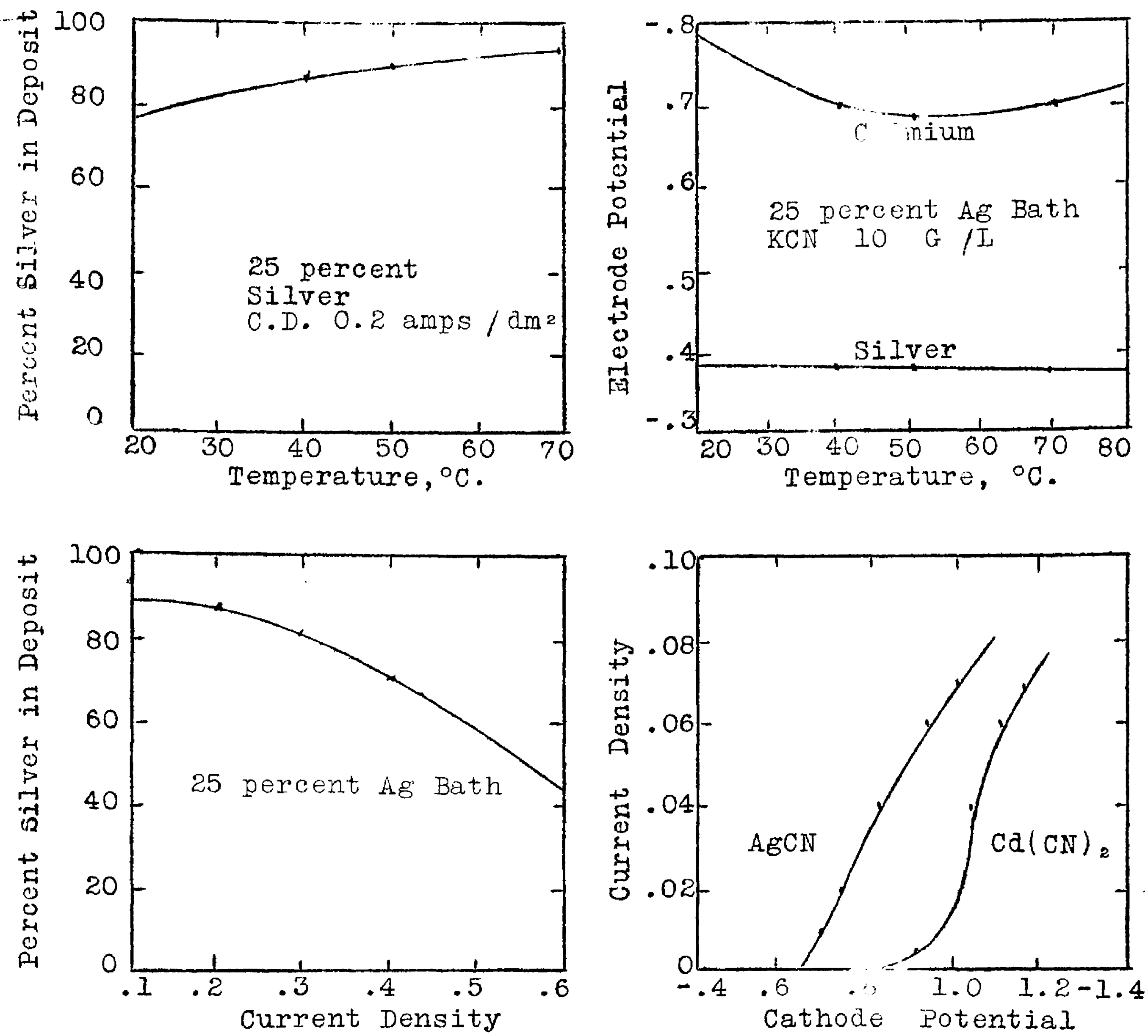
Effect of Current Density

Current Density Amps.per Dm²	Composition of Deposit Percent Ag
.1	90.2
.2	88.2
.4	72.5
.6	45.3

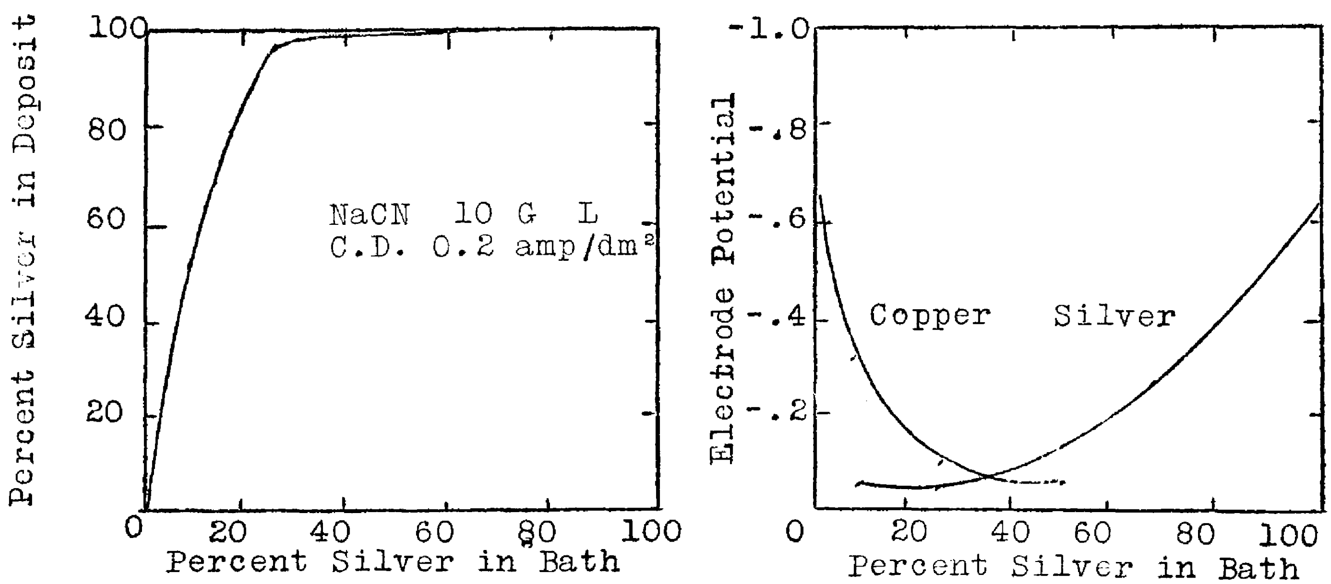
25 % Ag Bath; KCN 10 G/L



Silver-Cadmium Alloys



Silver-Cadmium Alloys



Silver-Copper Alloys

SILVER-COPPER ALLOYS

Effect of Metal Ratio of Bath

Composition of Bath Molal % Ag	Composition of Deposit Molal % Ag	Electrode Potentials		Decomposition Potential
		Silver	Copper	
0	0	----	-.635	-.735
5	37.1	-.083	-.311	-.097
10	49.3	-.076	-.284	-.089
15	61.0	----	----	----
25	99.7	-.054	-.083	-.071
50	100.0	-.114	-.052	-.065
100	100.0	-.618	----	-.056

NaCN 10 G/L   Current Density, 0.2 amps. per Dm^2.

Effect of Free Cyanide

NaCN G/L	Composition of Deposit Molal Percent Silver		Electrode Potential		Decomposition Potential
	5 % Ag Bath	10 % Ag Bath	Silver (5 percent Ag Bath)	Copper	
0	27.7	55.8	-.016	-.215	-.027
5	29.2	44.3	-.059	-.252	-.068
10	37.1	49.3	-.083	-.311	-.097
20	68.8	98.9	-.127	-.388	-.157
30	80.1	100.0	-.188	-.466	-.240

Effect of Alkalie

NaOH G/L	Composition of Deposit Molal Percent Silver
0	55.8
5	66.8
10	53.6
15	49.0
25	39.9

10 % Silver Bath. No Free Cyanide
Current Density, 0.2 amps per Dm^2

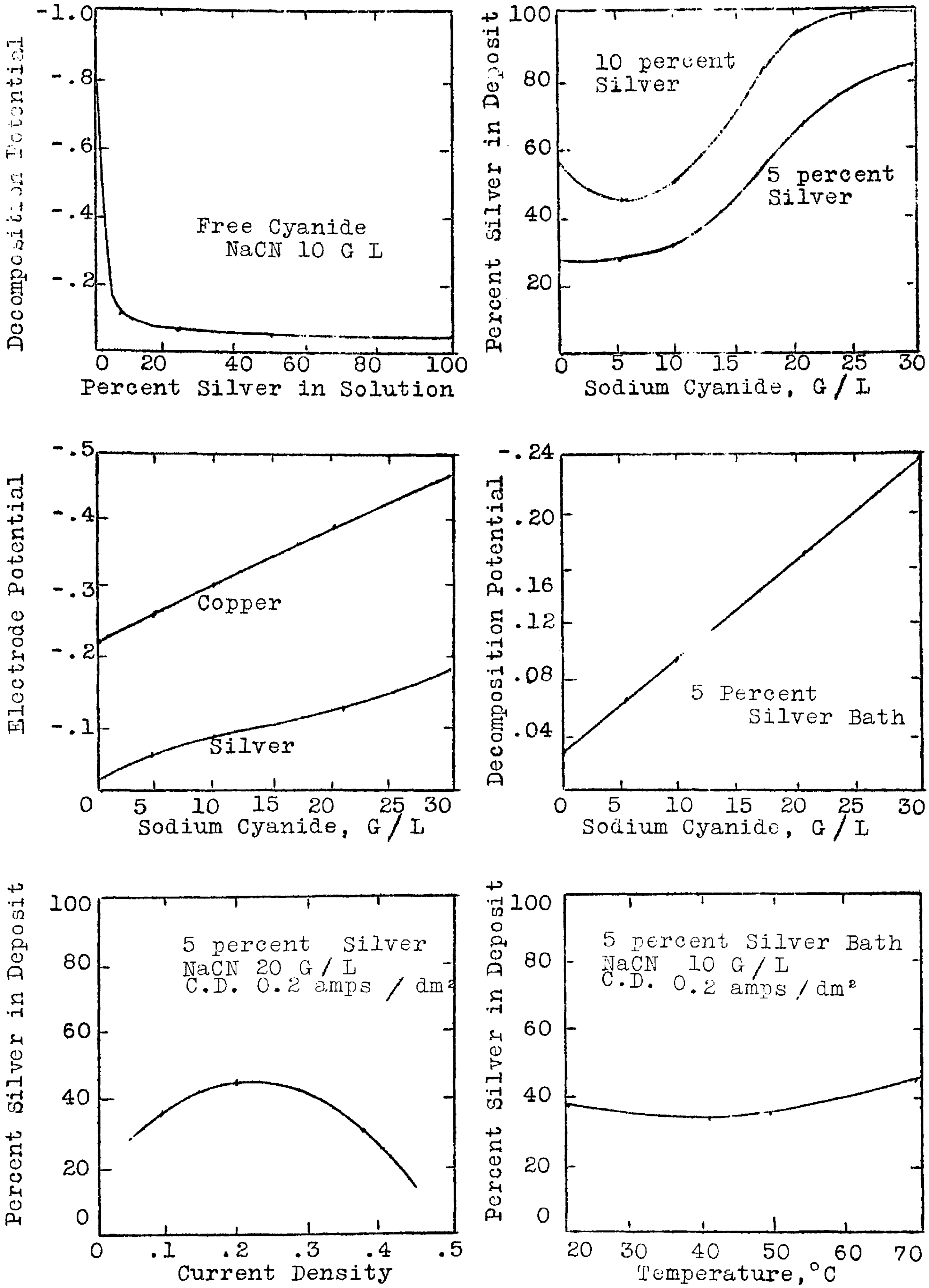
Effect of Temperature

Temp. °C.	Composition of Deposit Molal Percent Ag.	
	10 Ag Bath	5 Ag
20	98.9	38.5
40	97.7	36.0
50	98.2	37.5
70	100.0	44.7

NaCN 10 G/L
Current Density, 0.2 amps/Dm^2

Effect of Current Density

Current Density Amps/Dm^2	Composition of Deposit	
	5 % Ag Bath NaCN 20 G/L	10 [illegible] Bath Na[illegible] [illegible]0 G/L
.1	38.0	100.0
.2	45.6	100.0
.3	35.2	100.0
.4	25.2	94.3



Silver-Copper
Alloys

SILVER-TIN ALLOYS

Effect of Metal Ratio

Composition of Bath Percent Ag	Composition of Deposit Percent Silver: Theo. CN	Composition of Deposit Percent Silver: NaCN 10 G/L	Electrode Potential (NaCN 10 G/L): Silver	Electrode Potential (NaCN 10 G/L): Tin	Cathode Decomposition Potential
0	0	0	--	-.662	-.778
5	79.5	80.4	-.211	-.327	-.270
10	97.0	91.0	-.201	-.313	-.260
25	97.4	98.1	-.160	-.290	-.166
50	100.0	100.0	-.205	-.265	-.140
100	100.0	100.0	-.618	---	-.056

Current Density 0.2 amps. per dm^2

Effect of Free Cyanide

NaCN G/L	Composition of Deposit Percent Ag, From Baths: 5 % Ag	10 % Ag	25 Ag	Electrode Potentials (10 percent Ag): Silver	Tin	Cathode Decomposition Potential
0	79.5	97.0	97.4	-.089	-.276	-.140
5	80.0	91.8	98.2	-.150	-.295	-.221
10	80.4	91.0	98.1	-.201	-.313	-.260
20	80.1	90.2	98.0	-.220	-.316	-.281
30	79.3	91.2	97.6	-.239	-.317	-.301

Effect of Alkalie

NaOH G / L	Composition of Deposit Percent Ag
0	97.4
5	96.3
10	95.2
15	94.0
25	91.3

No Free Cyanide

Effect of Metal Concentration

Total Mols per Liter	Composition of Deposit Percent Ag
.1	80.2
.2	82.6
.3	85.7
.4	88.5
.5	91.2

Effect of Temperature

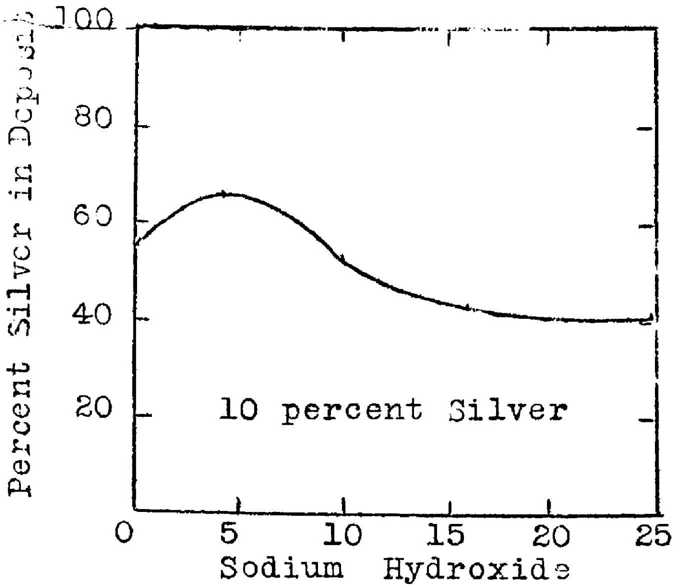
Temperature Deg. Cent.	Composition of Deposit Percent Ag
20	91.0
40	93.9
50	95.2
70	98.2

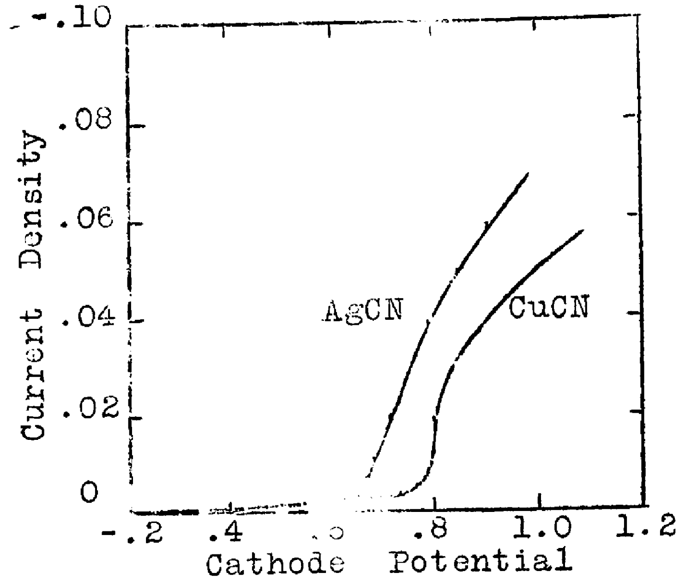
10 Ag Bath.
NaCN 10 G L

Effect of Current Density

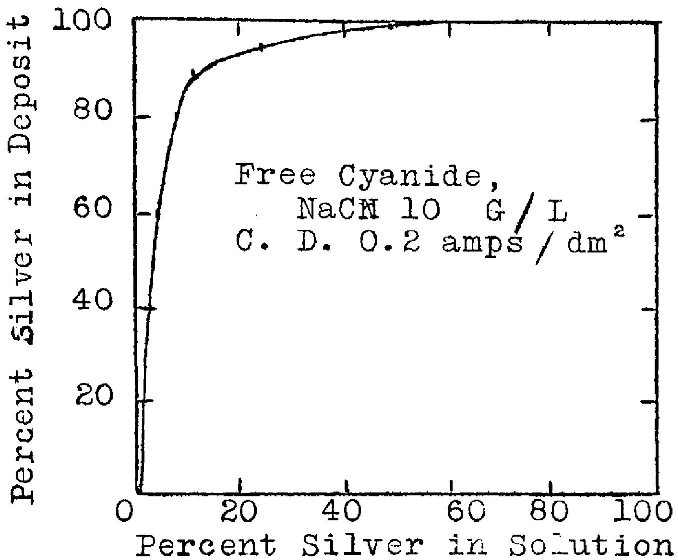
Current Density Amps. per Dm^2	Composition of Deposit Percent Ag
.10	100.0
.15	94.5
.20	91.0
.30	91.3
.40	91.7
.50	92.4

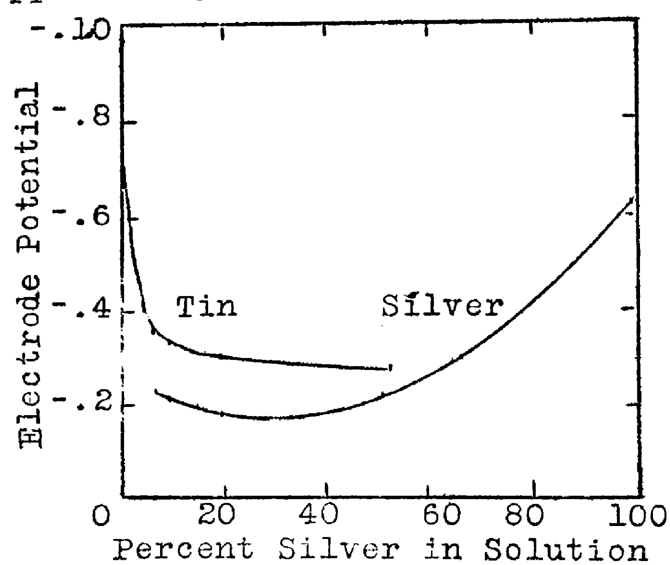
10 Ag Bath. NaCN 10 G L

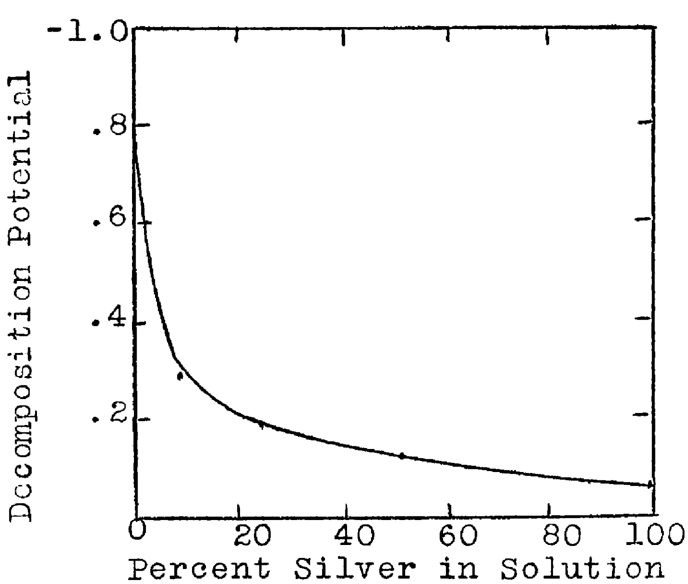


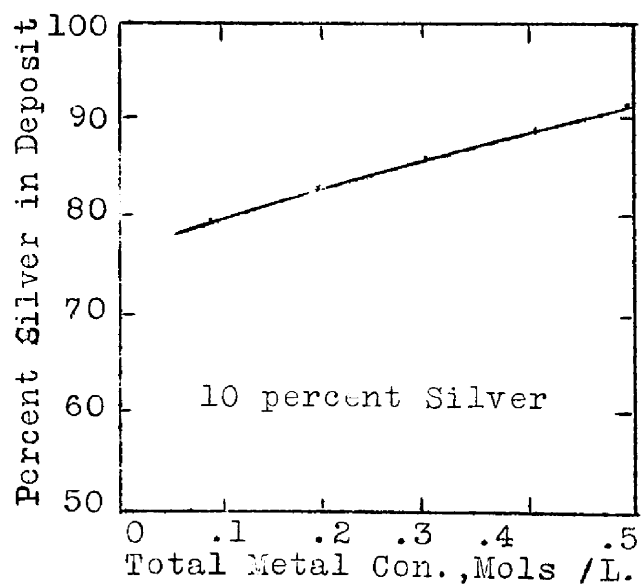


Silver-Copper Alloys

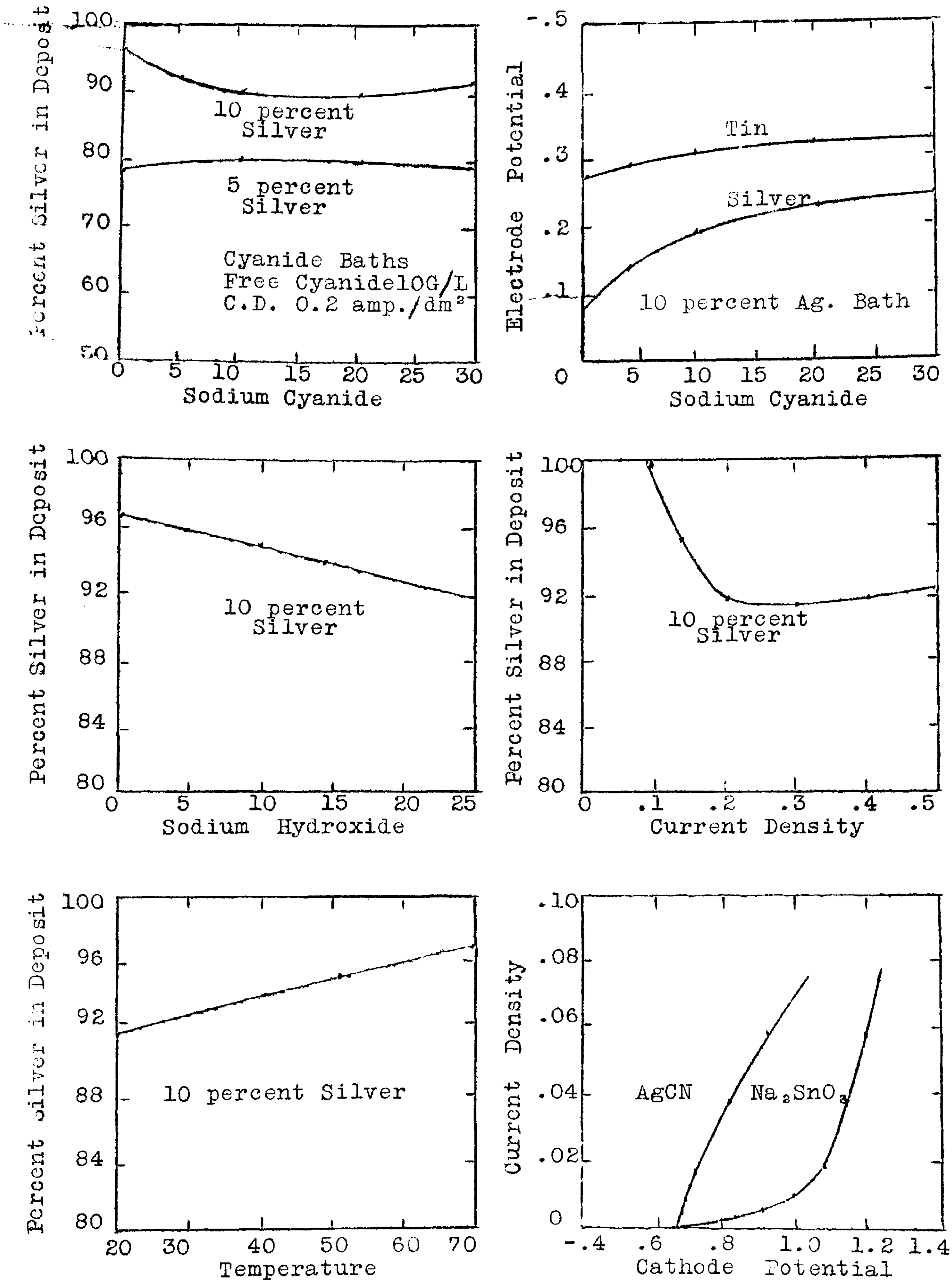








Silver-Tin Alloys



Silver-Tin Alloys

COBALT-NICKEL ALLOYS

Effect of Metal Ratio

Composition of Bath Percent Co	Composition of Deposit Percent Co	Cathode Decomposition Potential
0	0	-.595
5	15.5	----
10	45.6	----
25	74.0	-.584
50	98.5	-.582
100	100.0	-.580

Total Metal Conc. 1 Normal

Effect of Metal Concentration

Total Metal Concentration Normality	Composition of Deposit Percent Co
0.25	24.5
0.50	33.0
0.75	39.4
1.00	45.6

10 percent Co-Ni Bath Ratio
Current Density 1 amp. Dm².

Effect of Temperature

Temperature °C.	Composition of Deposit Molal Co	Decomposition Potential	
		Co	Ni
20	54.4	-.580	-.595
40	48.0	-.400	-.410
50	----	-.370	-.383
60	43.3	---	---
70	----	-.330	-.335
80	38.8	---	---

10 percent Co-Ni Bath

Effect of Current Density

Current Density Amps. per Dm².	Composition of Deposit Molal Co
0.5	38.0
1.0	45.6
1.5	51.5
2.0	57.0

1 Normal Solutions
10 percent Co-Ni Bath
Current Density 1 amp. Dm²

Effect of Ammonium Chloride

NH_4Cl G / L	Composition Of Deposit Percent Co	Decomposition Potential	
		Co	Ni
0	44.3	-.580	-.595
5	44.5	-.573	-.594
10	45.0	-----	-----
15	45.6	-.558	-.580
30	46.3	-.502	-.550

10 percent Co-Ni Bath
Current Density, 1 amp. per Dm²

Effect of Ammonium Sulfate

$(NH_4)_2SO_4$ G / L	Decomposition Potential	
	Co	Ni
0	-.580	-.595
10	-.612	-.640
30	-.662	-.690
60	-.720	-.750

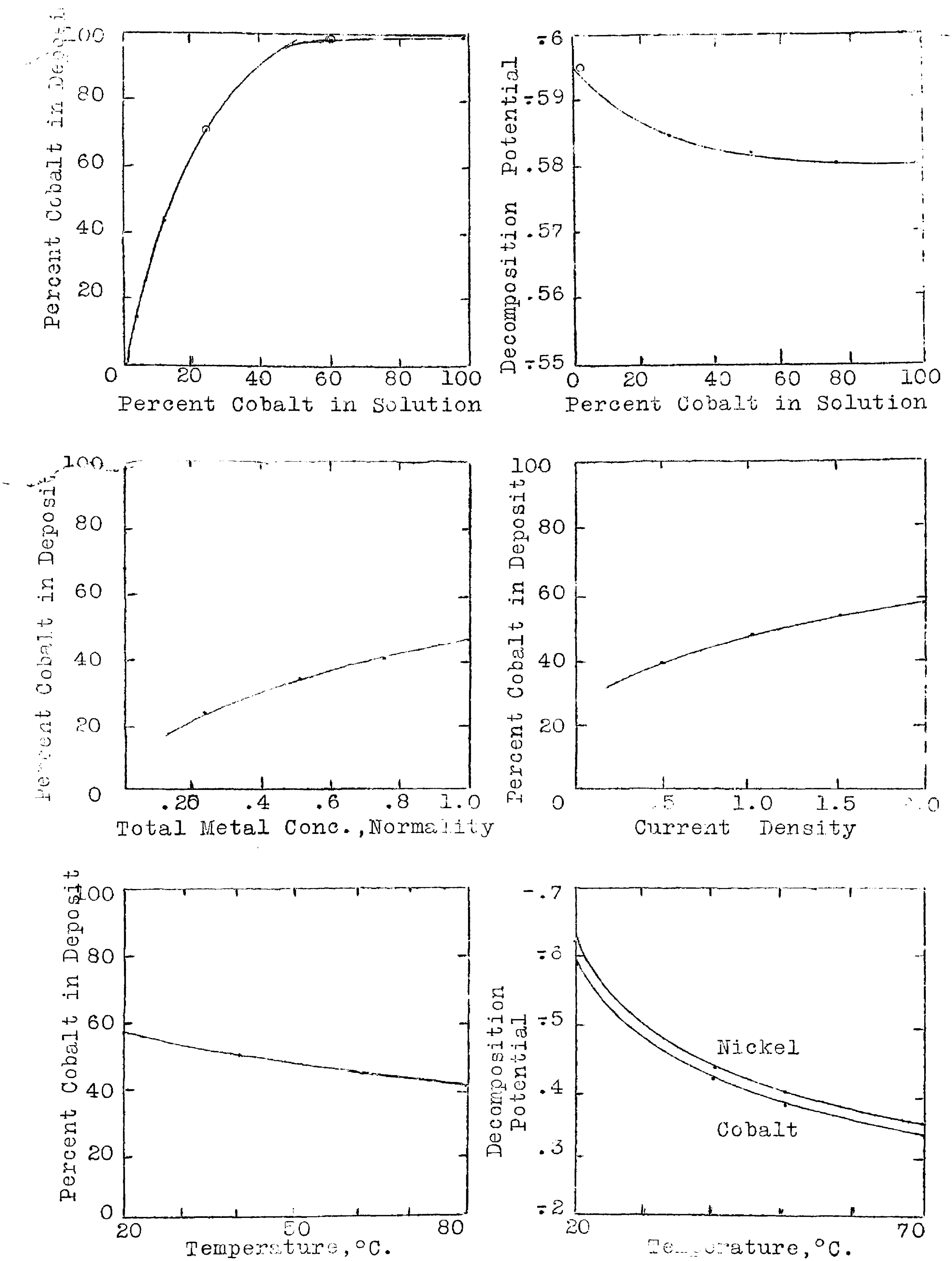
Effect of Boric Acid

H_3BO_3 G / L	Composition of Deposit Molal Co	Decomposition Potential	
		Co	Ni
0	49.2	-.580	-.595
5	----	-.525	-.540
15	45.6	-.508	-.525
25	41.2	-.507	-.525

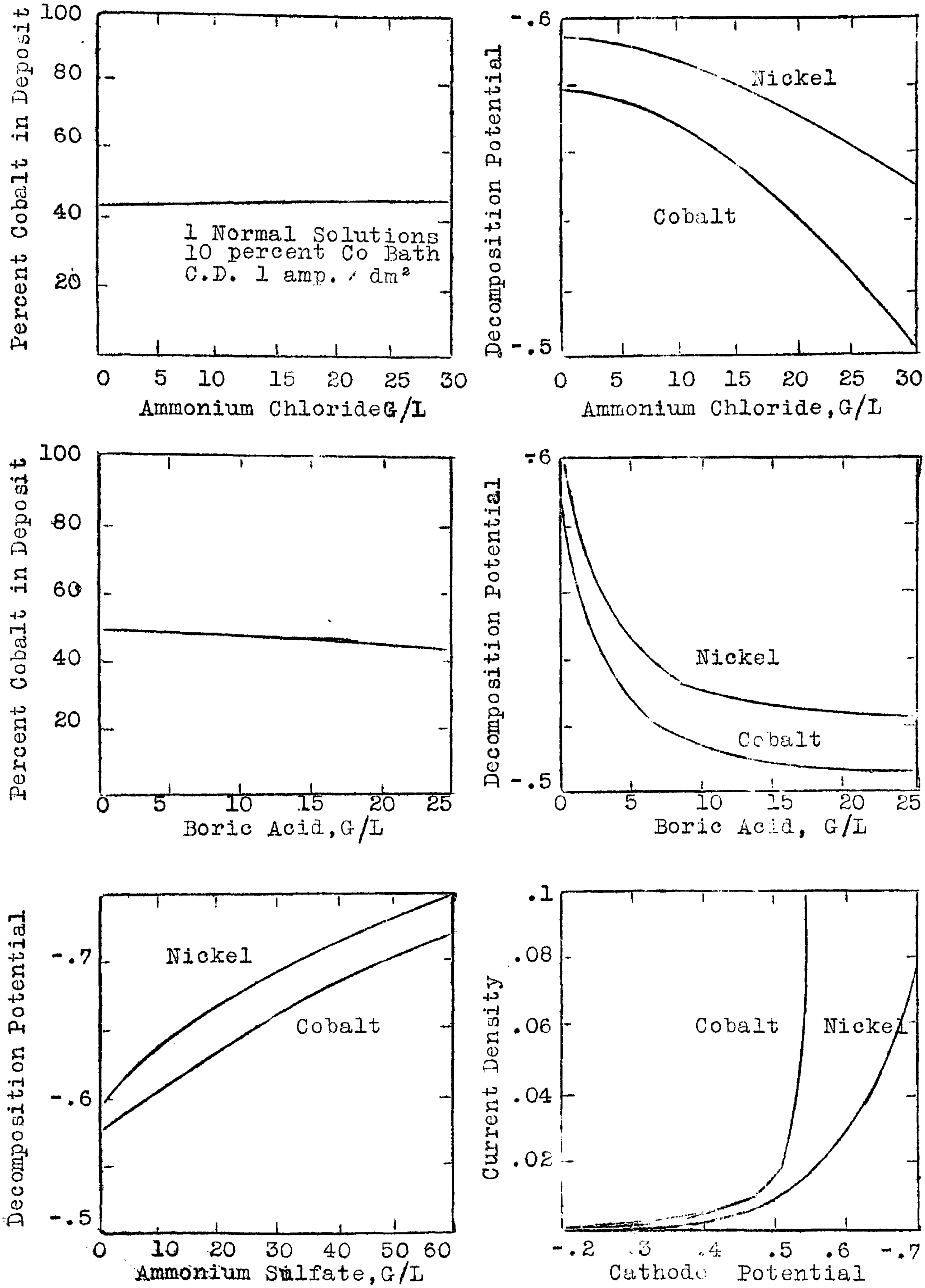
10 percent Co-Ni Bath
Current Density, 1 amp. Dm²

Effect of Current Density

Current Density Amp. /Dm²	Cathode Potential	
	Co in $CoSO_4$	Ni in $NiSO_4$
0	-.215	-.295
.0010	-.[illegible]	-.398
.0025	-.352	-.440
.0050	-.410	-.465
.0100	-.480	-.499
.0300	-.525	-.602
.0600	-.528	-.695



Cobalt-Nickel Alloys



Cobalt-Nickel Alloys

SUMMARY OF RESULTS

Copper-Tin Alloys

1. Copper content of the deposit varies with changes in conditions as follows;
   (a) Copper has the greater tendency to deposit, increasing rapidly with increasing copper to tin ratio in bath.
   (b) Increases with increasing total metal concentration.
   (c) Decreases with the addition of free cyanide.
   (d) Decreases with the addition of alkalie.
   (e) Decreases with increasing temperature.
   (f) Decreases with increasing current density.

2. Increasing Copper to Tin ratio in the bath;
   (a) Rapidly increases copper to tin ratio in the deposit.
   (b) Decreases(more positive) the copper equilibrium potential, while that of tin is affected very little.
   (c) Decreases cathode decomposition potentials.

3. Increasing total metal concentration;
   (a) Increases(linearly) the copper content of the deposit.
   (b) Increases the equilibrium electrode potential of tin, while that of copper changes but very little.
   (c) Increases(more negative) decomposition potentials.

4. Addition of free cyanide;
   (a) Rapidly decreases copper content of the deposit.
   (b) Rapidly increases the electrode potentials of copper, but that of tin is affected but very little.
   (c) Rapidly increases(more negative) the decomposition potential of copper, and that of tin to a lesser extent.

5. Addition of alkalie;
   (a) Slowly decreases the copper content of the deposit.
   (b) Decreases the equilibrium electrode potentials of Copper, and increases that of tin.
   (c) Rapidly changes the decomposition potential of copper to a more negative value, while that of tin to a more negative one.

6. Increase of temperature;
   (a) Decreases the copper content to a minimum value, again increasing as the temperature rises.
   (b) Increases the electrode potentials of both copper and tin.

7. Increasing current density decreases copper content of deposit.

Silver-Cadmium Alloys

1. Silver content of the deposit varies with changes in conditions, as follows;
   (a) Silver has the greatest tendency to deposit, increasing rapidly with increasing silver to cadmium ratio of bath.
   (b) Increases with increasing total metal concentration.

(c) Decreases with the addition of free cyanide.
(d) Decreases with the addition of alkalie.
(e) Increases with rising temperature.
(f) Decreases with increasing current density.

2. Increasing silver to cadmium ratio in the bath;
    (a) Rapidly increases silver content of the deposit.
    (b) Increases(more negative) the equilibrium electrode potential of silver, while that of cadmium is decreased.

3. Increasing total metal concentration of bath;
    (a) Increases silver content of the deposit.
    (b) Decreases the equilibrium electrode potentials of both silver and cadmium, but cadmium at the greater rate.

4. Addition of free cyanide;
    (a) Decreases the silver content of the deposit.
    (b) Increases the electrode potentials of both metals.

5. Addition of alkalie;
    (a) Decreases the silver content of the deposit.
    (b) Decreases the equilibrium electrode potential of cadmium to a slight extent,but increases that of silver.

6. Increase of temperature;
    (a) Slowly increases the silver content of the deposit.
    (b) Apparantly has no effect upon the equilibrium electrode potential of silver, but rapidly lowers that of cadminm.

7. Increasing current density rapidly lowers the silver content of the deposit.

Silver-Copper Alloys

1. Silver content of the deposit varies with changes in conditions, as follows;
    (a) Silver has the greater tendency to deposit,increasing rapidly with decreasing copper to silver ratio of the bath.
    (b) Increases with increasing total metal concentration.
    (c) At first decreases with the addition of free cyanide, but quickly passes thru a minimum and rapidly increases.
    (d) Decreases with the addition of alkalie, giving the reverse effect of free cyanide.
    (e) Increases very slowly with rising temperature.
    (f) Increases with increasing current density, passing thru a maximum at moderate current density,and rapidly falling off.

2. Increasing silverv to copper ratio in the bath;
    (a) Rapidly increases the percent silver in the deposit.
    (b) Decreases the equilibrium potentials of both metals.
    (c) Decomposition potentials become more positive.

3. Increasing total metal concentration of the bath;
   (a) Increases the silver content of the deposit.
   (b) Decreases the equilibrium electrode potentials of both metals, but to a greater extent for the silver.

4. Addition of free cyanide;
   (a) Causes a slight drop in the silver content of the deposit, passing thru a minimum, and rapidly increasing.
   (b) Rapidly shifts the equilibrium electrode potentials of both silver and copper to more negative values.
   (c) Causes the decomposition potentials to rapidly become more negative.

5. Addition of alkalie;
   (a) Decreases the silver content of the deposit.
   (b) Decreases the equilibrium electrode potential of copper, but increases that of silver.
   (c) Causes the decomposition potentials to become more negative.

6. Increasing temperature;
   (a) Slowly increases the silver content of the deposit.
   (b) Increases the equilibrium electrode potential of copper, but has very little effect upon that of silver.

7. Increasing current density causes the silver content of the deposit to decrease, after passing thru a maximum value.

Silver-Tin Alloys

1. Silver content of the deposit varies depending upon conditions, as follows;
   (a) Silver has the greater tendency to deposit, increasing very rapidly with increasing silver content of the bath.
   (b) Increases as the total metal concentration increases.
   (c) Decreases slowly upon addition of free cyanide.
   (d) Decreases(linearly) with addition of alkalie.
   (e) Rapidly decreases with increasing current density.
   (f) Increases slowly with temperature, as a linear function.

2. Increasing silver to tin ratio in the bath;
   (a) Rapidly increases the silver content of the deposit.
   (b) Both silver and tin equilibrium electrode potentials becomes more positive.
   (c) Shifts the decomposition potentials to more positive values.

3. Increasing total metal concentration of the bath;
   (a) Increases the silver content of the deposit.
   (b) Decreases the equilibrium electrode potentials.

4. Addition of free cyanide;
   (a) Slightly lowers the silver content of the deposit.
   (b) Shifts the equilibrium electrode potentials of both silver and tin to more negative values.
   (c) Rapidly shifts decompositions potentials to more negative values.

5. Addition of alkalie;
   (a) Gradually lowers the silver content , as a linear function.
   (b) Shifts both silver and tin electrode potentials to more negative values, but that of tin more rapidly.
   (c) Shifts decomposition potentials to more negative values.

6. Increase of temperature;
   (a) Slowly increases silver content of deposit(linearly).
   (b) Causes the tin electrode potential to slowly become more negative, but that of silver is practically unaffected.

7. Increasing current density rapidly decreases the silver content of the deposit.

Cobalt-Nickel Alloys

1. Cobalt content of the deposit varies with changes in conditions, as follows;
   (a) Cobalt has the greater tendency to deposit,increasing very rapidly with increasing cobalt to nickel ratio.
   (b) Increases with increasing total metal concentration.
   (c) Slowly increases with increasing temperature.
   (d) Slowly increases with increasing current density.
   (e) Is practically unaffected by the presence of chlorides or boric acid.

2. Increase of cobalt to nickel ratio of bath;
   (a) Rapidly increases cobalt content of the deposit.
   (b)Changes equilibrium electrode potentials of both cobalt and nickel but very little.

3. Increase of total metal concentration;
   (a) Increases cobalt content of the deposit.
   (b) Shifts the equilibrium electrode potentials to more negative values.

4. Addition of ammonium chloride;
   (a) Has no apparent affect upon the composition of the deposit.
   (b) Slightly lowers the decomposition potentials.

5. Addition of boric acid;
   (a) Slightly lowers the cobalt content of the deposit.
   (b) Slightly lowers the decomposition potentials.

6. Increasing temperature;
   (a) Slightly decreases the cobalt content of the deposit.
   (b) Rapidly decreases the decomposition potentials of both metals.

7. Increasing current density slowly increases the cobalt content of the deposit.

CONCLUSIONS

When two or more different cations are present in solution, deposition of one may be preferred over that of the other, for causes such as; (1) Metal ratio in solution, (2) Total metal concentration, (3) Degree of ionization, (4) Electrode potentials, (5) Temperature, (6) Current Density, (7) Addition agents, (8) Mobility of ions, and , (9) Overvoltage.

The composition of deposits obtained under otherwise similar conditions depend upon the metal ratio in the solution. In general, an increase in a metal ratio in solution increases that metal ratio in the deposit. The rate of increase of a metal in the deposit varies from one combination to another depending upon the other factors involved, such as relative degrees of ionization, which determines the ratios of metal ions present, relative electrode potentials, current density, and relative mobilities of the ions.

In general, with increasing total metal concentration, there is an increase in that metal deposited which ordinarily has the greater tendency to deposit. This may be attributed to;

(a) The increase in the number of prefered metal ions in the vicinity of the cathode which eliminat any possibility of a shortage of these ions available.

(b) Increase in resulting common ions which may, according to the law of mass action, further shift the equilibrium potentials of the more negative one having the smaller degree of ionization.

Due to the fact that the addition of substances with a common ion, or substances which form complex ions with the metal ions, and thus reduce the concentration of the metal ions present, according to the Nernst equation, and the equilibrium electrode potential is repidly shifted to a more negative value. This may in turn reverse the relative equilibrium potentials of the two metals in question, depending upon their degree of ionization, and greatly change the composition of the deposited alloy.

Deposited alloys, in general, have a much finer structure than either of the component metals deposited separately under similar conditions. It may be assumed that each metal acts as an addition agent with respect to the other, in that each metal prevents the growth of the crystals of the other.

In every case, the predominating metal present in the deposit, is the one having the most positive electrode potential. Addition of complex ions, as cyanide, or common ions, reduced the simple metal ion concentration and rapidly changed the electrode potentials. Due to relative degrees of ionization of the complex metal ions, the addition of complex ions changes the single electrode potentials at widely different rates and results in relatively complete reversed value. In agreement with these, in all cases, radical changes in composition of the deposited alloys resulted. As a general rule, it can be seen from the results obtained that the proportion present has a relation to the proximity of the single electrode potentials to each other.

Increase of temperature, in general, tends to favor the deposition of the more negative, less preferred metal. This may be due to a combination of the following reasons, which depending upon their relative values, give different net results.

(a) Reduces polarization and overvoltage, favoring the deposition of the more electropositive metal.

(b) Increases mobility of the ions. The resulting change in composition of the deposit is due to the difference in the change in their mobilities.

(c) Increases migration of ions, due to convection current. This results in the same effect as agitation, favoring the more electronegative metal.

(d) Rise in temperature may have the affect of changing the deposition potentials of one constituent more than the other, consequently, the composition of the deposited alloy will be such that there will be an increase in the percent of the matal having the lowest(most positive) potential.

Increasing current density, in nearly all cases, tends to decrease the percentage of the more easily deposited metal. In other words, increased current density tends to increase the percent of the metal deposited having the more negative potential.

Other factors which no doubt enter into the problem of alloy deposition make certain cases difficult to explain, and fit any general rule. The formation of an entirely new phase on the cathode, solid solutions, with their own potentials, may result in further complicated facts, rendering it almost impossible to apply conclusions drawn from a study of the individual component metals.

The evidence that has been submitted here, has been restricted to an attempted consideration of one factor at a time. In actual practice, all of these numerous factors act together, and it is difficult to distinguish or isolate the effect of any one variable. The actual deposit is the net result of all of these factors.