

THE ELECTRODEPOSITION OF COPPER-BISMUTH ALLOYS FROM
A PERCHLORATE BATH

by

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By

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THE ELECTRODEPOSITION OF COPPER-BISMUTH ALLOYS FROM
A PERCHLORATE BATH

I. Introduction

The electrodeposition of copper-bismuth alloy has been studied for theoretical rather than practical reasons. The codeposition of these two metals seemed to be simpler than in many other alloy systems and it was hoped, by such a study, to gain some insight into the mechanism of alloy deposition. Before discussing this system in detail, a short review of alloy deposition in general will be given as a back-ground.

The art of electrodepositing alloys is about 100 years old. Patents for bronze and brass plating baths were issued before 1850 (1). The electrodeposition of certain alloys are now processes of commercial importance. Brass has been commercially electrodeposited for many years. Bronze, cadmium-zinc and mercury-zinc alloys are now deposited commercially. One of the most recent alloy plating processes is the deposition of bright nickel-cobalt alloys. Even the electrodeposition of tungsten-nickel alloys is being attempted commercially. This latter process is interesting because tungsten cannot be deposited by itself. In addition to these alloys, satisfactory plating baths have been developed for plating a large number of other binary and even ternary alloys. Practical studies of the deposition of alloys, such as silver alloys, are now in progress for the purpose of developing methods of plating out bearing metals.

The development of a satisfactory alloy plating process is done rather empirically. There are few useful guiding principles and these are mainly qualitative. The bulk of the literature on alloy deposition is concerned with the practical problem of determining the conditions for the production of a good deposit. A relatively small number of papers deal with the theoretical side of the subject. An understanding of the factors involved in alloy deposition is of practical as well as theoretical interest, because it would decrease the amount of work required in the development of new alloy plating processes.

The problem of alloy deposition is two-fold. First, it is necessary to find a bath from which the alloy can be deposited. To merely codeposit two metals is usually not difficult; but much research may be required to find the conditions for producing an alloy of the required physical properties and composition. The second problem is to study the factors which affect the composition of the deposit. This study, by itself, would be a straightforward matter of electrodeposition followed by analysis, and the results would not be of general interest. Such an investigation, however, would not be complete unless the cathode potentials were also measured, so that some information could be obtained about the electrode processes. It is desirable to be able to predict the composition of the deposit from a knowledge of the plating conditions, the bath composition, and the electrochemical behavior of the individual metals (i.e. their static potentials and their cathode potentials during deposition). This ideal cannot be realized in general, because some metals, for

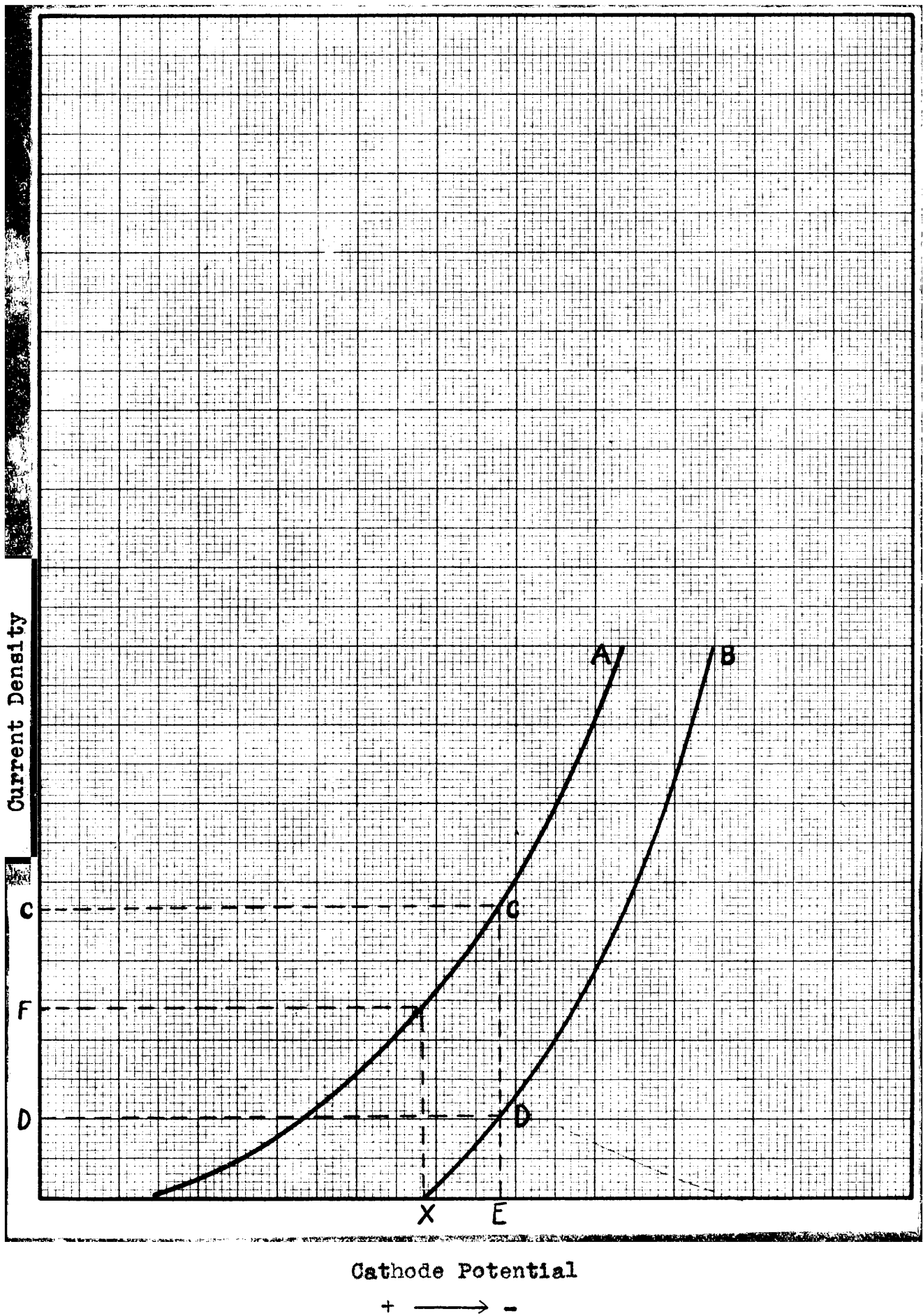
example the iron group, behave in an anomalous manner when co-deposited with each other or with some other metals. However, if studies were made of the codeposition of those pairs of metals which exhibited the simplest behavior, an idea could be obtained of the nature of alloy deposition under ideal conditions. The principles gained in such a study could be used as a standard for interpreting the behavior of other alloy systems. If a system should deviate in some respect from the ideal system, then an investigation would be in order to find the complicating factor.

II. Theory of the Electrodeposition of Alloys

The following is a brief discussion of the theory of the electrodeposition of alloys (2), (3), (4). The curves A and B in Fig. I represent the cathode potential curves for the separate deposition of two metals from solutions in which they are of the same concentration as in the alloy bath. If the cathode potential, during the electrolysis of the mixed solution, is below X, (the deposition potential of the less noble metal) only the nobler metal, A, deposits. For the two metals to codeposit, the cathode potential must be more negative than X. This cathode potential can be attained, and the two metals codeposited, by raising the current density to a value above F. If the alloy formed by the two metals is a solid solution or compound, which has a reversible potential intermediate between those of the two metals, then metal B will deposit at a more positive potential than corresponds to X, and its deposition is said to be depolarized. The

FIG. 1.

Conditions for the Codeposition of the Two Metals A and B



Cathode Potential

+ → -

most striking example of this is the deposition of sodium from an aqueous solution on a mercury cathode. In addition to the depolarization effect of the amalgam formation, the high overvoltage of hydrogen on mercury is a contributing factor. If the equilibrium potentials of the two metals are far apart, it is difficult to codeposit them satisfactorily by simply raising the current density. The potentials of the nobler metal can be made more negative by reducing its ion concentration in solution, either by employing a smaller concentration of its salt, or by forming a complex ion. An example of this is the codeposition of copper and cadmium, at high current density, from a sulphate solution which contains a larger amount of cadmium than copper. A better deposit is more easily obtained by using a cyanide solution, which forms complex ions. With this bath a high current density is not required. By adding excess potassium cyanide, the cadmium can be made more noble than copper, so that it will deposit more readily than copper.

The above statements are qualitative. Very little of a general nature can be said concerning the quantitative relations between the composition of the deposit and the conditions of deposition. The following ideas have been discussed in the literature. (I). If an alloy is deposited reversibly from a bath which contains the metal ions in the equilibrium ratio, i.e., from a solution in which the two metals have the same static potential, then the deposit will contain the metals in the same ratio as the bath. (II). In codeposition attended by polarization, the ratio of the two metals can be computed

from the separate cathode potential curves for the two metals. If the cathode potential is E (Fig. I), the ratio of the two metals A:B in the deposit will be in the ratio of $GE:DE$. (III). At high current densities, the metal ratio of the deposit will be the same as that of the solution.

The latter relationship seems obvious, and it has been experimentally demonstrated, (6),(7). Relationship (I) also seems rather obvious and follows from thermodynamics. It has been experimentally demonstrated by Blum and Haring (8) in their work on the electrodeposition of lead-tin alloys. Relation (II) seems reasonable but so far has received no experimental proof. It is probably an oversimplified picture of codeposition, as it assumes that the metals behave during codeposition in the same manner as when they alone are present in solution. This is seldom the case.

The alloy systems may be divided into three groups with regard to the simplicity of their behavior. Group A contains most of the alloy baths composed of simple salts. The effect of the plating variables on the composition of the deposit can be qualitatively predicted from the general principles of alloy deposition. Group B includes the simple salt baths containing the iron group metals, iron, nickel and cobalt. The codeposition of these metals with one another or with zinc is anomalous, as frequently the less noble metal deposits more readily than the nobler one. For example, the alloy obtained from a sulphate bath containing zinc and one of these metals has a higher zinc:metal ratio than the bath (9),(10),(11). The codeposition of binary alloys of iron, nickel, or cobalt with each other is complicated

and the results of different investigators are often contradictory (12), (13), (14), (15), (16), (17), (18), (19). At elevated temperatures, these metals codeposit in a more orthodox manner. Group C includes the baths containing complex ions. The relative positions of the cathode potentials of the metals give some qualitative information about the composition of the deposit. The structures of the baths are not well known, however, and the effect of changes of bath composition on the alloy can not always be predicted. Also, the complex ion baths, such as the cyanide baths, are usually unstable.

In the selection of an alloy system for a theoretical study, only the members of group A were given consideration. However, a bath composed of a mixture of the simple salts of two metals has the disadvantages that the alloy deposits are usually of poor quality, and the standard electrode potentials of most metals are so far apart that they can be codeposited only at high current densities.

The copper-bismuth alloy system was chosen for study because from a preliminary survey it seemed to be a simple system. An examination of the literature showed that the electrodeposition of this alloy has not been investigated previously. Both metals are more electropositive than hydrogen and they deposit, either singly or together, with above 99 percent efficiency. Their electrode potentials are only about 30-50 mv. apart, so that they can be codeposited over a wide range of current density. The two metals do not form either solid solutions or

compounds (5), hence, their codeposition ought not be complicated by the depolarization effect. The alloy deposits are usually smooth and adherent. As the following study will show, this system behaved in a simple fashion as regards the effect of the plating conditions and bath composition on the composition of the alloy; but the cathode potentials were rather anomalous.

III. Experimental

A. Apparatus

Investigators of alloy deposition have shown that a homogeneous deposit is not obtained from a still bath. If the bath is stirred the difficulty is not entirely obviated, as the agitation is not uniform over all parts of the cathode. The best method is to agitate the cathode. The only geometrical arrangement of anode and cathode, which readily lends itself to the production of a uniform degree of agitation and a uniform current density over all of the cathode surface, is a rotating cylindrical cathode surrounded by a concentric cylindrical anode. Some investigators have used a rotating disc as a cathode; this arrangement is not satisfactory, as the cathode surface has neither a uniform current density nor a uniform degree of agitation.

The apparatus used was patterned after that of Boulach (20). A diagram of the apparatus is shown in Fig. II. The cathode, H, consisted of a steel tube 9.0 cm long and 2.0 cm in diameter. It was nickel plated, polished, and then plated with a coating of gold 0.0025 cm (0.001 in.) thick. The gold

FIG. II

Rotating Cathode Assembly Used for Alloy Deposition

- A. Bakelite coupling.
- B. Commutator.
- C. Brushes, with leads to potentiometer and battery.
- D. Glass cup.
- E. Ammonium nitrate bridge leading to calomel half-cell.
- F. Capillary for measurement of cathode potentials.
- G. Electrical connection from shaft to cathode.
- H. Gold plated cathode
- K. Bakelite cylinder.
- L. Rubber collar.

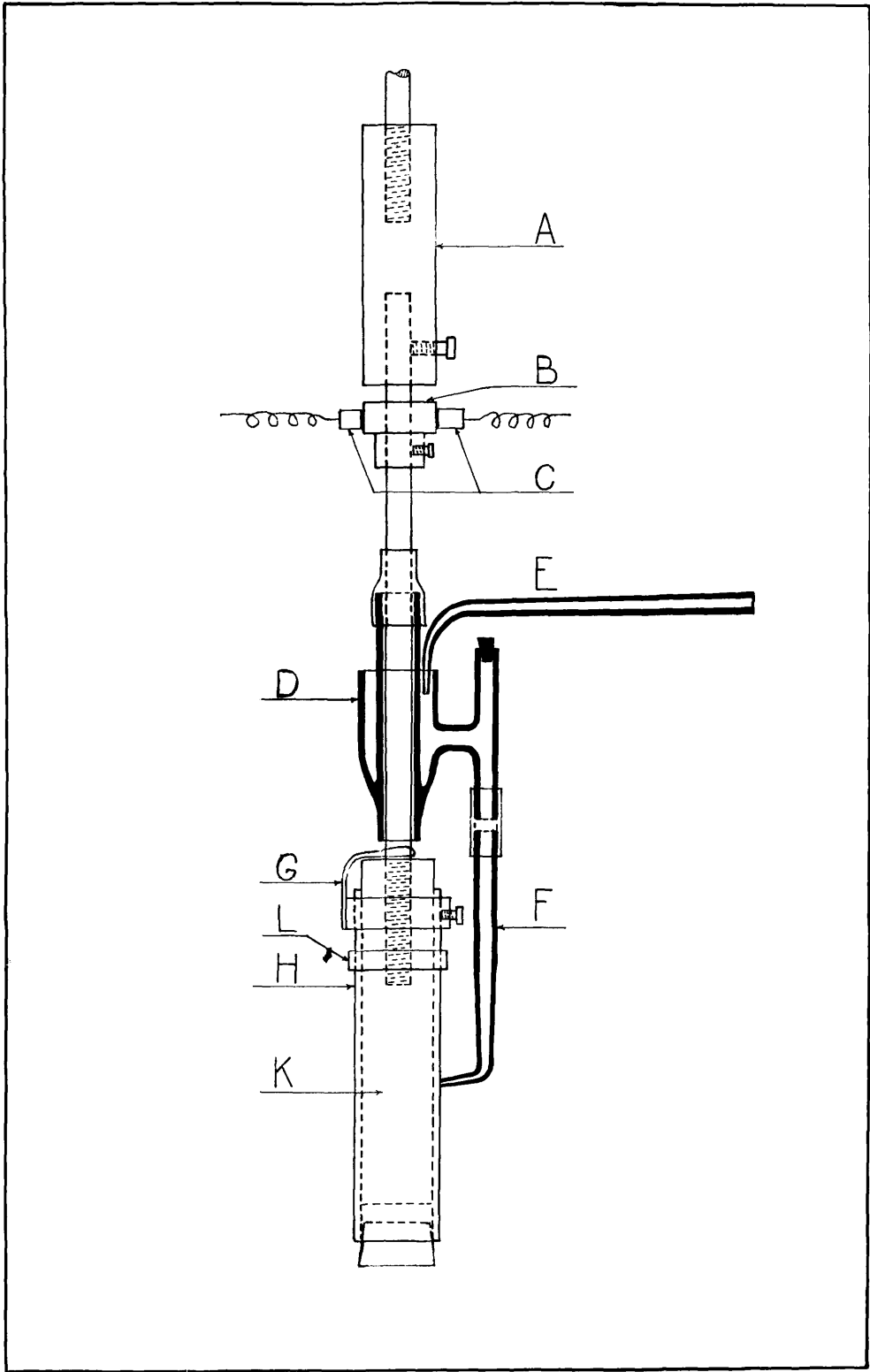


plate was polished. It was nonporous, and the alloy deposit could be dissolved off in nitric acid without attack of the basis metal. A 6.0 cm length of the gold cathode was plated with the alloy. This area was defined by a rubber collar, L. The lower end of the tube was closed by a rubber stopper, and the tube was then slipped on the bakelite cylinder, K, and the electrical connection to the steel shaft was made by the thumb-screw. The current was led from the battery to the rotating cathode by means of one of the brushes, C, and the commutator, B. The commutator was provided with a second brush which led to the potentiometer.

The capillary tube, F, was held firmly pressed against the cathode by a rubber band. The tip of the capillary had an external diameter of 0.5 mm. The end of the capillary did not rest flush against the cathode but it was cut obliquely, according to the suggestion of Boulaeh (20), so that it made a 20-30° angle with the surface of the cathode. The glass cup, D, to which the capillary is connected was partly filled with glass wool and a gel, consisting of 2.0 M ammonium nitrate and 5 g of agar-agar per 100 ml. This served to prevent the ammonium nitrate solution from running into the plating bath. The rest of the cup was filled with ammonium nitrate solution to make connection with the calomel cell. The capillary and the side tube of D was filled with the plating bath. In some cases, a stationary capillary was pressed against the rotating cathode, and potential measurements were made at the same time with both the rotating and the stationary capillaries. The difference in their readings usually amounted to several millivolts. Therefore,

most of the measurements were made with the capillary which rotated with the cathode, as this was the more convenient method.

The cathode assembly was connected to the shaft of a variable speed motor by an insulating coupling of bakelite, A. The speed of rotation was 100 rpm. in most of the experiments, and it was constant within about 5 percent. Since the circumference of the cathode was about 6 cm, this corresponds to a linear speed of 600 cm/min. (24 ft./min.). When high speeds of rotation were used the glass cup and side tube unbalanced the shaft and caused much vibration. In this case, they were removed and the stationary capillary was used.

Cathode potentials were measured against a saturated calomel half-cell, and these were converted to the hydrogen scale by adding +0.246 V. The liquid junction potential formed by the gel was found to vary several mv. after it had been used for one or two experiments. The variation of E.M.F. due to the liquid junction was determined after an experiment by comparison with another calomel cell which had a fresh ammonium nitrate junction. This was more convenient than preparing a new agar plug each time.

The anode, which is not shown in the diagram, was a cylinder concentric with the cathode. The anode consisted either of copper, or copper heavily plated with bismuth. The anode selected for use in any experiment was the one which would produce the smallest change in the metal ratio of the bath. The plating was done in a 1-liter beaker which was provided with a glass plate ground to fit the curved bottom. A thermostat maintained the temperature of the bath constant within 0.5°.

The plating bath had a volume of about 525 ml and the amount of alloy plated out was 0.2-0.3 g. This changed the composition of the bath by less than 2 percent.

B. Analysis of Deposits

The total weight of deposit was obtained by weighing the cathode. The deposit was analyzed by dissolving it in 5 ml of concentrated nitric acid diluted to 15 ml. The solution of the alloy was diluted to 300 ml, made alkaline with ammonia, so that all the copper was dissolved, and the precipitation of the bismuth completed with ammonium carbonate. The solution was allowed to stand on the steam bath for several hours or over night. It was filtered and the filtrate was evaporated with sulphuric acid to fumes and electrolyzed for copper. The precipitate was dissolved in nitric acid, the solution evaporated in a platinum dish and the residue ignited to Bi_2O_3 . Usually only one of the metals was determined as the other could be obtained by difference.

Swift (21) states that the carbonate method is not satisfactory for separating small amounts of copper from large amounts of bismuth. He found that when separating a few hundredths of a gram of copper from about 1 g of bismuth, 10-15 percent of the copper was carried down. Instead he recommended Moser's method (22), which consists in precipitating the bismuth as phosphate from a solution 0.3-0.4 N in nitric acid. However, Swift's objections to the carbonate method could not be confirmed. The bismuth carbonate precipitate obtained by a single precipitation in the separation of about equal amounts of copper and bismuth was analyzed by Moser's method. Only about 0.0002 g of

copper was carried down by the carbonate. Also, 3 mg of copper was separated from 1.0 g of bismuth with an error of only 0.0001 g. For most of the analyses the carbonate method was used since bismuth is best weighed as the oxide. In those cases where only a small quantity of copper was to be determined, Moser's method was used, as the precipitate of phosphate was more easily filtered and washed than the carbonate and the precipitation could be made from a smaller volume of solution.

In most of the experiments, a copper coulometer was used. Since the equivalent weight of bismuth (69.7) is more than twice that of copper (31.8), the composition of the alloy deposit could be calculated from the weight of the alloy and the weight of copper deposited in the coulometer. This served as a rough check on the analyses.

The composition of the deposit and the metal ratio of the bath are expressed in this paper as equivalent percent of copper. This equals $100 \text{ Cu} / (\text{Cu} + \text{Bi})$ where Cu and Bi here represent the amounts of the two metals expressed in equivalents.

C. Preparation of Plating Baths

The plating bath consisted of a mixture of copper and bismuth perchlorates. Harbaugh and Mathers (23) investigated the bismuth perchlorate plating bath and found it gave satisfactory deposits. Bismuth can also be electrodeposited from acid solutions of the nitrate or chloride, but the advantage of the perchlorate bath is that the basic bismuth perchlorate is soluble and the solution can be diluted without precipitating the bismuth. However, if an anion, such as chloride or sulphate is

added to the diluted solution, immediate precipitation occurs. Smith (24) has studied the constitution of bismuth perchlorate solutions by conductivity methods. He showed that one mole of bismuth (as oxide) was dissolved by one mole of perchloric acid so that the solution must have contained the soluble basic salt BiOClO_4 . According to the conductivity measurements, the bismuth is partly present as this salt even when the solution contains considerable excess of perchloric acid. When the ratio of perchlorate to bismuth (moles) is 4:1 only about 50 percent of the bismuth is converted into the less basic salt $\text{BiOH}(\text{ClO}_4)_2$. In agreement with Smith's statements, it was found that on titrating a bismuth perchlorate solution, which corresponded to a 1.0 molar solution of $\text{Bi}(\text{ClO}_4)_3$, with sodium hydroxide, two-thirds of the perchlorate was neutralized before a permanent precipitate formed. However, on heating this solution, the precipitate dissolved and additional alkali (the total alkali added corresponding to four-fifths of the perchlorate present) could be added to the boiling solution before a permanent precipitate was formed.

The bismuth perchlorate stock solution was made by dissolving Bi_2O_3 in perchloric acid to form a solution corresponding to the composition 1.0 molar $\text{Bi}(\text{ClO}_4)_3$. The copper stock solution was prepared from copper carbonate and perchloric acid. The chemicals used were of reagent quality, and the bismuth oxide gave no qualitative test for lead or silver. For checking some of the earlier cathode potential measurements, some new

solutions were later made up from copper and bismuth oxides which had been heated to 800°C to decompose any organic matter that might be present. The plating baths were made up by mixing measured volumes of the stock solutions, and the required amount of a standardized solution of perchloric acid. As pointed out above, the amount of free acid in a bismuth perchlorate solution is not definitely known. Therefore, as a matter of convenience in stating the composition of the plating baths, the term "free acid" has been used to mean the amount of perchloric acid in excess of that theoretically required to form the normal salts $\text{Bi}(\text{ClO}_4)_3$ and $\text{Cu}(\text{ClO}_4)_2$.

Most of the alloys were deposited from a bath 1.0 N in total metal concentration and 0.5 N in free acid. The temperature was 25°C and the cathode was rotated at 100 rpm.

IV. Appearance of the Deposits

Copper and bismuth plated separately from a perchlorate bath give smooth dull deposits. However, over a fairly wide range of conditions, almost mirror bright deposits were obtained from the alloy bath. The appearance of the deposits depended on the conditions of deposition. The deposits from a bath 0.5 N in copper, 0.5 N in bismuth, and 0.5 N in free perchloric acid, were white in color and quite bright when plated on a polished cathode at current densities from 4 to 10 amp/dm². At lower current densities the deposits were copper colored and dull. In order to get bright deposits from a bath containing more bismuth, the amount of free perchloric acid had to be

decreased. For example, a bath 0.75 N in bismuth and 0.25 N in copper did not give bright deposits over a very wide range of current density, if it contained any "free" perchloric acid, but it gave bright deposits from 1.5-8.0 amp/dm² in its absence. A bath 0.95 N in bismuth and 0.05 N in copper did not give smooth deposits as long as the bath was very acid. To secure a bright deposit it was necessary to neutralize even the perchloric acid resulting from the hydrolysis of the bismuth perchlorate. The deposits obtained under unsatisfactory conditions were dull, striated and usually coated with a black dust or bloom.

The color of the deposits depended on their composition. Bright deposits which contained below 60 percent (by weight) of copper had a white color, similar to that of steel; deposits containing above 60 percent of copper, were copper colored and usually dull. However, a dull copper colored deposit containing only 30 percent of copper was obtained at a low current density from a bath high in bismuth.

The bright deposits maintained their appearance for a week or more without appreciably tarnishing. The deposits were very brittle, and although they adhered well to the cathode, they could be flaked off by bending. Because of their brittleness, they do not offer promise of any commercial use.

V. Cathode Potentials

The current density vs. cathode potential curves for copper and bismuth singly and for the alloy deposition are shown in Fig. III. All measurements were made at 25°C with solutions having a total metal content of 1.0 N. The cathode was rotated at 100 rpm. Most of the curves are the average of two sets of measurements. The reproducibility of the measurements depended on the system measured, but usually was about ±10 mv. for current densities below 1 amp/dm²; about ±20 mv. for current densities between 2 and 5 amp/dm²; and somewhat more uncertain at the higher current densities, especially as the limiting current density was approached. No correction was made for the liquid junction potential. It was probably fairly constant for the different solutions, since they varied little in total metal content or acidity. A correction would have resulted simply in displacing all the curves by the same amount.

It would be desirable for the comparison of different baths to be made in solutions of the same acidity. As already pointed out, the amount of uncombined acid in a bismuth perchlorate solution is uncertain. If a solution is 1.0 N in Bi(ClO₄)₃, the amount of uncombined acid due to hydrolysis is between 1/3 and 2/3 N. As a rough approximation it will be assumed that 1/2 of the perchlorate is present as uncombined acid. Thus, the plating baths, which have a total metal content of 1.0 N and a "free" acid content of 0.5 N, actually have 0.5 to 1.0 N uncombined acid. Fortunately, the acidity of the bath does not appreciably affect the composition of the deposits, hence, the

FIG. III

Cathode Potentials for the Electrodeposition of Copper,
Bismuth and Copper-Bismuth Alloys.

Curve	Bath Composition		
	Normality		
	Cu	Bi	"Free" HClO ₄
A	1.00		0.50
B	1.00		1.00
C		1.00	0.50
D	0.05	0.95	0.06
E	0.25	0.75	0.50
F	0.50	0.50	0.50
G	0.75	0.25	0.50

The cathode was rotated at 100 rpm.

Temperature = 25°C.

Current Density
amp/cm²

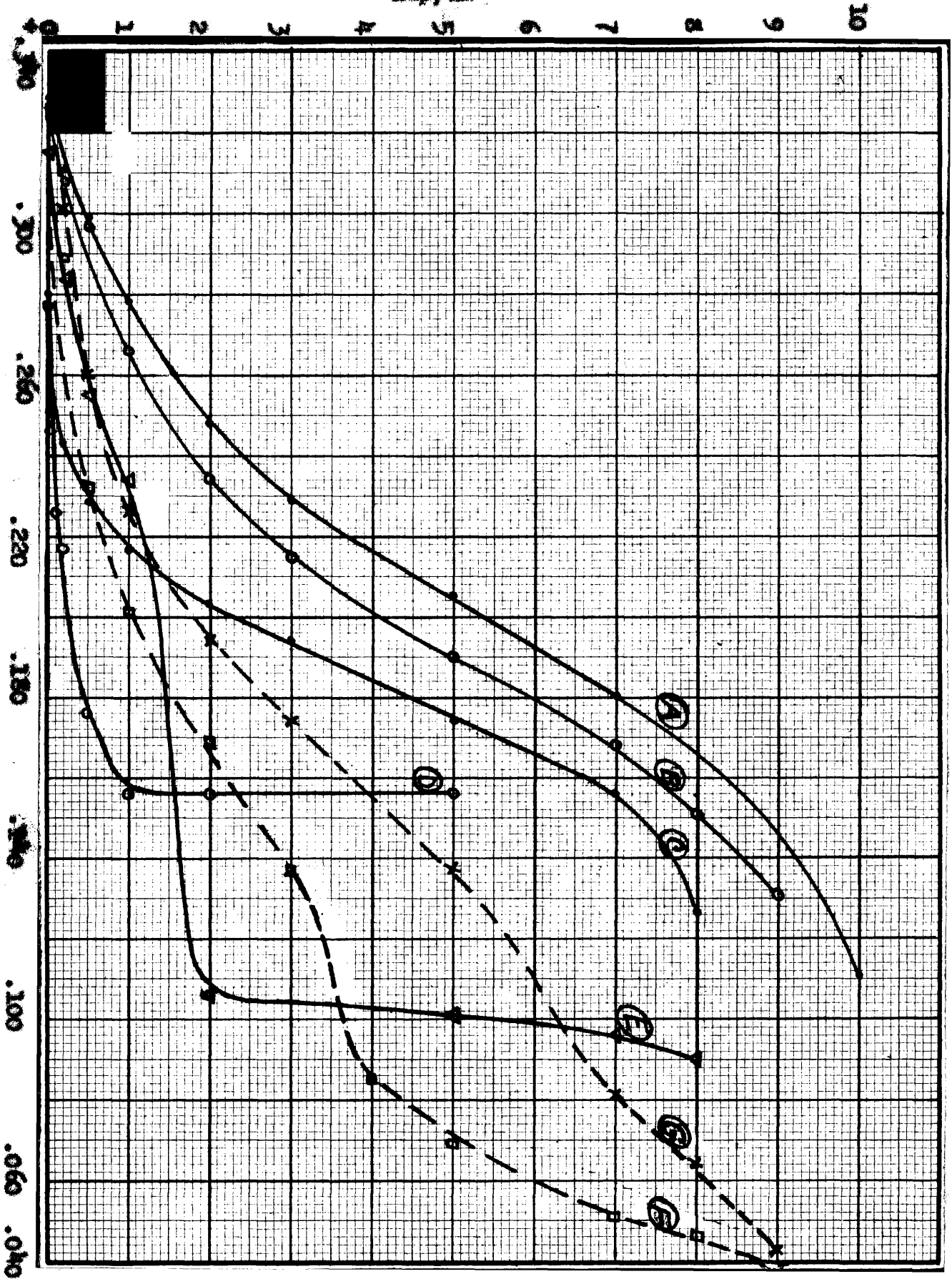


FIG. III.

baths need not be of exactly the same acidity in order to be compared.

The cathode potential curves for copper and bismuth (Fig. III) show the relative tendency of these metals to deposit. The cathode potential curves for the alloy deposition are peculiar, because they become more negative than the curve for bismuth, which is the less noble of the two metals. The curves for the alloy baths should be compared with curves for bismuth solutions which contain the same concentration of bismuth as the bath. However, the curve for a 0.75 N solution of bismuth lies close to curve C for a 1.0 N solution. Thus, the alloy curves D and E for baths containing 0.95 and 0.75 N bismuth, respectively, can be compared with curve C. No example of an alloy deposition, occurring at a more negative potential than that of the less noble metal, appears to have been reported in the literature. Since the cathode potentials for alloy deposition were rather anomalous, no attempt was made to test the relation II discussed on page 5.

In spite of the unexpected nature of the cathode potential curves, the alloy deposition behaved as a simple system with respect to the composition of the deposit, and, qualitatively, the effect of the different variables on the composition of the deposit could be predicted or explained by a consideration of the relative ease of deposition of the two metals and the rate of replenishment of ions to the cathode film. It is customary to interpret the results of electrodeposition entirely on the basis of cathode potentials. If the significance of the cathode

potential is known, it serves as a convenient means of following the progress of the reaction at the electrode. However, the relation of the potential to some electrode processes, such as electrodeposition in the presence of addition agents, is not understood; and the potential, rather than helping to explain the phenomenon, must itself receive explanation. In the present investigation, the cathode potential curves of the alloy deposition do not offer much information about the process, although the cathode potentials of the individual metals are of some help.

VI. Effect of Variables on the Composition of the Deposit

A. Current Density

The effect of current density on the composition of the deposit is shown in Fig. IV. The curves have the characteristic shape for simple alloy baths. The curves for the baths containing 0.5 N copper or less have a sharply descending portion, representing an abrupt change from a copper-rich deposit at low current densities to a bismuth-rich deposit at high current densities. The dotted lines in Fig. IV represent the cathode potential curves for copper deposition alone. The concentration of copper and the actual (not "free") acidity of the baths used for the copper deposition were about the same as in the corresponding alloy baths. The asterisks on these curves mark the limiting current density of the copper deposition.

FIG. IV

Effect of Current Density on the Composition of the Deposit

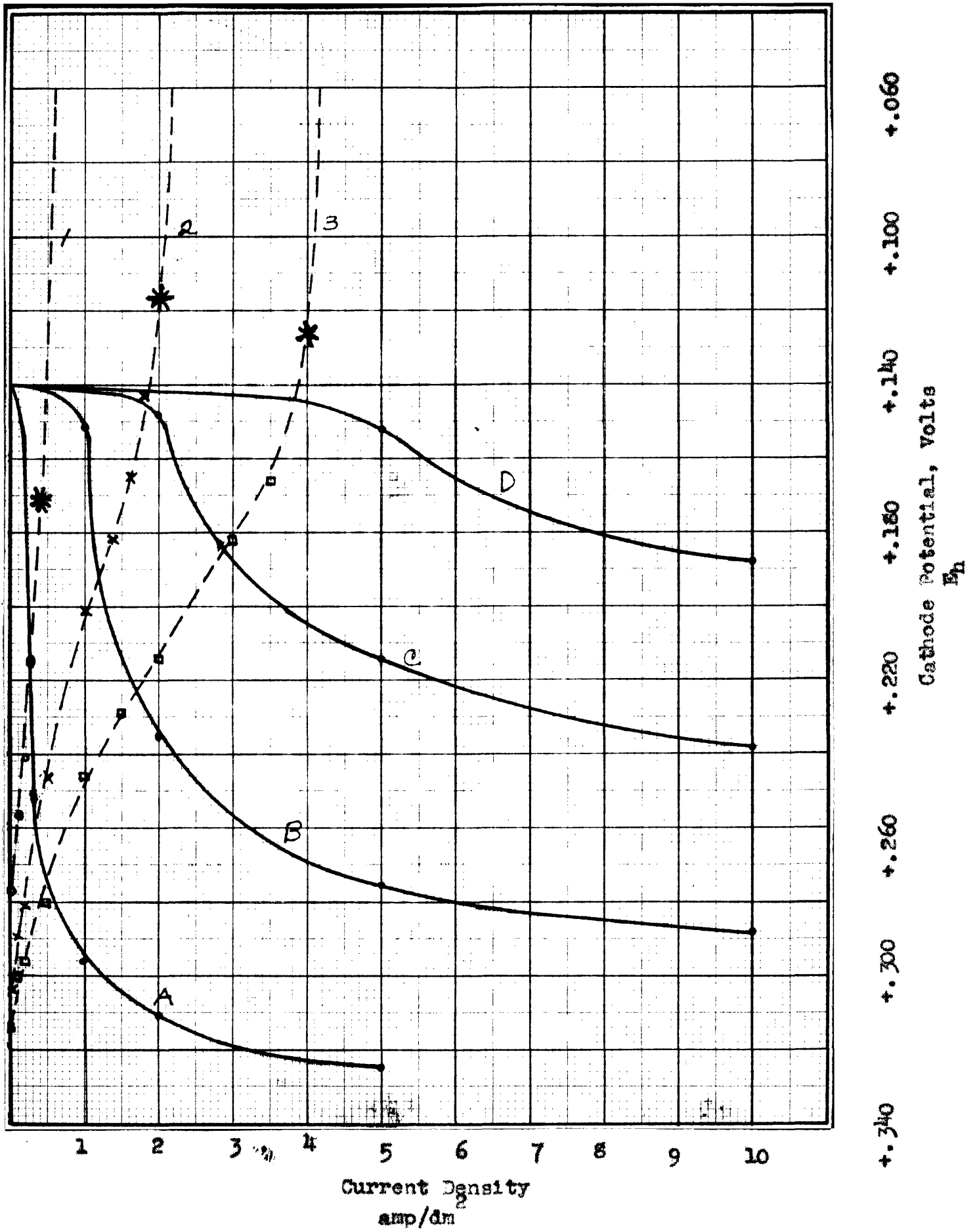
Curve No.	Bath Composition Normalities		
	Cu	Bi	"Free" HClO ₄
A	0.05	0.95	0.06
B	.25	.75	.50
C	.50	.50	.50
D	.75	.25	.50
1	.05		.50
2	.25		.75
3	.50		.75

The heavy lines are the composition vs. current density curves for the alloy deposition. The dotted lines represent the current density vs. cathode potential curves for the copper deposition.

The cathode was rotated at 100 rpm.

Temperature = 25°C.

FIG. IV



It is well known that a high current density must be used to codeposit two metals which have widely separated electrode potentials. The current density must be sufficient to deplete the nobler metal ions in the cathode film, so that the deposition potential of the less noble metal can be reached. In the copper-bismuth system, the electrode potentials are fairly close together. Nevertheless, some relationship can be shown between the shape of the cathode potential curves for copper deposition and those for the variation in the copper content of the deposit with current density. For curves A, B, and C, the abrupt change in the deposit from a copper-rich to a bismuth-rich alloy occurs at a current density in the neighborhood of the limiting current density for the copper deposition, although the potential at which bismuth can codeposit has already been reached at a much lower current density (a few tenths of an amp/dm²). Thus it seems that in this alloy bath, a large proportion of the current is used in depositing copper, until the limiting current density for the copper deposition has been exceeded. At this current density, the cathode film is not supplied with copper ions rapidly enough by diffusion or convection, and the current, in excess of that required for the limiting current density, must go to deposit bismuth. On this basis, some rough calculations of the composition of the deposit can be made for deposits plated at current densities exceeding the limiting current density for the copper deposition. The calculated result will give too high a value for the percent copper, because

even before the limiting current density is reached, some bismuth codeposits with the copper. As an example, the limiting current density of copper deposition from a 0.05 N solution is 0.4 amp/dm². Therefore, the deposit obtained from an alloy bath 0.05 N in copper, at a current density of 2.0 amp/dm², should contain 0.4/2.0 = 20 equivalent percent copper. The actual value for a bath 0.05 N in copper and 0.95 N in bismuth is 15 percent (Fig. IV, Curve A). The following table I shows some calculations made on this basis. It may be pointed out that the calculation would not be valid for current densities in excess of the limiting current density for the alloy bath itself.

TABLE I.

Calculation of the Composition of Copper-Bismuth Alloys from the Limiting Current Density for Copper Deposition.

Concn. of Cu in bath Normality	Limiting c.d. of Cu dep. amp/dm ²	c.d. of alloy dep. amp/dm ²	Equiv. percent Cu in alloy	
			Calc.	Found
0.05	0.04	1	40	22
0.05	0.04	2	20	15
0.05	0.04	5	8	7
0.25	2.0	5	40	32
0.50	4.0	5	80	63

B. Composition of Bath

Fig. V shows how the composition of the deposit varies with the bath composition, the current density being held constant. The curves have steeply sloping intermediate portions

FIG. V

Effect of Bath Composition on the Composition of the
Deposit.

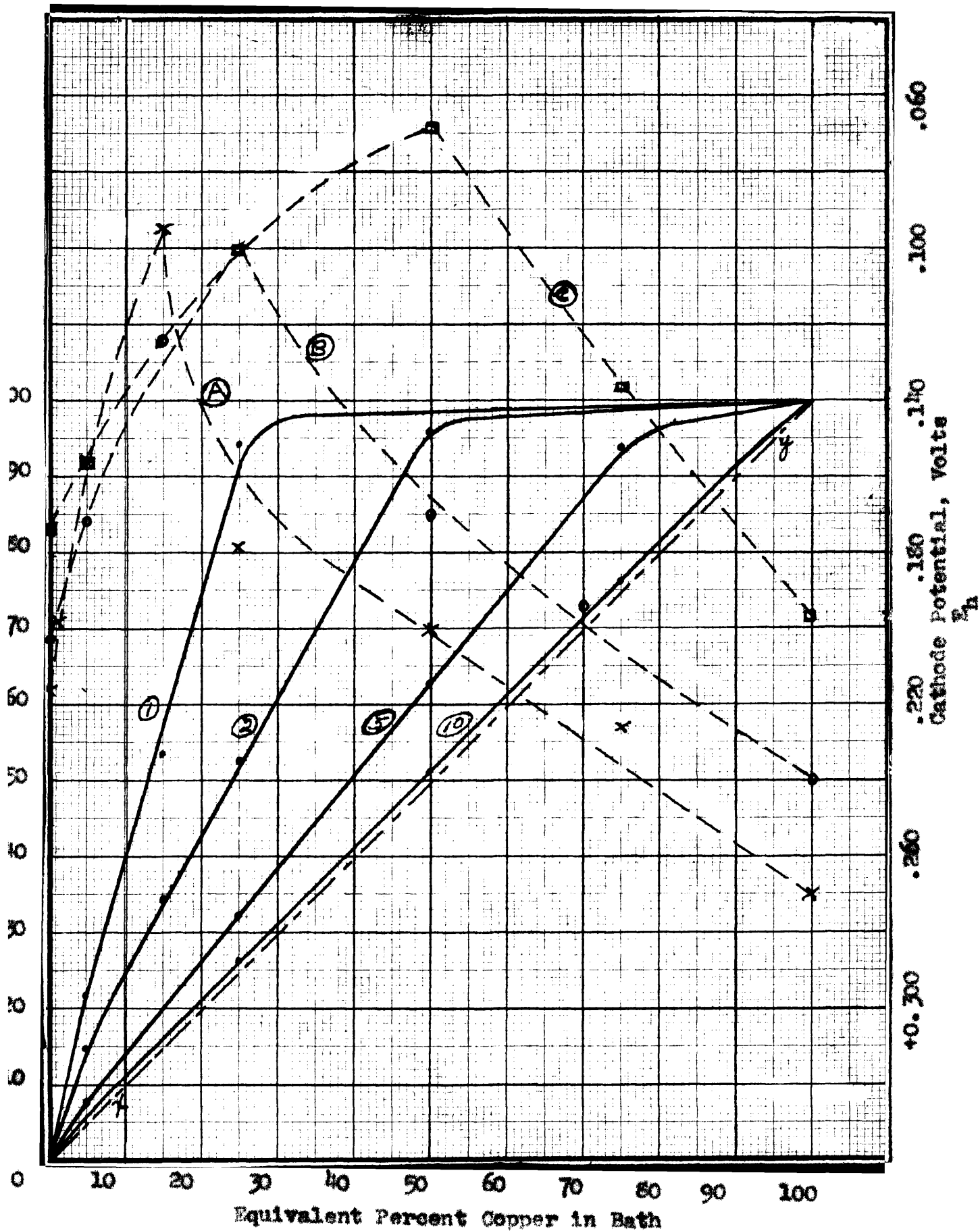
Curves 1, 2, 5, and 10 are for current densities of 1, 2, 5 and 10 amp/dm², respectively. All baths were 1.0 N in total metal content. The baths for curves 2, 5, and 10 contained 0.5 N "free" perchloric acid. The bath for curve 1 was 0.06 N in "free" perchloric acid.

The dotted lines are cathode potential curves. Curves A, B, and C represent the potentials corresponding to curves 1, 2, and 5.

The cathode was rotated at 100 rpm.

Temperature = 25°C.

FIG. V.



which are almost straight lines and show a rapid increase in the percent of copper in the deposit with increase of copper in the solution. The upper parts of the curves are flat and represent deposits containing almost pure copper. The copper;bismuth ratio of the deposit is larger than that of the bath. As the current density is increased, the curves for the various current densities approach the diagonal, XY, along which line the metal ratio of the deposit would be the same as that of the bath. The deposits obtained at 10 amp/dm² have almost the same metal ratio as the bath. Creutzfeld (7) has shown this to be the case in the deposition of copper-cadmium alloys from sulphate solutions, and Sauerwald(6) has shown a similar tendency to exist in the deposition of zinc-copper alloys from sulphate solutions.

The cathode potentials of alloy deposition are shown by the dotted lines. They show decided maxima, which for each current density, occurs in a bath of different composition. But the composition of the deposits corresponding to these maxima are closely alike. At 1.0 amp/dm² the deposit contains 53 equivalent percent of copper; at 2.0 amp/dm², 52 equivalent percent copper; and at 5 amp/dm², 62 equivalent percent copper. No satisfactory explanation has been found for this relation between alloy composition and cathode potentials.

C. Agitation of the Cathode and Total Metal Concentration of the Bath

It is well known that the effect of agitation of the cathode or an increase in the total metal concentration of a bath (keeping the metal ratio constant) is similar, and result

FIG. VI

Effect of Agitating the Cathode on the Composition of
the Deposit.

The plating conditions are as follows:

Bath composition: 0.25 N in Cu; 0.75 N in Bi;
0.5 N in "Free" acid

Current density: 2.0 amp/dm²

Temperature: 25°C

The solid line represents the alloy composition curve.

The dotted line represents the cathode potentials.

Equivalent Percent Copper in Deposit

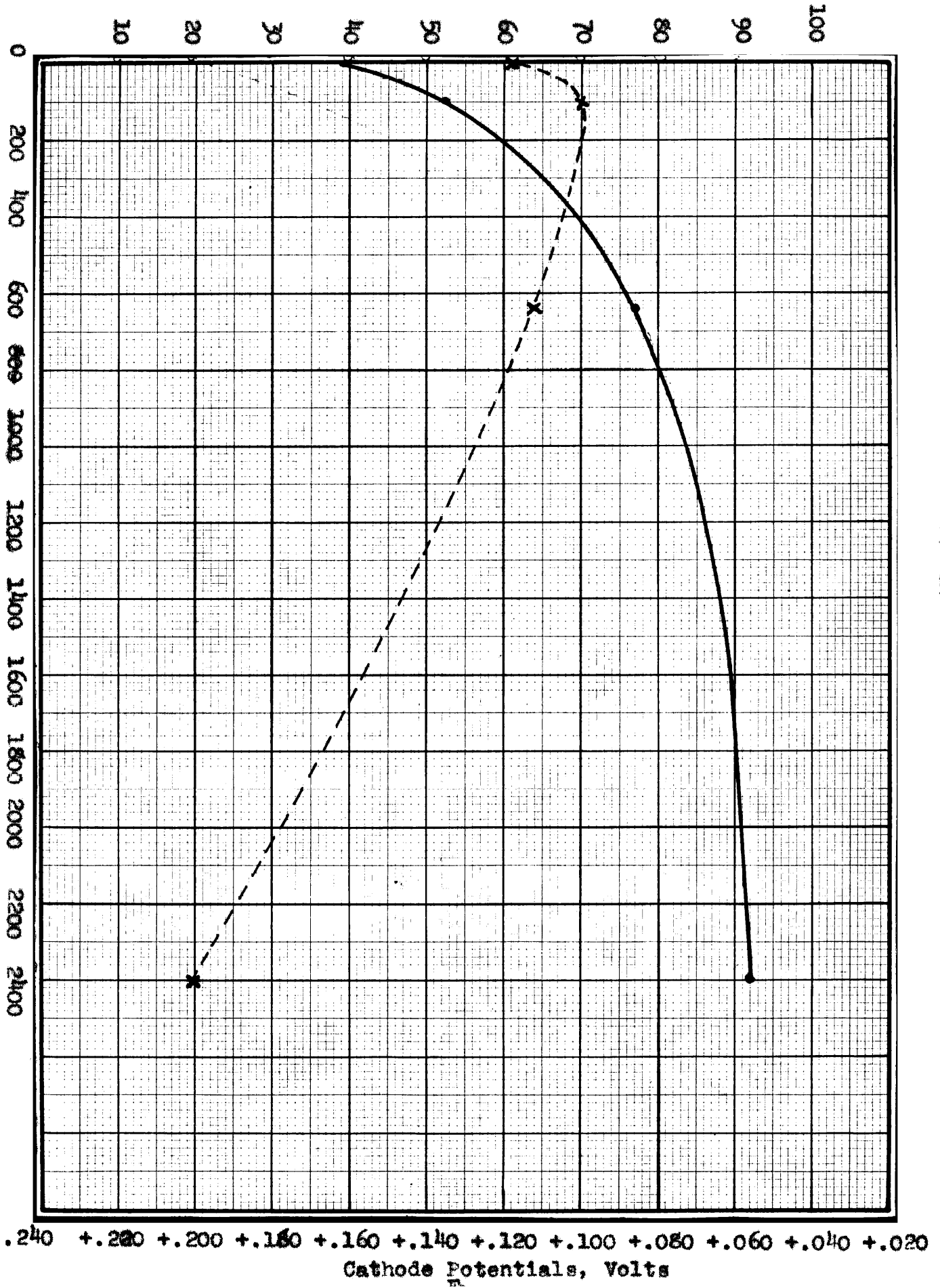


FIG. VI.

in an increase in the amount of the nobler metal in the deposit. This is because the cathode film is kept from being depleted in those ions which are discharging most rapidly. The effect of these two variables in increasing the copper content of the alloy are shown in Fig. VI and VII. These results are similar to those found by Fink and Young (25) in the deposition of cadmium-zinc alloys from a sulphate bath. The cathode potentials are also shown in the Figures. In Fig. VII, the curves have been extrapolated to touch the ordinate at points corresponding to the composition of the solution, since in a dilute solution, a current density of 2.0 amp/dm² would be sufficient to cause the metals to deposit in the same ratio as they occur in the solution.

Agitation, and increase of total metal content are equivalent, as the data in the following Table II show. Deposits of about the same composition can be obtained from baths of different total metal content (but of the same metal ratio) by varying the rate of rotation of the cathode. The cathode potentials also are about the same thus showing that the cathode film and the cathodic process must be the same in both cases.

TABLE II.

Agitation of the Cathode is Equivalent to an Increase in Total Metal Concentration of the Bath

The equivalent percent copper in all baths is 25%.

Current density = 2.0 amp/dm². Temperature = 25°C.

Total metal Conc. of bath. N	rpm of cathode	Equiv. % Cu in deposit	Cathode potential E_p
1.0	2400	92	+0.200
2.0	100	95	+0.200
1.0	0	39	+0.115
0.5	100	38	+0.107

FIG. VII

Effect of Total Metal Concentration (But the Same
Metal Ratio) on the Composition of the Deposit.

Curve A is for baths containing 25 equivalent percent
copper.

Curve B is for baths containing 15 equivalent percent
copper. Both baths are 0.5 μ in "free"
perchloric acid.

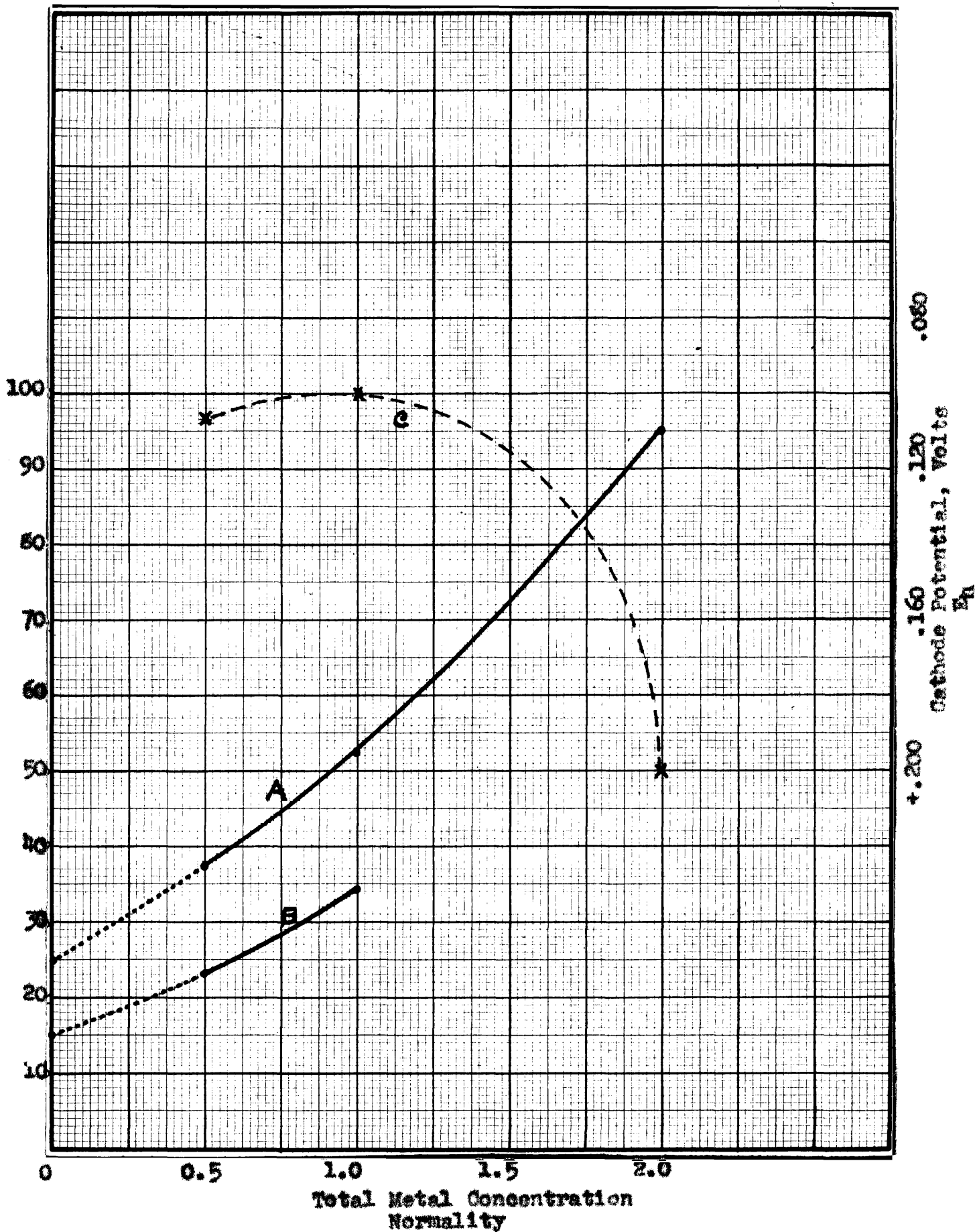
Curve C represents the cathode potentials for Curve A.

The cathode rotation was 100 rpm.

Current density - 2.0 amp/dm².

Temperature - 25°C.

FIG. VII



D. Temperature

An increase in temperature affected the composition of the deposit in the expected manner, and the results are not of any special interest. An increase in temperature increased the proportion of copper in the deposit as Table III shows. The reason for the increase in the proportion of the nobler metal is that at elevated temperatures the diffusion of its ions into the cathode film becomes greater than their rate of discharge. In some other alloy systems, the reduction in cathode polarization is also a contributing factor.

TABLE III

Effect of Temperature on the Composition of the Deposit

Bath composition: -

Bi = 0.75 N
Cu = 0.25 N
"Free" HClO₄ = 0.5 N

Current density amp/dm ²	Equiv. Percent Cu in Deposit	
	25°	70°
2.0	52	98
5.0	32	69

E. Bath Acidity

The acidity of the bath did not materially affect the composition of the deposit. As Table IV shows, an increase in acidity slightly increased the equivalent percent of copper. It would have been expected that the acidity would have a larger effect, since it affects the degree of hydrolysis of the bismuth

perchlorate. The effect of acidity on the composition of a deposit is not readily predictable. In the deposition of cadmium-zinc alloy, Fink and Young (25) found that the amount of zinc in the deposit increased with the acidity of the bath. In the deposition of iron-zinc alloys, Foerster (10) found that an increase in the acidity of the bath increased the amount of zinc in the deposit. In these two latter examples, the amount of the less noble metal was increased by increasing the acidity of the bath, whereas in the deposition of the copper-bismuth alloy the proportion of the nobler metal was increased. In the deposition of iron-nickel alloys, Glasstone and Symes (18) found that a variation in pH had no effect on the deposit.

TABLE IV.

Effect of Bath Acidity on the Composition of the Deposit.

Bath composition: -

Cu = 0.25 N

Bi = 0.75 N

Cathode agitation = 100 rpm. Temperature = 25°C

<u>"free" perchloric acid</u> Normality	<u>Equiv. percent Cu in deposit</u>
1.0	55.3
0.5	52.5
0.06	49.4

F. Addition Agents

Fink and Young (25) found that the use of addition agents in a cadmium-zinc sulphate alloy bath resulted in considerable decrease in the amount of cadmium in the deposit. They considered this to be a new phenomenon; however, Blum and

FIG. VIII

Effect of Glue on the Composition of the Deposit.

Bath composition: Cu = 0.25 M; Bi = 0.75 M
"Free" HClO₄ = 0.5 M

Current density: 1.0 amp/dm².

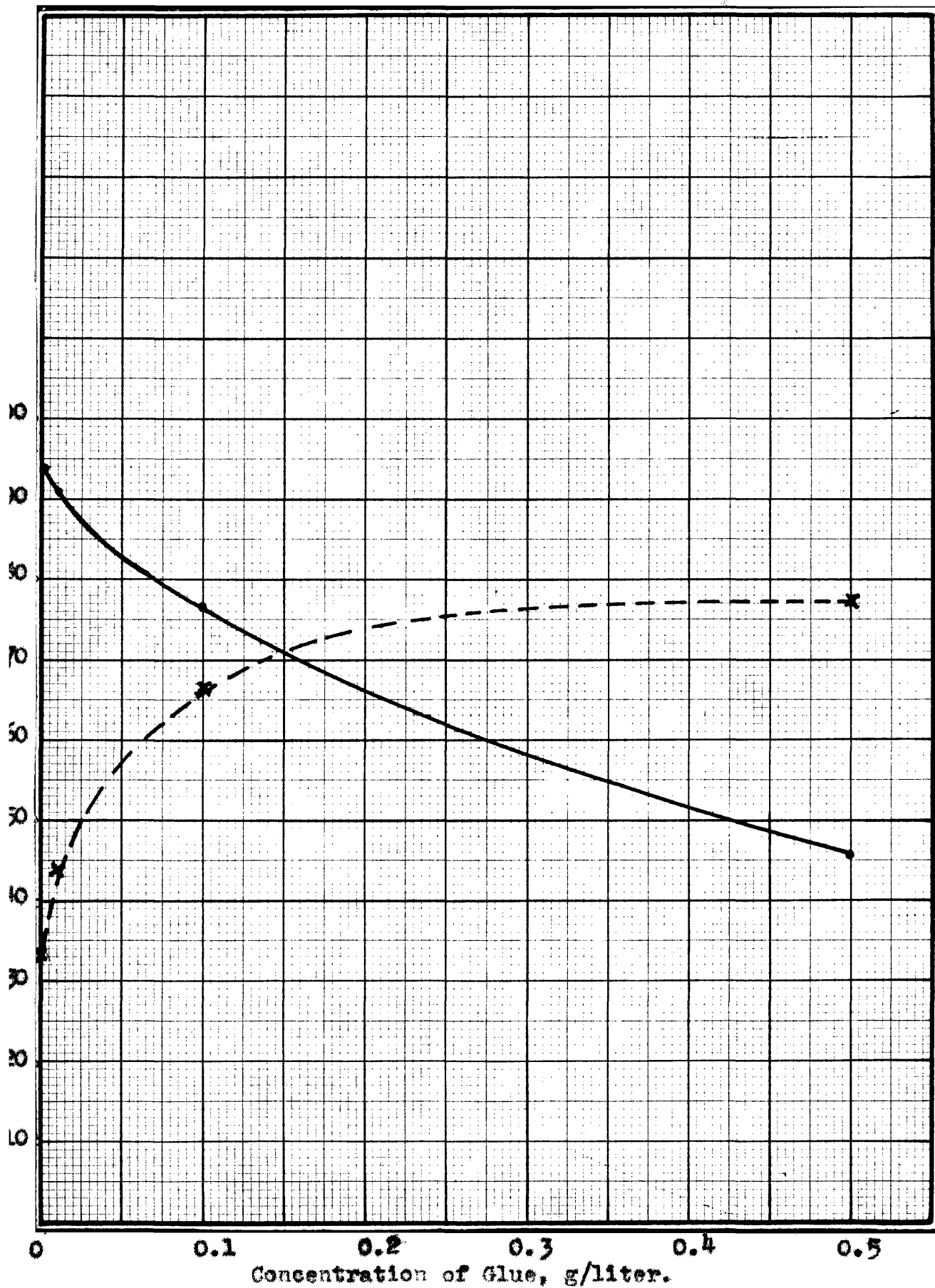
Cathode rotation: 100 rpm

Temperature: 25°C

The solid line is the alloy composition curve.

The dotted line is the cathode potential curve.

FIG. VIII



+ .260 + .240 + .200 + .180 + .160 + .140 + .120 + .100 + .080 + .060
Cathode Potential, Volts
E_h

Haring (8) in 1921 had observed that the addition of glue to a lead-tin alloy bath increased the amount of tin in the deposit and stated that the effect was similar to an increase in current density. Addition agents do not always affect the composition of the deposit, as Fink and Young found little effect on the deposition of copper-zinc alloy from a sulphate solution, and Young and Gould (15) found that gelatin had no effect on the composition of the plate, when added to a nickel-cobalt sulphate alloy bath.

In the electrodeposition of copper-bismuth alloy, the addition of glue was found to considerably increase the amount of bismuth in the deposit, as Fig. VIII shows. The cathode potential, as is usually the case, became more negative when the glue was added.

The effect of the addition agent in the case of the electrodeposition of cadmium-zinc, lead-tin, and copper-bismuth alloys is to decrease the amount of the nobler metal, and this appears equivalent to an increase in current density, as stated by Blum and Haring. However, Fink and Young also found that in the deposition of copper-cadmium alloy, the proportion of copper was increased by the addition agent, which is opposite to the result obtained by increasing the current density.

To gain more insight into the effect of addition agents, the cathode potentials of copper and bismuth deposition were measured with and without the addition of glue. (See Fig. IX.) The glue, as is well known, caused the potentials of copper deposition to become about 0.1 volt more negative. However, the cathode potentials of bismuth were not affected,

FIG. IX

**Effect of Glue on the Cathode Potentials of Copper
and Bismuth Electrodeposition.**

Curve A is for a bath 1.0 N in copper perchlorate
and 0.5 N in perchloric acid.

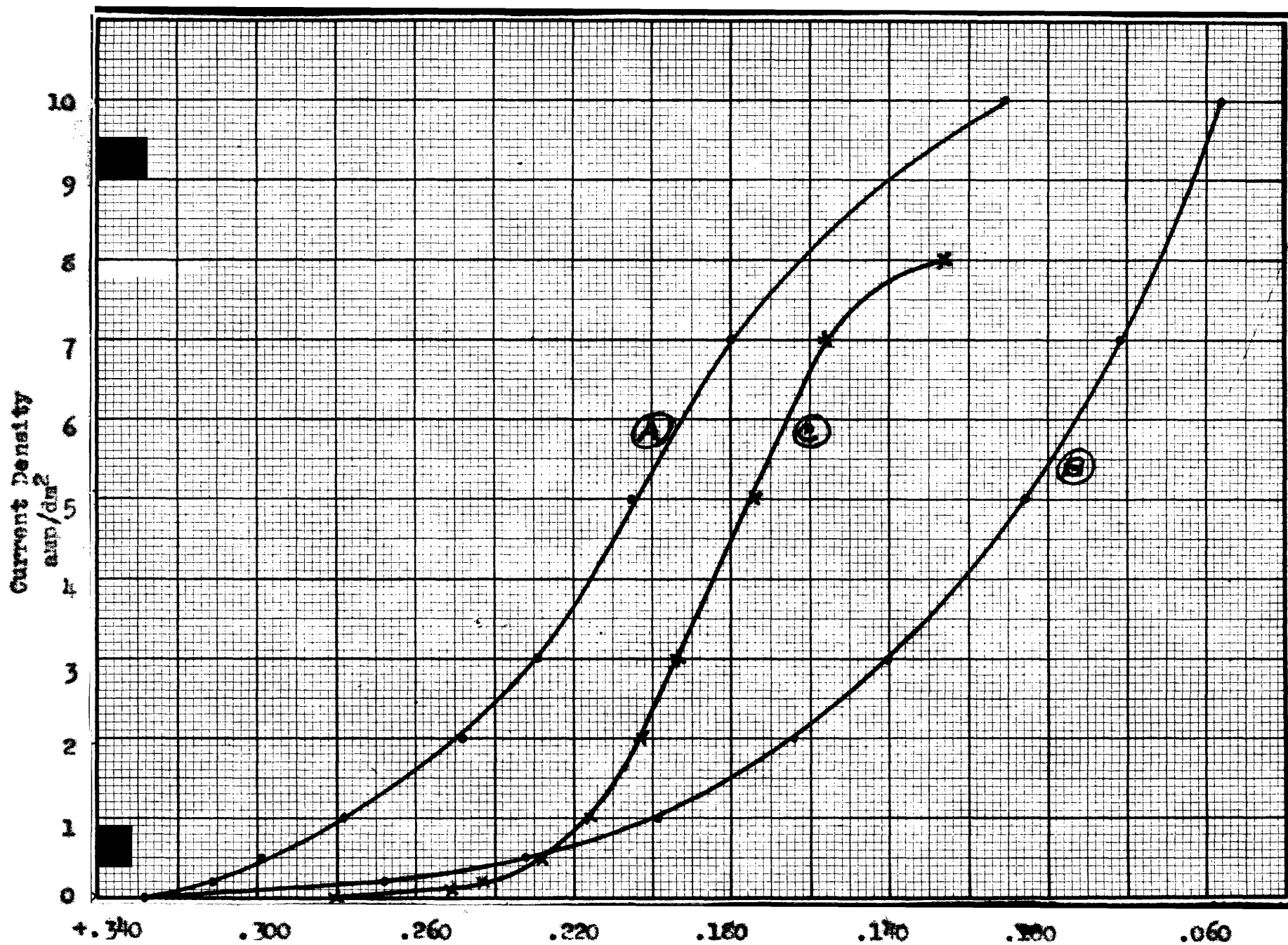
Curve B is for bath A to which 0.1 g/l of glue has
been added.

Curve C is for a bath 1.0 N in bismuth perchlorate
and 0.5 N in "free" perchloric acid. The
addition of 0.1 g/l of glue has no effect.

Cathode rotation - 100 rpm.

Temperature - 25°C

FIG. IX.



although the deposits obtained at the higher current densities were smoother. The glue apparently affected only the copper during the alloy deposition, and by making its cathode potential more negative decreased its ability to plate out. The deposition potentials of copper in the presence of glue are actually more negative than those of bismuth, and if the alloy deposition followed the course predicted from the relative positions of the curves, the deposit should contain more bismuth than copper. Actually, the bath has to contain about five times the quantity of glue, that was used in obtaining the data in Fig. IX, before this occurs.

Thus the addition agent affects the deposit by causing the cathode potentials of one of the metals to become more negative. This does not constitute a complete explanation of the effect of glue on the composition of the deposit, but it does relate the effect to a more general problem, namely the increase in the cathode potential produced by certain addition agents.

VII. The Equilibrium Concentrations of Copper and Bismuth

Since the standard electrode potentials of copper and bismuth are not far apart, the difference being only about 0.030 to 0.050 V, the equilibrium solution of the two metals should contain an appreciable amount of copper. It was of interest to determine the equilibrium concentration by electrodeposition. It was pointed out in the discussion of theory that two metals will codeposit from their equilibrium mixture in the same ratio as they exist in the solution, although this is strictly true

only for a reversible electrodeposition, in which case both metals have the same electrode potential. Thus the equilibrium concentration can be found by altering the composition of the solution until the deposit obtained from it at low current density has the same metal ratio as the solution.

By chemical means, Blum and Haring (8) determined the equilibrium concentration of lead and tin in a fluoborate solution and found the equilibrium ratio was approximately $(N \text{ of tin}) / (N \text{ of lead}) = 4.3$. The alloy deposits from a bath containing the metals in this proportion were found to have the same metal ratio as the bath. The deposits were made at a current of 0.8 and 1.6 amp/dm². These conditions are rather far removed from an equilibrium codeposition, and the deposit would not be expected to have the equilibrium composition unless the cathode polarizations were small and the cathode potential curves for lead and tin were close together.

The equilibrium between copper and bismuth perchlorates, was determined by Swift (21), who used the data for the calculation of the molal electrode potential of bismuth. The hydrolysis of bismuth perchlorate is affected by the acidity, and the acid concentration was also included in the equilibrium.

The reaction is:



assuming the bismuth to exist as Bi(OH)^{++} ions. Some also exists as BiO^+ and perhaps Bi^{+++} ions. At equilibrium

$(\text{Bi} \times \text{H}) / (\text{Cu})^{3/2} = K$. The electrode potential of bismuth was

determined from the equation $E_{Bi} = E_{Cu} - RT/3F \log K = E_{Cu} - 0.020 \log K$. The value of E_{Bi} is not very sensitive to variations in the value of K . A 100 percent error in the determination of K would change the value of E_{Bi} by only 6 mv.

Swift did not give values of K in his paper. Using his data, the following values in Table V were calculated for K . Concentrations were expressed in moles, and the ionizations were assumed to be complete.

TABLE V.

Values of the Equilibrium Constant $K = \frac{Bi \times H}{(Cu)^{3/2}}$

Exp. No.	K
1a	32
1b	27
2a	39
2b	45
3a	60
3b	56
4b	38
Av.	$\frac{38}{42} \approx 23\%$

The equilibrium concentration of copper and bismuth was determined electrochemically by codepositing copper and bismuth at a current density of 0.03 amp/dm² from solutions 1.0 N in total metal, but having a varying metal ratio. The data are shown in Fig. X. The dotted diagonal line corresponds to deposits which have the same metal ratio as the bath. Points below this line correspond to deposits which have a smaller

FIG. X

Determination of the Equilibrium Concentration of
Copper and Bismuth by Electrodeposition.

Curve A is for deposits plated at 0.03 amp/dm^2 .

Curve B is for deposits plated at 1.0 amp/dm^2 .

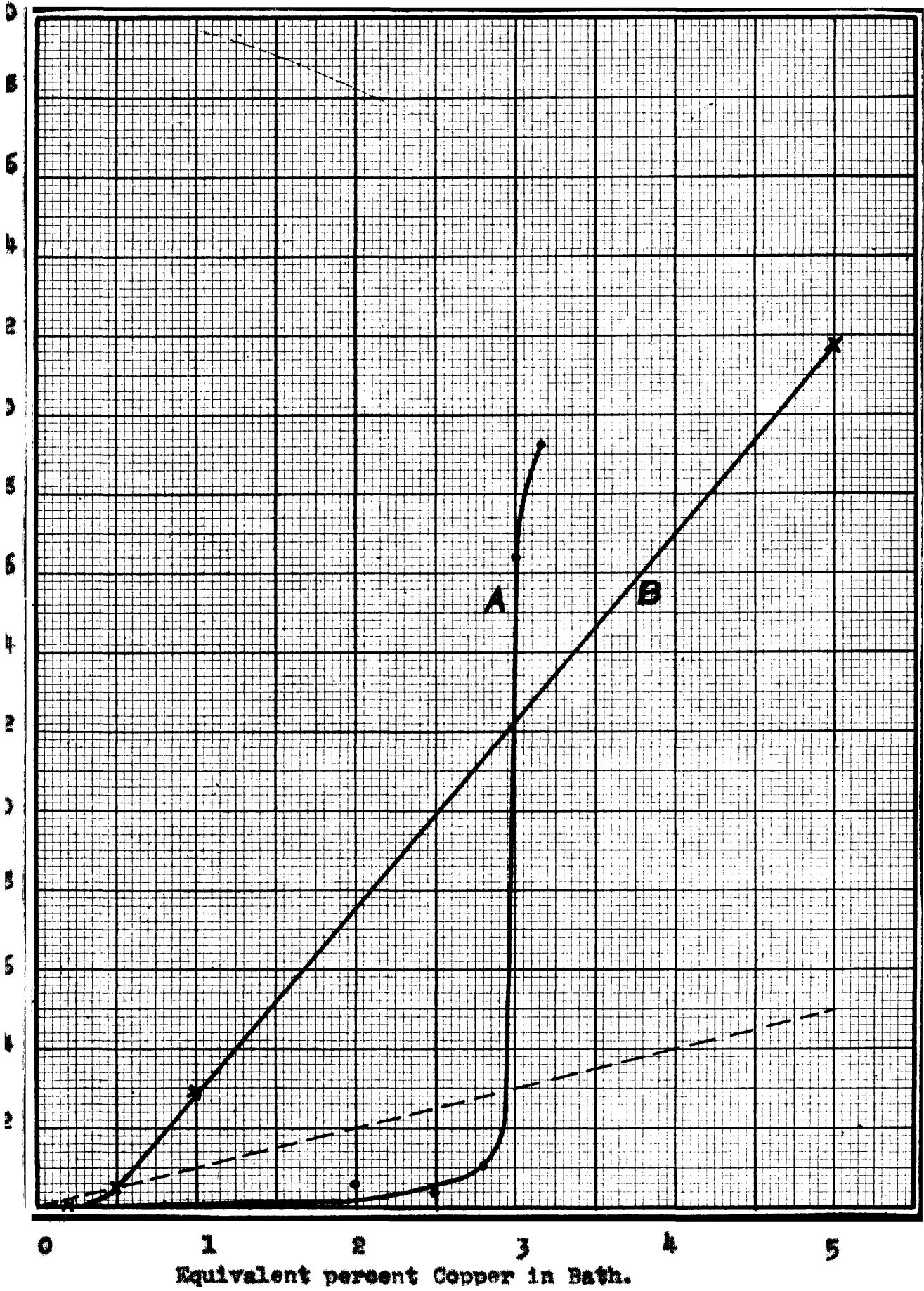
All baths were 1.0 in total metal and

0.06 N in "Free" perchloric acid.

Temperature - 25°C

Cathode rotation - 100 rpm.

FIG. X



Cu/Bi ratio than the bath and points above the line to a Cu/Bi ratio in the alloy greater than that in the bath. The curve for 0.03 amp/dm^2 shows a sudden break at the equilibrium concentration and crosses the dotted line at a point corresponding to a solution 0.03 N in copper and 0.97 N in bismuth. Using the chemically determined equilibrium constant, the calculated equilibrium concentration of copper for a bath 0.97 N in bismuth (0.323 M) and 0.056 N in "free" acid (H^+ conc. = $0.323 + 0.056 = 0.379 \text{ M}$ assuming the Bi present as $\text{Bi}(\text{OH})^{++}$) is 0.04 N . This agreement is satisfactory, as the values of K in Table V show a considerable variation.

The curve of 1.0 amp/dm^2 in Fig. X shows the effect of using too high a current density, as the equilibrium concentration appears to come at a bath 0.005 N in copper. This curve shows that for baths between 0.01 and 0.03 N in copper, the equivalent percent copper for the deposit is greater than for the bath. This is rather unexpected, since for solutions containing less than the equilibrium concentration of copper, the copper should behave as the less noble metal and the Cu/Bi ratio should be less than that of the bath. This result may be worth further investigation.

VIII. Structure of the Alloy

The occurrence of the maxima in the cathode potential curves (Fig. V) at a fairly definite composition of deposit (52-62 equiv. percent copper), seemed to indicate that a compound formation had taken place. Thus, it was of interest to study the structure of the alloy. According to the thermal

study of the alloy by Jeriomin (5), copper and bismuth form neither solid solutions nor compounds.

Creutzfeld (7) and Sauerwald (6) studied the structure of some electrodeposited alloys by means of E.M.F. measurements. The potential of the alloy was measured in a salt solution of the less noble metal. According to the results of their measurements the electrodeposited alloys possess a different structure than the thermal alloys, in having a random arrangement of the atoms. These results are at variance with X-ray studies of electrodeposited alloys. Roux and Cournet (26) made an X-ray examination of electrodeposited copper-zinc, cadmium-silver, cadmium-tin, and cadmium-nickel alloys and showed that they were not a simple mixture of the two metals but probably solid solutions and compounds. Stillwell (27) showed by X-rays that the silver-cadmium alloys, electrodeposited from cyanide solutions, consisted of the same compounds and solid solutions as the thermal alloy. Fuseya and Sasaki (28) found from X-ray study that an electrodeposited chromium-iron alloy was a solid solution.

Three samples of the copper-bismuth deposits, corresponding approximately to the alloy of 50-60 equivalent percent copper, were examined by the powder X-ray method, using copper radiation. The alloys were compared with a mixture containing the two metals in about the same proportion as existed in the alloy. Two of the alloy samples were bright deposits and had been plated out at current densities of 2 and 5 amp/dm². The

X-ray diffraction patterns of these two samples showed only several very diffuse lines of copper, which however, apparently were not displaced. The diffuseness of the lines indicated that the grain size of the alloy was very small, perhaps below 10^{-6} cm. The third alloy sample was plated at 1 amp/dm^2 and was not bright. It showed the same lines as the mechanical mixture of copper and bismuth, although the intensities of many of the lines were quite different from those produced by the mixture. If the bright deposits have the same structure as the dull deposit, then the electrodeposited copper-bismuth alloys must be a mixture of crystals of the two metals. This result agrees with the other X-ray studies of electrodeposited alloys, which showed such alloys to be similar in structure to the thermal alloys.

The results of the X-ray examination do not give any information which might serve to explain the maxima in the cathode potential curves of Fig. V. The anomalous negative potentials obtained during alloy deposition may be due to the interference of the metals with each other's crystal growth. That is, each may act as an addition agent for the other, and thus produce the bright, fine-grained deposit. The significance of the maxima in the cathode potential curves coming at a certain alloy composition, may be that at this metal ratio, the interference with crystal growth is at a maximum.

IX. Summary

(1). The investigation of the electrodeposition of copper-bismuth alloys has shown the system to behave in a simple and predictable manner with respect to the effect of the plating variables on the composition of the alloy. However, the cathode potentials were anomalous, being more negative than those for the deposition of bismuth alone and showing maxima corresponding to deposits containing 50-60 equivalent percent copper.

(2). Smooth, bright, adherent alloy deposits can be obtained. The bright deposits are very little.

(3). At high current densities, the deposit has the same metal ratio as the bath.

(4). A relationship has been shown to exist between the limiting current density of copper deposition and the shape of the alloy composition vs. current density curves.

(5). The proportion of copper in the deposit is increased by agitation of the cathode, by increase of total metal concentration, and by increase of temperature. Agitation of the cathode and an increase in total metal concentration in the bath were shown to be equivalent.

(6). An increase in the acidity of the bath slightly increased the copper content of the deposit.

(7). The presence of glue in the bath considerably decreases the proportion of copper in the deposit. This was shown to be due to the glue causing the cathode potential of copper to become more negative than that of bismuth; the cathode potentials of bismuth were not affected by the glue.

(8). The equilibrium concentrations of copper and bismuth were determined by electrodeposition and found to agree fairly well with the chemical determination.

(9). X-ray diffraction patterns of the bright alloy gave diffuse lines, thus indicating a small grain-size. The lines given by a dull alloy deposit were the same as those of the separate metals, thus showing the alloy to be a mixture of crystals of copper and bismuth.

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