Half-title:

ADDITION AGENTS IN DEPOSITION OF COPPER.

Hospadaruk

THE EFFECT OF CHLORIDE ON THE DEPOSITION
OF COPPER, IN THE PRESENCE OF ARSENIC,
ANTIMONY AND BISMUTH.

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ANTIMONY AND BISMUTH.

by

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INTRODUCTION

The importance of addition agents in the electro-deposition of metals is well established. Although it is widely known that these substances, when added to an electrolyte, are capable of modifying the physical nature of a metal deposit, the problem of how they function has yet to be solved. To gain an insight into the mechanism by which addition agents act, many studies have been made, a large body of data, much of which is contradictory, has been obtained and various theories of their action have been proposed. A considerable proportion of the work that has been done has been concerned with the effect of gelatin on the electro-deposition of copper from acid copper sulphate solutions, in the absence and presence of foreign ions, and it is with this particular aspect that the present study is mainly concerned. However, before discussing such a relatively complex system it seems advisable to outline briefly the main views held on the mechanism of electrodeposition in the absence of addition agents or foreign ions.

It is generally agreed that during electrodeposition a very thin layer of solution adjacent to the cathode, known as the cathode film, rapidly acquires properties different from those of the bulk electrolyte. The properties of this cathode film have been studied by Read and Graham (1, 2) and

Brenner (4, 5). Read and Graham obtained samples of the film for analysis by withdrawing the electrolyte through a hole in the cathode. However, their data have been questioned since there is some indication that the samples included some of the bulk electrolyte. Brenner employed other methods. In one, the electrolyte surrounding a hollow cylindrical cathode film was suddenly frozen and successive 0.003 to 0.004 inch layers were turned off on a lathe for analysis. In the other method a planar cathode was removed from the solution, and after allowing the bulk of the electrolyte to drain, the thin layer adhering to the cathode was collected and analyzed. His experimental work showed that:

- (1) The thickness of the cathode film is about 0.25 centimetres and is approximately the same at room temperature for electrolytes of different compositions. Hickling (5) gave the same value, on the basis of polarization data.
- (2) The metal ion concentration in the film increases linearly with the distance from the cathode.
- (3) The film thickness decreases with rotation of the cathode or with hydrogen evolution.
- (4) The current density increases continuously from the top to the bottom of the cathode.

It is well established that as a consequence of deposition, the supply of metal ions in the film is constantly

depleted by their removal as neutral atoms entering the deposit. Agitation causes a physical breakdown of the film, while increased temperature should increase the diffusion rate of the ions, thereby decreasing the thickness of the cathode film. With the convection currents from the bulk of the electrolyte flowing up the cathode face, the metal ion concentration, and therefore the current density, is greater at the bottom of the electrode than at the top.

Studies of the process at the cathode and the adjoining film have led to two main views of the mechanism of ion discharge and integration of the resulting atom into the crystal lattice of the deposit. One considers that ionic discharge and incorporation into the lattice occur simultaneously; the other suggests the existence of an intermediate stage prior to crystallization.

Blum and Rawdon (6) have postulated simultaneous discharge and crystallization, i.e., that the discharge of ions occurs on the electrode surface. They assumed that the forces causing atomic orientation or crystallinity are attractive and, consequently a metal crystal should have a lower solution pressure than an unorientated atom. It follows that the discharge potential, being a function of the metal ion concentration and the solution pressure, must be greater when an ion is discharged in a position unrelated

to that of a previously discharged ion, than when the growth of a crystal is continued. Similarly, the potential must be higher to discharge an ion upon a small crystal than on a large one. Conversely, all factors tending to increase the polarization, or potential difference between cathode and solution, will favour nucleus formation.

Blum and Rawdon showed that increase of current density, addition of a colloid, or increase of viscosity, all of which increase polarization, favour smooth, finely grained deposits; while higher temperatures, higher metal ion concentrations, or agitated electrolytes, which decrease polarization, favour coarse, crystalline deposits. There is considerable experimental evidence which seems to support Blum and Rawdon's theory (7, 8, 9, 10). Some relation between grain size (the degree of fineness of the deposit) and polarization has been observed (11, 12, 13, 14). Other workers claimed that no definite relation could be found between cathode polarization and the grain size of the deposit (15, 16, 17, 18). Hunt (19) criticized Blum and Rawdon's assumption that cathode polarization is the primary cause of the decrease of grain size. He suggests that polarization be regarded as a parallel result of other operating factors.

The theory that electrodeposition takes place in stages was favoured by Hughes (20) who assumed that there

exists an intermediate state of metallic ions in the solution adjacent to the cathode and that the grain size depends on the extent of supersaturation of these atoms before they crystallize. Volmer and Erdey-Gruz (21, 22) developed the concept further by postulating deposition in layers of atoms. They believed that until a given layer is complete, a certain proportion of the ions is in a state intermediate between that in solution and that which the ions will assume in the crystal lattice.

A more recent view of electrodeposition assumes that there is an adsorption of metal ions at the cathode and a subsequent conversion of the ions to metal atoms by electron transition. Gurney (23) derived, by quantum mechanics, the conditions necessary for the electron transfer to occur. The neutral atoms become part of the cathode surface on which further adsorption of cations can take place.

It is fairly well established that electrodeposition does not take place atom by atom as postulated by Blum and Rawdon. However, there is disagreement concerning the size of the groups of cations deposited. Hunt (24) believed that a continuous lattice layer of ions must be held over a crystal before neutralization takes place. Kasper (25), however, contended that neutralization can occur before the layer is complete.

ELECTRODEPOSITION IN THE PRESENCE OF ADDITION AGENTS

An addition agent may be defined as a substance which, when added in small amounts to an electrolyte, gives a smooth, fine-grained, hard deposit of high tensile strength and good adherence.

A large number of substances are known to behave as addition agents. Many elaborate systems for classifying addition agents have been proposed, but, in the light of our scanty knowledge of the subject, it is doubtful whether this procedure is warranted. It seems of little purpose to include any detailed classification in the present review.

Briefly, however, addition agents may be classified as colloids, crystalloids, and inorganic salts. The very important group of colloidal addition agents (particularly gelatin) has been extensively studied. Amino acids, amines, and sugars are examples of the crystalloids; while an outstanding example of an inorganic addition agent is sodium chloride, used so extensively in the electrorefining of copper.

An interesting feature of addition agents is the relatively small concentrations needed to produce their spectacular effects. Concentrations of a few parts per million generally increase cathode polarization and uniformity of the deposit, but do not appreciably change the

composition, degree of dissociation and the conductivity of the electrolyte (12, 26, 27). Another outstanding property of addition agents is the high degree of specificity in their behaviour. While an addition agent may exert a marked effect on the deposition of a particular metal, it may be totally ineffective for another metal.

Several mechanisms of general applicability have been proposed for the action of addition agents. Most of these have been based on data obtained from the deposition of copper from acid solutions. Of the many studies of systems involving addition agents, the effect of gelatin on copper deposition has probably received the greatest attention.

GELATIN IN THE ELECTRODEPOSITION OF COPPER

In general, studies on the effect of gelatin on copper electrodeposition have consisted of the measurement of the physical properties of the deposits, cathode polarization and excess weights. The majority of the work used concentrations of gelatin in copper sulphate solutions greatly in excess of that used commercially. The commercial concentration is about 2-3 mg. per litre (or its equivalent in form of glue), while investigators have generally used from 0.2 to 2 gm. per litre or higher.

No strict comparison between the results that various workers have obtained with gelatin can be made. Samples of "pure" gelatin can be quite different, depending on their origin and treatment (28).

In 1906 Muller and Bahntje (29) observed excess weights (gain in weight over that of a deposit obtained in a coulometer in series without addition agents) in the deposits obtained from electrolytes containing gelatin. Some twenty years later, Marie and Buffat (30) investigated the effect of gelatin, at higher concentrations, on excess weight and showed that the excess weight-gelatin concentration curve resembled an adsorption isotherm with the equation $S = KC^{\frac{1}{2}}$, where S is the excess weight, K a constant and C the gelatin concentration. The excess weight consisted of about 66 per cent gelatin and 33 per cent copper sulphate which they assumed to be in its pentahydrate form. They found that there was practically no dependence on current density. However, Taft and Messmore (28) did find that the excess weight was a function of current density for a similar copper-gelatin system.

Marie and Claudel (31) studied the effect of pH on the excess weight. Using a fixed gelatin concentration of 0.2 per cent and measuring the excess weight of the deposit for various pH values (0.88 to 3.57) they obtained

a smooth excess weight -pH curve which passed through a maximum for pH 3.2. This is analogous to other properties of gelatin, such as viscosity, swelling, osmotic pressure, etc., which all pass through a maximum at pH 3.2 - 3.6, and through a minimum at its iso-electric point (pH = 4.7). They were unable to measure the excess weight at the iso-electric point because a pH higher than 3.57 could not be obtained even by the addition of copper carbonate to a 12 per cent copper sulphate solution.

Muller and Bahnjete's excess weight studies led them to believe that during electrodeposition of copper from copper sulphate solutions in the presence of gelatin, colloidal particles are formed near the cathode (29). The particles, consisting of the metal surrounded by gelatin, then serve as crystal nuclei for deposition of the metal. This, and other similar mechanisms, suggested by other investigators (32, 33), are able to account for the effect of gelatin on the grain size of the deposit.

The presence of an addition agent in the electrolyte is also generally reflected in an increase in the cathode polarization (34, 35, 32). Clark and Jones (12) have examined the effect of several addition agents on cathode polarization. With gelatin, peptone, dimethylaniline, starch, and others, at a fixed concentration of 0.5 gm. per litre, they found that the polarization was invariably increased

by the addition agents. The addition agents were found to reduce the grain size of the deposit, and they attempted to express mathematically a relation between polarization and grain size, but concluded that there was no simple relation.

Taft and Messmore (28) found that the addition of gelatin to an acid-free copper sulphate solution increased the polarization considerably and an inflection at 0.8 amps. per dm.² was obtained in the corresponding polarization-current density curve. Lower polarization values were obtained when a copper cathode was replaced by platinum. After deposition for some time the deposits were independent of the base metal (platinum, gold, silver, brass) but, initially, the base metal did affect their appearance.

In 1926 Haring (37) stated that a definite relation exists between cathode polarization and the concentration of glue used as addition agent in the electrodeposition of copper. He suggested the estimation of addition agent concentration by measurement of the cathode polarization in a special electrolytic cell which bears his name. The Haring cell was used subsequently by many workers, but the results obtained show very poor agreement (12, 28, 37, 38, 39, 40, 41, 42). Believing the Haring method to be fundamentally sound, Gauvin and Winkler (43, 44) undertook an

investigation to determine the conditions under which reproducible cathode polarization measurements might be made with the cell. A slightly modified form of the original cell was used. It consisted simply of a relatively long, narrow box, both ends of which were copper blocks used as anode and cathode. Two intermediate electrodes of copper gauze were so situated between the anode and cathode as to divide the cell into three equal compartments. The potential drop across the cathode compartment, less the IR drop across the same thickness of solution, (measured as the potential drop across the middle compartment) gives the cathode polarization.

Gauvin and Winkler (43) made some preliminary experiments, using polished electrodes in a solution containing no gelatin, 125 g. of reagent grade copper sulphate and 50 g. of concentrated sulphuric acid per litre. At first, measurements of the cathode polarization were not reproducible. However, when a study of the change of cathode polarization with time was made, it was found that with electrolysis at current densities above 0.6 amp. per dm.², definite values of the cathode polarization were attained, providing sufficient time was allowed for the cathode surface to attain a steady state corresponding to the conditions of electrolysis. These polarization values were called "the steady state cathode polarizations." At lower current

densities, the base metal structure was perpetuated in the deposit, and it was shown that the cathode polarization at these current densities depended upon the surface condition of the electrode.

On the basis of their results, Gauvin and Winkler concluded that the lack of agreement in cathode polarization values obtained by former workers using the Haring cell was attributable to the fact that their measurements generally did not correspond to steady state values.

Using a gelatin-free acid copper sulphate electrolyte at 25°C., Gauvin and Winkler studied the effect of change in current density on cathode surfaces. After depositing at a relatively low apparent current density, to obtain a comparatively coarse crystalline deposit, the current was switched off for about 10 minutes to allow complete dissipation of the cathode film. The electrolysis was resumed at a higher apparent current density to promote rapid nuclear formation, hence a finer crystalline deposit. The change from a coarsely crystalline surface to a fine-grained deposit resulted in a decrease in cathode polarization. The reversion to a coarse-grained deposit was accompanied by an increase in cathode polarization. The results are in contradiction to the Blum and Rawdon (6) theory, according to which change from a coarsely crystalline surface to a

fine-grained deposit should be associated with an increase in cathode polarization, and vice versa. Gauvin and Winkler suggested that a change from a coarsely crystalline surface to a fine-grained deposit is accompanied by an increase in total, or true, cathode area. This true area may be many times the apparent or geometric area. There is then a decrease in true current density with a corresponding reduction in cathode polarization. Conversely, a change to a more coarse deposit results in an increase in true current density and a higher cathode polarization. Thus, they believe that crystal size is fundamentally related to true current density, rather than to cathode polarization.

Recently, Shreir and Smith (45, 46), using a Haring cell and gelatin-free acid copper sulphate electrolytes, studied the effect of change in current density on various cathode surfaces. They believed their results to support the view of Blum and Rawdon that the cathode polarization is related to crystal size.

Gauvin and Winkler (47) continued their study of the effect of cathode surface on cathode polarization by adding gelatin to the acid copper sulphate electrolyte. Cathodes with finely crystalline surfaces were prepared by deposition from electrolytes containing 10 and 2 mg. per litre of gelatin respectively. They were then used during electrolysis at 26.4°C. with an apparent current density of 2 amp. per dm.²,

in an electrolyte containing 125 mg. per litre of copper sulphate, 150 g. per litre of sulphuric acid, but no gelatin. Starting with a high cathode polarization, the value decreased to the steady state polarization value usually obtained for the gelatin-free electrolyte. The final surfaces had the coarsely grained characteristic of deposits obtained in the absence of gelatin. That is, a change from a finely crystalline surface to a coarsely grained deposit was accompanied by a decrease in polarization in the presence of gelatin. Exactly the opposite effect was obtained in the absence of gelatin. Also, it was found that a more finely crystalline deposit, obtained by increasing the gelatin concentration in the electrolyte, was accompanied by an increase in cathode polarization. Since a fine structure was always associated with a large true area, Gauvin and Winkler reasoned that gelatin must be able to impart to such a fine-grained surface the characteristics normally associated with a coarser surface of smaller true area.

In 1904, Bancroft (50) suggested that the decrease in crystal size of a deposit in the presence of an addition agent was due to adsorption of the addition agent. Fischer (51, 52) extended the theory by assuming adsorption of addition agents, such as gelatin, on the active centres of cathode surfaces. He believed the adsorption causes a rise in cathode polarization by inhibiting further deposition on

the active centres. In 1931, Erdey-Gruz and Volmer (22) showed that deposition always starts from crystal corners, although it may sometimes start from an edge, but never from a crystal face. These corners were called "active centers."

Gauvin and Winkler, too, assumed that only a certain fraction of the total area of a cathode is active during deposition. They believed that although gelatin may favour formation of a deposit of greater total area the active area may be considerably reduced due to adsorption of gelatin. This would result in an increase in the true current density, accompanied by an increase in cathode polarization. Thus, the true current density is determined, not by the total area, but by the active area. According to these views, a very small amount of gelatin should be sufficient to exert a beneficial action on the deposit. On the other hand, a large amount of gelatin should so reduce the active area that nucleus formation may become excessive, and result in a loose, powdery deposit. Indeed, this is borne out in practice.

Strong support for the mechanism of adsorption on the cathode surface is given by Jacquet (48). He found that alternate immersion of the cathode in a protein (ex. gelatin) solution, and deposition in the absence of the addition agent

gave the same crystal structure as did deposition in the presence of the addition agent. He found that repeated hot water rinsings of the protein-treated surfaces still gave fine-grain deposits (49). This demonstrates how strongly the addition agent can be adsorbed on the electrode surface.

The adsorption mechanism, proposed to explain the effect of gelatin during the deposition of copper, has been the most satisfactory theory up to the present time (53, 54). However, other mechanisms have received some attention in the past, and it is perhaps interesting to note their main features briefly.

The cathode interference theory proposed by Hunt (19) states that the crystalline structure of a deposit is governed by the relation of the metal ion concentration in the cathode film to the concentration of the other constituents of the film. The introduction of an addition agent into the film should decrease the ratio of the metal ions to the other constituents and, therefore, reduce the grain size. Confirmation of this awaits the direct analysis of the cathode film in the presence of addition agents.

Froelich (36) and Machu (55) suggested that electro-deposition takes place through the intermicellar spaces of a porous, viscous film of gelatin accumulated at the cathode.

This mechanism, which assumes that gelatin acts as a diaphragm on the cathode surface, has been held untenable. Fischer (56) has said that it allows only for concentration polarization to increase by obstructing the diffusion of metallic ions. He showed that gelatin began to increase concentration polarization (by preventing diffusion) only at an exceedingly high concentration of 10 grams per litre.

Glazunov and co-workers (57) were of the opinion that complex ion formation is responsible for the effectiveness of an addition agent. They showed that the primary process is the discharge of the complex ion at the cathode, and that the discharged radical may then migrate a short distance before the deposition of the metal takes place (58). They assumed that since the discharged metal precipitates in the form of individual atoms on the entire surface of the cathode, the number of effective crystallization centres is thereby greatly increased and a smooth surface results (59).

Isgarischev's (60) views that a copper-gelatin complex is discharged at the cathode has been strongly contradicted by Taft and Messmore (28). They claimed that if Isgarischev's mechanism were valid, the excess weight should increase steadily with increasing gelatin concentrations. Their observations show that there is an upper limit at which the excess weight no longer increases.

Gauvin and Winkler (44) extended their investigations into copper deposition from acid sulphate electrolytes by studying the effect of temperature and acidity on cathode polarization in the absence and presence of gelatin. Using a Haring cell and a gelatin-free electrolyte containing 125 g. per litre of copper sulphate pentahydrate (a standard amount, used in all their experiments) and 150 g. per litre of concentrated sulphuric acid, the cathode polarization was determined at different temperatures for a range of current densities. The measurements showed that the polarization decreased as temperature increased, with the decrease observed being larger for a change below room temperature than for a change at higher temperatures, at any current density.

Since there seems to be little agreement among different investigators on the effect of acidity on the cathode polarization (37, 38, 39, 40, 41), Gauvin and Winkler measured, at various current densities, the steady state cathode polarization values for gelatin-free electrolytes containing various amounts of sulphuric acid. They found that an increase in acidity had little effect on the polarization (except for low acidities) at apparent current densities below 2 amp. per dm.², while it resulted in an increase in polarization above that value. They then made experiments to determine the effect of increasing gelatin concentrations on the cathode polarization for a wide range of concentrations (0 to 1000 mg. per litre). The electrolyte used contained

50 g. per litre of sulphuric acid. Taking measurements at current densities ranging from 0.2 to 4 amp. per dm.², they found that the increase in cathode polarization per unit increase in gelatin concentration was greater at lower than higher gelatin concentrations.

Commercial electrolytes generally contain concentrations of acid higher than that used in the preceding study. Studies were made, therefore, using electrolyte containing 150 g. per litre of concentrated sulphuric acid. The effect of gelatin concentrations (1, 5, and 10 mg. per litre) on cathode polarization was determined at current densities of 0.2 to 6.5 amp. per dm.². For a given temperature, the relative increase in cathode polarization was found, as with electrolytes of lower acidity, to be greater at smaller gelatin concentrations. For a given gelatin concentration, the relation of temperature to cathode polarization was quite analogous to that in the absence of gelatin.

THE EFFECT OF CHLORIDE IONS ON COPPER DEPOSITION IN THE
PRESENCE OF GELATIN

Chloride, as sodium chloride or hydrochloric acid, is added quite generally with glue (or gelatin) to acidified copper sulphate refinery electrolytes. Its addition is considered essential, since it keeps the silver ion concentration very low by causing the silver to accumulate in the anode slime. Thus, it prevents the loss of silver in the copper refining operations. Also, the presence of chloride in the electrolyte minimizes the codeposition of antimony and bismuth with copper. The chloride concentration used is usually from 10 to 50 mg. per litre (61, 62).

Little information is available on the effect of chloride ion on copper deposition. Arndt (63) reported that the presence of chloride decreased the grain size of the deposit, though this has been contradicted (41).

Yu-lin Yao (64), working with acidified copper electrolytes, in the absence of addition agents, found that an increase of chloride concentration at low concentrations resulted in small increases in cathode polarization and hardness of deposit, and a large decrease in the grain size. At concentrations greater than about 15 mg. per litre, however, cathode polarization and hardness decreased sharply with chloride concentration, while an increase in grain size

was observed. Yao claimed that the effects of chloride on the deposit are masked by the addition of gelatin.

Gauvin and Winkler (65) studied the effect of chloride in the presence of gelatin. The composition of the electrolyte for all experiments consisted of 125 g. per litre of copper sulphate pentahydrate and 150 g. per litre of sulphuric acid. In preliminary experiments, they observed that addition of chloride ion as sodium chloride to the electrolyte had no obvious effect on deposition below minimum concentrations of 9 mg. per litre at 25°C. and 19 mg. per litre at 50°C. Above the minimum concentration, the deposits became finer grained and gradually changed to a salmon pink colour. Increased concentrations gave increased fineness to the deposits. Above the minimum concentration, the anode processes were also affected. A great deal of fine copper powder accumulated at the anode, at both 25°C and 50°C. At still larger concentrations, less and less copper was formed, but greyish white cuprous chloride began to appear on the anodes. Analysis of the electrolyte showed that the chloride ion concentration became depleted at a fairly rapid rate especially at higher concentrations. The effects were shown to be due to chloride ion rather than sodium ion by the observation that addition of sodium sulphate instead of sodium chloride had no effect on the electrode processes.

Working at comparatively high chloride concentrations (100 to 500 mg. per litre), Gauvin and Winkler found that, in the presence of 10 to 50 mg. per litre of gelatin, chloride did not enter the deposit as it did in the absence of the addition agent. In the presence of addition agent a maximum chloride content in the deposit was observed at a chloride ion concentration in the electrolyte of about 500 mg. per litre.

The excess weights of copper deposits obtained in the presence of 50 mg. per litre of gelatin and increasing amounts of chloride ions were determined relative to the weight of a deposit obtained in series under the same conditions, but in the absence of these ions. The solutions were at 25°C. At low chloride concentrations there was no increase in the excess weight, while at concentrations above 100 mg. per litre there was a sharp decrease. In the absence of gelatin, there was an increase in excess weight at low chloride concentrations, while at concentrations above 50 mg. per litre there was a sharp decrease, similar to that observed in the presence of gelatin.

In the absence of gelatin, an increase in reflectivity was observed up to a chloride concentration of approximately 100 mg. per litre. The slight decrease in reflectivity at higher concentrations was ascribed to a roughening of the

cathode surface and not to an increase in crystal size. The reflectivity due to the presence of gelatin was not decreased by the addition of chloride up to 100 mg. per litre. At higher concentrations, however, irregularities began to appear, which decreased the reflectivity. As with reflectivity, the hardness of deposits obtained in the presence of gelatin was not affected when chloride was added to the electrolyte.

Gauvin and Winkler observed no effect on the steady state cathode polarization measured in the presence of gelatin when 20 mg. per litre or more of chloride ion were added to the electrolyte. In the absence of gelatin, the polarization increased with increase in chloride ion concentration from 20 mg. to 100 mg. per litre, while a decrease in polarization was observed with an increase in chloride concentration from 10 to 20 mg. per litre.

The effect of relatively small additions of chloride, in the absence of gelatin, on cathode behaviour was explained by the adsorption of cuprous chloride on the cathode surface. It was assumed that the adsorption was the cause of the addition agent effect of chloride at low concentrations. At high concentrations, the cuprous ions in the cathode film will be depleted to a much greater extent (by cuprous chloride formation) and the reduction of cupric to cuprous ion will

proceed to an increasing extent, resulting in decreased deposition efficiency. These assumptions are in accord with the excess weight observations cited above. Gauvin and Winkler assumed that, in the presence of gelatin, the effective concentration of cuprous chloride in the solution is reduced considerably by the formation of a gelatin-cuprous chloride complex. The formation of this complex also explains the prevention of cuprous chloride adsorption at the deposit by gelatin.

In the work just reviewed, the chloride concentrations used were in excess of 10 mg. per litre. In their study of the effects of halides on copper deposition in the presence of gelatin, Mandelcorn, McConnell, Gauvin and Winkler (66, 67, 68) extended the investigations to lower concentrations of chloride. Using Haring cells, cathode polarization-halide concentration relations were determined for all four halides.

The effect of fluoride ion on copper deposition in the presence of 25 mg. per litre of gelatin and at a current density of 2 amp. per dm.² was investigated at concentrations ranging from 0 to about 110 mg. per litre. Neither the polarization nor the structure of the deposits was affected by the addition of fluoride ions.

Successive increases of chloride, bromide and iodide ion concentrations, in the presence of 25 mg. per litre of

gelatin and at 2 amp. per dm.², first decreased the polarization and then increased it, thereby yielding polarization-halide concentration curves with minima. Iodide was least effective, since the minimum of the polarization-iodide concentration curve occurred at a greater concentration and at a greater polarization than the other two ions. Chloride and bromide affected polarization to about the same extent. The minimum in the polarization-chloride ion concentration curve corresponded to a chloride concentration of about 2 mg. per litre. In general, the polarization-halide concentration curves were found to be altered by changes in current density, gelatin concentration, and temperature but not by changes in acid concentration. Thus, the minima for chloride and bromide shifted to higher halide concentrations and higher polarizations with increased gelatin concentration (from 25 to 75 mg. per litre) or increased current density (from 1 to 3 amp. per dm.²). With a temperature change from 25° to 40°C., the minimum of the polarization-chloride concentration curve shifted to a lower polarization and a lower chloride ion concentration.

Mandelcorn and co-workers found that the shape of the polarization-halide concentration curves remained unaltered when measurements were made in a cell in which the anode was surrounded by a parchment membrane. This precluded the possibility that the observed minima were due to

insoluble material originating at the anode.

The structure of the deposits was found to depend upon the chloride concentration used. Increasing the chloride concentration, the deposits became increasingly bright until the concentration corresponding to the minimum polarization was reached. At higher concentrations, the deposits became progressively more striated, and had passive areas where little or no deposition seems to occur. At still higher chloride concentrations, such that the polarization was equal to, or greater than, that observed in the absence of chloride, the deposits again became uniform but dull in appearance.

Excess weights, and gelatin and chloride contents, were determined for deposits obtained from electrolytes containing 25 mg. per litre of gelatin and various amounts of chloride. It was found that excess weights increased slowly with increasing chloride concentration, until the concentration corresponding to the minimum in the polarization-chloride concentration curve was passed, beyond which there was a rapid increase to a constant excess weight value with further increase in chloride content of the electrolyte. The gelatin content of the deposits was constant over the whole range of chloride concentrations (0 to 9 mg. per litre), while the chloride content passed through a maximum at

approximately the chloride concentration in the electrolyte corresponding to the minimum in the polarization-chloride concentration curve.

In seeking an explanation of the observations reviewed above, Mandelcorn and co-workers dismissed the likelihood that at the low halide ion concentrations used, cuprous halide should form in the electrode films and be adsorbed on the cathode in the manner suggested previously by Gauvin and Winkler (65) for higher chloride concentrations. They believed that the minima in the polarization-halide concentration curves suggest a balance between two processes that operate simultaneously to alter the polarization when both gelatin and halide are present in the electrolyte. One of the processes may be the adsorption of gelatin on active centers of the cathode surface (47), resulting in a reduction of the active area of the electrode. The essentially constant gelatin content of the deposits obtained from electrolytes containing various amounts of chloride seems to indicate that the adsorption of gelatin is relatively unaffected in the presence of chloride. The other process was believed to be the attack of halide at the relatively inactive crystal faces on the cathode surface, with a resultant increase in active area. This action could account for the decrease in polarization at low halide concentrations.

According to Mandelcorn and co-workers, further increase in the halide content of the electrolyte should result in greater formation or adsorption of cuprous chloride on the cathode surface. The cuprous chloride should then exert an addition agent effect similar to gelatin. If this effect eventually becomes predominant over the tendency for halide to increase the active area of the cathode, the polarization should pass through a minimum as observed.

THE DEPOSITION OF COPPER IN THE PRESENCE OF ARSENIC,
ANTIMONY AND BISMUTH

The copper anodes used in the copper refinery cells usually contain many impurities. The eight major impurities are gold, silver, selenium, tellurium, arsenic, antimony, lead, and nickel. Traces of other metals are to be found in the anodes, such as zinc, cobalt, iron, bismuth, tin, etc., but usually in such small amounts that it is said that they do not influence the refinery practice.

According to Mantell (69), the most important impurities in the acidified sulphate electrolyte are arsenic, antimony and (occasionally) bismuth because of their bad effects on properties of the refined copper and the ease with which they enter solution and are cathodically precipitated. It is generally believed that the presence of small amounts of

soluble chlorides in the electrolyte prevents the codeposition of antimony and bismuth with copper, by causing the formation of insoluble oxychlorides of the two impurities, which fall into the slime.

Although gelatin (as glue) and chloride ion are being used widely in refinery electrolyte to produce hard, smooth copper deposits of high purity, few investigations had been undertaken into the effect of the two addition agents on copper deposition from electrolytes containing arsenic, antimony and bismuth.

In 1911, Wen and Kern (70, 71) studied the effect of various organic (colloid) and inorganic addition agents on copper deposition from electrolytes of high arsenic content. The purpose of the investigation was to find conditions which would prevent (1) deposition of arsenic and antimony on the cathode, and (2) the formation of "trees".

In all experiments, the electrolytes were stirred. They contained 150 g. per litre of copper sulphate pentahydrate and 100 g. per litre of concentrated sulphuric acid. The apparent current density was 4.4 amp. per dm.² and the anodes were approximately 98 per cent copper, one per cent arsenic and one per cent antimony.

The following observations were made:

1. In a series of experiments with electrolytes containing 2 to 8 per cent arsenic and no addition agents, a sticky coating of arsenic and antimony oxides was formed at the anodes. The anodes had to be scraped several times during the electrolysis. At 35°C., with the electrolytes containing 2 to 6 per cent arsenic, coarse, brittle deposits were obtained. The surfaces became dark as soon as they were exposed to air. Analysis showed that the deposits were high in arsenic and antimony. With 8 per cent arsenic in the electrolyte the deposit was bright and coherent; it was low in arsenic and antimony content. There were some "trees" and nodules at the edge of the deposit. When the above electrolytes were at 50°C., the deposits were essentially similar in appearance to those obtained at 35°C. No appreciable change was observed when the experiments were repeated with the anodes surrounded by muslin diaphragms intended to prevent particles of impurity from depositing mechanically on the cathode. Wen and Kern believed that the arsenic acid in the electrolyte containing 8 per cent arsenic acted as an addition agent since it prevented, to some extent, the co-deposition of arsenic and antimony and retarded the formation of "trees".

2. Experiments were also made with electrolytes containing 1.5, 3.0, 6.0 and 8.0 per cent arsenic, at 40° and 50°C.

The effects of various inorganic addition agents were:

A. In the presence of 165 mg. per litre of sodium chloride, i.e., 100 mg. per litre of chloride ion and 65 mg. per litre of sodium ion, the deposits were bright, smooth, hard, and free of "trees". They were low in arsenic and antimony content in every case. The deposits obtained at 50°C. were brighter and more crystalline than those at 40°C.

B. In the presence of 100 mg. per litre of chloride ion, added in the form of hydrochloric acid, the deposits at 40° and 50°C. were quite similar to those obtained in the presence of sodium chloride. However, they were slightly more nodular at the edges, and analysis showed they were less pure. Wen and Kern concluded that sodium chloride was a more effective inorganic addition agent than hydrochloric acid.

C. Electrodeposition in the presence of 65 mg. per litre of sodium ion, added in the form of sodium sulphate, gave deposits that were bright, solid, free from "trees", and quite low in arsenic and antimony, especially those from electrolytes at 50°C. Thus, small amounts of sodium sulphate had a good effect, chemically and physically on copper deposition. Electrodeposition in the presence of larger amounts of sodium sulphate gave poorer deposits. Likewise, deposits from electrolytes containing 0.5 or 1.0 g. per litre of chloride

ion (as sodium chloride) were not as bright, smooth, or pure as those obtained in the presence of 0.1 g. per litre of chloride ion.

3. The individual effects of 100 and 200 mg. per litre of gelatin, glue and tannin on copper deposition from electrolytes containing 3 to 6 per cent arsenic were studied. All three addition agents produced remarkably beneficial effects upon the copper deposits. The deposits were smooth, ductile and contained very little arsenic or antimony.

4. Deposits obtained from electrolytes containing 3 to 6 per cent arsenic, 100 mg. per litre of gelatin and chloride ion (from sodium chloride) each were similar to those formed in the presence of gelatin alone. They were slightly lower in arsenic and antimony content. When sodium chloride was replaced by hydrochloric acid the beneficial effect with gelatin was somewhat decreased.

Wen and Kern were unable to offer an explanation of the effect of organic addition agents and of the combined effect of organic and inorganic addition agents on copper electrodeposition in the presence of arsenic. They felt that the chemistry of organic addition agents, such as gelatin, must be better known before any answer to the problem could be given.

However, Kern (72) postulated a mechanism to explain "the physical action of sodium ion" during electrodeposition. He believed that the formation of smooth, ductile deposits from electrolytes containing salts, such as sodium chloride or sodium sulphate, are due to the "reducing" effect of metallic ions which, by aid of the electric current, form a menstruum around the cathode. In other words, this menstruum of metallic ions has the influence, or property, of more or less changing the copper crystals to an amorphous form. He states that the higher the metal of the inorganic addition agent stands in the Electromotive Series, the purer, smoother and less brittle the deposit.

In addition to the physical action of sodium ion, Wen and Kern have assumed that the beneficial effect of a salt, such as sodium chloride, can be ascribed to the chemical behaviour of sodium and chloride ions in the electrolyte. They believed that the arsenic in the anode passes into solution as arsenious sulphate which hydrolyzes to form arsenious acid having the structural formula, $\text{As}(\text{OH})_3$. The acid undergoes slight dissociation, as a base, to trivalent arsenic ion and hydroxyl ion. According to Wen and Kern, the undissociated arsenious acid reacts with the sodium ions which surround the cathode:

that is, arsenic cation is changed to arsenite anion. Thus, sodium ions diminish the arsenious acid concentration and, therefore, the amount of trivalent arsenic ion. The net result is the prevention of arsenic deposition on copper. Wen and Kern believed that chloride ions, too, prevent the deposition of arsenic. It was proposed that chloride ions surrounding the anode, convert arsenic from the cationic to anionic state. Chloride ions prevent the hydrolysis of arsenious sulphate (formed at the anode) by oxidizing it, at the moment of its formation, to arsenic sulphate:

It was noted that the chloride ion concentration is not decreased. They assumed that the pentavalent arsenic cation is then converted to the arsenate anion by the hydrolysis of arsenic sulphate:

Spear (73) claimed that Kern's theory, which relates the structure of the copper deposit to the "reducing" effect of metal ions of the inorganic addition agents, is untenable. He has shown that shiny, good deposits are obtained in the presence of nitric or chloric acid (74).

Wen and Kern did not explain how antimony co-deposition with copper was reduced so drastically by the addition of inorganic addition agents such as sodium chloride.

There is some doubt concerning the mechanism by which arsenic, antimony and bismuth enter the deposits. Addicks (75) believed that impurities may enter the cathode copper in the refinery by (1) electrodeposition, (2) inclusion of electrolyte, or (3) inclusion of slime. He assumed that arsenic cannot be electrodeposited but must be included as slime or electrolyte. On the other hand, Johnson (76) believed that arsenic and antimony exist in the electrorefined copper as compounds in solid solution (ex. cuprous arsenide and antimonide in copper), while bismuth is in copper as a nearly negligible, insoluble constituent (as the metal).

Kameyama and co-workers (77, 78, 79) studied the influence of antimony and bismuth on the electrorefining of copper from an electrolyte composed of 4 moles of sodium chloride, 0.8 mole cuprous chloride, 0.5 mole hydrogen chloride, 1 g. gelatin and 1000 g. of water, at 50°C. The current density was 2.3 amp. per dm.² and the time of deposition ranged from 30 to 70 hours. Mechanical stirring and passage of carbon dioxide displaced atmospheric oxygen. Adding potassium acid tartarate as addition agent, and various amounts of antimony to the electrolyte, it was found that the

cathode never contained more than 0.0009 per cent antimony. When more than 1 g. per litre of bismuth was present in the electrolyte the bismuth content in the cathode deposit was occasionally as high as 0.001 per cent. Under these conditions, the cathode deposit became highly crystalline. Increasing the gelatin and copper concentrations in the electrolyte eliminated these effects.

It is obvious, of course, that one of the more effective methods of minimizing the entrance of soluble impurities into electrodeposits is the precipitation of the impurities by the formation of an insoluble compound (resulting from the addition of a chemical substance to the electrolyte), or by the creation of conditions favouring decreased solubility. Pletenev and Kuznetzova (80) studied the effects of temperature, and concentrations of chloride ion, sulphuric acid, arsenic, zinc and nickel on the solubility of antimony as antimony sulphate in a copper sulphate solution containing 40 g. per litre of copper. A constant amount of antimony was used in the tests (1 g. per litre). It was found that the presence of chloride ion up to 25 mg. per litre has no effect on the solubility of antimony in the copper sulphate solution at 50°C., but higher concentrations increased the solubility. Increasing the concentration of sulphuric acid from 100 to 200 g. per litre almost doubled the solubility

of antimony. An increase of arsenic from 0.5 to 1.0 g. per litre increased the solubility of antimony, but above this amount the solubility decreased sharply with increase in arsenic concentration. The effects of zinc and nickel were insignificant. Lowering the temperature of the electrolyte from 50° to 18°C. decreased the solubility of antimony by about 20 per cent.

Pletenev and Kuznetzova then studied the solubility of antimony during the electrolysis of an electrolyte containing 150 g. per litre of sulphuric acid, 40 g. per litre of copper, and 0.65 g. per litre (maximum solubility) of antimony. Various temperatures and concentrations of chloride ion were used. Pure copper anodes were used in one series of experiments and anodes containing 1.42, 0.9, and 0.18 per cent antimony were used in another series. It was found that the amount of antimony in solution was independent of the amount in the anode and depended only on the temperature and acidity. The presence of chloride ion, even up to 300 mg. per litre, did not reduce the concentration of antimony in the electrolyte, and did not seem to affect the process of anodic oxidation of antimony from the tri-valent to pentavalent cation.

Yu-lin Yao (61) repeated some of Pletenev and Kuznetzova's work and found, in confirmation, that chloride ion did not

decrease the solubility of antimony in an acid sulphate electrolyte. He did not agree with some metallurgists in the copper refinery industry who believed that the co-deposition of antimony with copper is minimized by chloride ion through antimony precipitation as antimony oxychloride. He actually found that with an increase in chloride ion concentration there was an increase in antimony solubility. Likewise, bismuth oxychloride is not formed, because bismuth is more soluble than antimony in the copper-refining electrolyte (81). He concluded, from his experimental work on slime analysis and from bismuth determinations in copper deposits, that bismuth was occluded by the cuprous chloride precipitate. The precipitate carried down with it the bismuth derived from the anodes into the anode slime. Cuprous chloride reached its minimum solubility at a chloride ion concentration of about 15 mg. per litre. At this minimum, the bismuth content in the cathode deposit represents the sum of mechanical inclusion of anode slime and of electrolyte.

THE PROBLEM

No information seems to be available on the effect of arsenic, antimony or bismuth on the cathode polarization during copper deposition, nor has there been much mention in the literature of the effect of addition agents on copper deposition in the presence of these impurities. Practically all of the investigations have been confined to the practical problem of preventing the entrance of the foreign metals into copper deposits. The object of the present investigation has been to study the effect of gelatin and chloride ions on copper deposition from acidified sulphate electrolytes containing arsenic, antimony and bismuth. It has been of particular interest to determine the extent to which the presence of these metallic ions might influence the minima in the polarization-chloride ion concentration relations observed by Mandelcorn et al at low chloride ion concentrations in the presence of gelatin.

EXPERIMENTAL AND RESULTS

CATHODE POLARIZATION MEASUREMENT USING A HARING CELL

Polarization measurements were made with a Haring cell (37) of the design used by McConnell (68) and Mandelcorn (67). A sketch of the cell is given in Figure 1. It consisted of a narrow rectangular box made from $\frac{1}{8}$ -in. thick lucite sheets that had been machined to size. These were cemented together with chloroform and then secured with brass bolts. The anode and cathode consisted of strips of roller copper, $1/16$ in. thick, sealed with paraffin to lucite blocks. The copper and blocks were machined to fit exactly into the ends of the box. The strips of copper were allowed to project about $3/4$ inch above the blocks to facilitate electrical connection. These electrode units were then placed in position at the ends of the cell. Two intermediate electrodes of copper gauze, evenly spaced between the cathode and anode, were inserted into grooves that had been cut into the walls of the cell. They, too, projected above the cell to facilitate electrical connection. The interior dimensions of the cell with the electrodes in place were $15 \times 2.5 \times 9$ cm.³ and the 150 ml. of electrolyte, which was always added, covered 10 cm.² of each electrode.

During an electrolysis the cell was immersed in a water bath with temperature controlled to within 0.1°C .

Figure 1

The Haring Cell

HARING CELL

Figure 1

The cell was kept level by setting it on a platform permanently adjusted to a level position.

The electrical circuit used is schematically shown in Figure 2. A 6-volt storage battery served as the source of power, the current being measured with a Marsland Multi-meter, Model 2014, and regulated with three rheostats of 5, 23 and 110 ohms resistance. All potential measurements were made with a "Queen" Potentiometer, Model E-3040, in conjunction with a Weston Standard cell and a Leeds and Northrup Lamp and Scale type galvanometer. Not shown in the diagram are switches which made it possible to pass current in either direction through any section of the cell, and switches to provide for measurement of the potential drop across any section of the cell.

If the three compartments of the cell are of equal length, the IR drop across each may be taken to be the same, and the cathode polarization at D, in Figure 2, can then be obtained as the difference between the potential across the cathode compartment CD and that across the intermediate compartment BC. With the particular cell used, the correction for slight differences in length of compartments was negligible.

Electrolytes were made with doubly-distilled water, and contained 125 g. per litre of copper sulphate pentahydrate

Figure 2

Apparatus for Measuring Polarization

Figure 2

and 100 g. per litre concentrated sulphuric acid, both of reagent grade. Eimer and Amend gelatin from a single stock was used throughout. Chloride ion was introduced as reagent grade sodium chloride.

An electrolyte containing arsenic, antimony or bismuth was made by dissolving the appropriate amount of the C. P. metal in hot concentrated sulphuric acid, cooling the acid solution, and then adding it to acid-free copper sulphate solution. Since arsenic, antimony and bismuth have low solubilities in the electrolytes used, the amounts added were limited to concentrations which gave permanently clear, precipitate-free solutions.

Electrodes, attached to the lucite blocks, were prepared for electrolysis by polishing with emery cloth, etching in 40 per cent nitric acid and, finally, washing with distilled water.

Before an electrolysis experiment was undertaken, the cathode surface was brought to a standard condition (43, 44) by electrodeposition from an acid-copper sulphate electrolyte containing no gelatin, at a current density of 3 amp. per dm.² for 30 min., followed by deposition at a current density of 2 amp. per dm.² for one hour. This precluded the possibility of any variation in effect of surface on cathode polarization due to different initial cathode surfaces.

The procedure adopted to determine cathode polarization was as follows: 150 ml. of the desired electrolyte, kept in the constant temperature bath, was measured into the Haring cell, which had been previously rinsed with the electrolyte. The cell was lowered into the bath and the proper electric connections made. The current switch was closed and the current immediately adjusted to the desired amperage (200 milliamperes for a current density of 2 amp. per dm.²). The potential drop across the cathode compartment, and across the middle compartment, was then measured as quickly as possible. The difference between these two values gave the cathode polarization, uncorrected for error in electrode spacing. The potential measurements were repeated at intervals of about five minutes until further change in polarization did not exceed 0.2 mv. per min. . That is, the cathode polarization eventually attained a steady-state value (after 15 to 75 min., depending upon the system involved).

All experiments were conducted at 24.5°C. and 2 amp. per dm.², except where otherwise stated.

EFFECT OF ARSENIC, ANTIMONY AND BISMUTH ON CATHODE
POLARIZATION IN THE PRESENCE AND ABSENCE OF GELATIN

Experiments were made, in the absence and presence of gelatin, to determine the effect of arsenic, antimony and bismuth on the steady state polarizations for depositions at 2 amp. per dm.². The results are recorded in Tables I, II and III, respectively, and plotted in Figures 3, 4 and 5. It is evident that the presence of arsenic or antimony alone results in an increase of polarization while bismuth alone causes a decrease. The presence of gelatin (25 mg. per litre) rather drastically modifies all three cation effects.

Of the three cations, the presence of arsenic, whether alone or with gelatin produced the least effect on polarization, as indicated in Figure 3. The deposits obtained in the presence of addition agent were shiny, smooth, of a light salmon pink colour. However, with higher arsenic concentrations of 1.60 and 1.92 g. per litre the surfaces were slightly rough. In the absence of gelatin the deposits were less bright, though still smooth and light pink. At 2.0 g. per litre arsenic, the deposit was slightly rough.

The presence of antimony alone produced a greater increase in polarization than that attributed to arsenic.

TABLE I

Effect of Arsenic on Cathode Polarization

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$$

$$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$$

$$\text{Current Density} = 2 \text{ amp./dm.}^2$$

$$\text{Temperature} = 24.5^\circ\text{C.}$$

(No chloride present)

Gelatin conc. 0 mg./l.		Gelatin conc. 25 mg./l.	
As conc. (g./l.)	Polarization (millivolts)	As conc. (g./l.)	Polarization (millivolts)
0	112	0	244
0.4	114	0.8	248
1.0	121	1.2	251
1.6	134	1.6	232
2.0	136	1.9	243

Figure 3

Effect of Arsenic on Cathode Polarization

in the Presence and Absence of Gelatin

(Current Density = 2 amp. per dm.²)

(No chloride present)

Figure 3

TABLE II

Effect of Antimony on Cathode Polarization

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$$

$$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$$

$$\text{Current Density} = 2 \text{ amp./dm.}^2$$

$$\text{Temperature} = 24.5^\circ\text{C.}$$

(No chloride present)

Gelatin conc. 0 mg./l.		Gelatin conc. 25 mg./l.	
Sb conc. (mg./l.)	Polarization (millivolts)	Sb conc. (mg./l.)	Polarization (millivolts)
0	112	0	244
25	129	50	240
50	133	160	223
100	150	200	213
150	161	200	215
200	165	315	201
250	165	360	212
320	164	360	213
400	166	385	222

Figure 4

Effect of Antimony on Cathode Polarization

in the Presence and Absence of Gelatin

(Current Density = 2 amp. per dm.²)

(No chloride present)

Figure 4

TABLE III

Effect of Bismuth on Cathode Polarization

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$$

$$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$$

$$\text{Current Density} = 2 \text{ amp./dm.}^2$$

$$\text{Temperature} = 24.5^\circ\text{C.}$$

(No chloride present)

Gelatin conc. 0 mg./l.		Gelatin conc. 25 mg./l.	
Bi conc. (g./l.)	Polarization (millivolts)	Bi conc. (g./l.)	Polarization (millivolts)
0	112	0	244
0.1	108	0.1	205
0.2	105	0.2	190
0.5	105	0.44	172
1.0	94	1.0	151
1.5	82	1.0	142
		1.4	143

Figure 5

Effect of Bismuth on Cathode Polarization

in the Presence and Absence of Gelatin

(Current Density = 2 amp. per dm.²)

(No chloride present)

Figure 5

It gave smooth, salmon pink deposits. In the presence of 25 mg. per litre of gelatin, successive increases of antimony first decreased the polarization and then increased it, thereby yielding a polarization-antimony concentration curve with a minimum at about 316 mg. per litre of antimony (Figure 4). The deposits obtained in the presence and absence of gelatin were smooth, light pink. In the former case, however, they were brighter.

The presence of bismuth, whether alone or with gelatin, resulted in a decrease of polarization which was especially marked in the latter case (Figure 5). Smooth, pink deposits were obtained in all experiments.

EFFECT OF CHLORIDE ON CATHODE POLARIZATION IN THE PRESENCE OF ANTIMONY, ARSENIC AND BISMUTH

Before studying the effect of chloride ions in the presence of the metallic ions, the effect of the halide alone on cathode polarization was determined. The results are recorded in Table IV and plotted in Figure 6. They are comparable with those obtained by McConnell (68). A small addition of chloride ion to the electrolyte resulted in a relatively small increase in polarization. Increasing amounts of chloride ion, to a 9 mg. per litre concentration, had no further effect. Smooth, salmon pink deposits, free of

TABLE IV

Effect of Chloride on Cathode Polarization

 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$ $\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$ Current Density = 2 amp./dm.²

Temperature = 24.5°C.

(No gelatin present)

Cl ⁻ conc. (mg./l.)	Polarization (millivolts)
0	112
0.5	126
0.5	130
1	128
2	131
2	135
3	129
4	129
6	129
9	125

TABLE V

Effect of Chloride on Cathode Polarization
in the Presence of Antimony, Arsenic and Bismuth

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

(No gelatin present)

Sb conc. 200 mg./l.		As conc. 1.6 g./l.		Bi conc. 1.0 g./l.	
Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)
0	165	0	134	0	94
1	131	0	132	1	48
2	123	1	65	2	49
3	117	2	60	4	47
4	123	3	51	8	48
5	124	4	62		
6	125	5	73		
9	119	7	62		
		9	59		

Figure 6

Effect of Chloride on Cathode Polarization
in the Presence and Absence of Antimony, Arsenic
and Bismuth

(Current Density = 2 amp. per dm.², no gelatin present)

Figure 6

any striations, were obtained.

Experiments were then made, in the absence of gelatin, to determine the effect of chloride on steady state polarization, in the presence of antimony, arsenic and bismuth, and at 2 amp. per dm.². The results are recorded in Table V and plotted in Figure 6. The addition of chloride ion, with no gelatin present, caused comparable decreases in polarization in the presence of antimony and bismuth, but a relatively large decrease when the electrolyte contained arsenic.

The addition of chloride ion to an electrolyte containing 200 mg. per litre of antimony gave smooth, pink deposits and a decrease in polarization, to values approximating those obtained for chloride alone. Although the addition of chloride ion to an electrolyte containing 1.0 g. per litre of bismuth caused a decrease in polarization comparable with that obtained for chloride in the presence of antimony, the actual polarization values were much lower. Also, the structure of the deposits were quite different. In the presence of bismuth and chloride ion, the deposits were bright, highly crystalline.

The addition of chloride ion caused a substantial decrease in polarization in the presence of 1.6 g. per litre of arsenic, resulting in the formation of bright, highly

crystalline deposits. The polarization in the electrolyte containing arsenic and chloride corresponded to that for an electrolyte containing bismuth and chloride.

The above experiments were extended to determine the effect of chloride, in the presence of arsenic-antimony and arsenic-bismuth mixtures, on the steady state polarizations for depositions at 2 amp. per dm.². The results, recorded in Table VI and plotted in Figure 7, were similar to those obtained with electrolytes containing one of the cations and chloride ion. The deposits were crystalline.

The decrease in polarization brought about by addition of chloride to electrolytes containing the mixture, 200 mg. per litre of antimony and 1.6 (or 0.8) g. per litre of arsenic, paralleled the behaviour with chloride and arsenic (1.6 g. per litre) alone, while the polarization in the electrolyte containing the cation mixtures, with no chloride added, corresponded to that for an electrolyte containing only the antimony cation. Also, the polarization in an electrolyte containing 1.6 g. per litre of arsenic, 1.0 g. per litre of bismuth and no chloride was that corresponding to an electrolyte containing arsenic (1.6 g. per litre) alone.

TABLE VI

Effect of Chloride on Cathode Polarization
in the Presence of Antimony-Arsenic and Bismuth-
Arsenic Mixtures.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

(No gelatin present)

Sb = 200 mg./l. As = 0.8 g./l.		Sb = 200 mg./l. As = 1.6 g./l.		Bi = 1.0 g./l. As = 1.6 g./l.	
Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)
0	167	0	163	0	127
1	54	1	46	1	43
5	48	5	43	2	39
9	51	9	46	4	37
				8	37

Figure 7

Effect of Chloride on Cathode Polarization
in the Presence of Antimony-Arsenic and Bismuth-
Arsenic Mixtures.

(Current Density = 2 amp. per dm.²; no gelatin present)

Figure 7

EFFECT OF CHLORIDE AND GELATIN ON CATHODE POLARIZATION
IN THE PRESENCE OF ANTIMONY, ARSENIC AND BISMUTH

Experiments were made to determine the effect of chloride (0 to 12 mg. per litre) and gelatin (25 mg. per litre) on the steady state polarizations in electrolytes containing various antimony concentrations (0, 50, 200, 315 and 360 mg. per litre), and at 2 amp. per dm.². The results are recorded in Tables VII and VIII, and plotted in Figure 8.

With gelatin at a level of 25 mg. per litre, the effect of chloride in the presence of antimony was quite analogous to that observed in the absence of added cation. All of the polarization-chloride ion concentration curves have the characteristic minima, observed by Mandelcorn et al. (66) for depositions from electrolytes containing gelatin and chloride ion, but no antimony. The slightly lower polarization values obtained for the electrolytes containing gelatin, 315 mg. per litre of antimony and 0 to 3 mg. per litre of chloride ion are perhaps a reflection of the decrease in polarization brought about by the antimony itself in the presence of gelatin (Figure 4). The deposits were somewhat similar to those obtained in the absence of antimony (66). With increasing chloride ion concentration, the deposits were smooth and became increasingly brighter

TABLE VII

Effect of Chloride on Cathode Polarization in the Presence
of Gelatin and Different Antimony Concentrations

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Sb conc. 0 mg./l.		Sb conc. 50 mg./l.		Sb conc. 200 mg./l.	
Cl^- Conc. (mg./l.)	Polarization (milli-volts)	Cl^- conc. (mg./l.)	Polarization (milli-volts)	Cl^- conc. (mg./l.)	Polarization (milli-volts)
0	244	0	240	0	213
0.4	225	0.4	220	0	215
1	186	1	193	0.4	208
2	162	2	167	0.4	205
3	180	3	176	1	188
5	235	4	197	2	162
7	256	6	249	3	182
10	256	8	270	4	201
		12	261	6	250
				9	265
				12	259
				15	259

TABLE VIII

Effect of Chloride on Cathode Polarization in the Presence
of Gelatin and Different Antimony Concentrations

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Sb conc. 315 mg./l.		Sb conc. 360 mg./l.	
Cl ⁻ conc. (mg./l.)	Polarization (millivolts)	Cl ⁻ conc. (mg./l.)	Polarization (millivolts)
0	201	0	213
0.4	185	0	212
0.8	175	1	177
1.5	155	2	166
2	151	3	176
3	166	6	247
5	227	9	253
7	254		
10	257		

Figure 8

Effect of Chloride on Cathode Polarization
at Different Antimony Concentrations, in the
Presence of 25 mg./l. Gelatin.

(Current Density = 2 amp. per dm.²)

Figure 8

until the concentration corresponding to the minimum polarization was reached. At higher concentrations, the deposits became progressively more striated, and nodules appeared. The striations consisted of smooth vertical strips of deposit separated by apparently passive areas where very little or no deposition seemed to occur. At high chloride concentrations, corresponding to polarizations higher than those obtained in the absence of chloride, the deposits became uniform again with, however, a loss in lustre. In the presence of antimony, especially at lower chloride concentrations, the pink deposits were of a shiny silver hue.

To determine the effect of chloride (0 to 10 mg. per litre) and gelatin (25 mg. per litre) on cathode polarization in the presence of arsenic, experiments were made with electrolytes containing 0.8 g. and 1.6 g. per litre of arsenic. The results are recorded in Table IX and plotted in Figure 9.

In the presence of arsenic, as with antimony, the effect of chloride, in the presence of gelatin at a level of 25 mg. per litre, is quite analogous to that observed in the absence of added cations. The minimum in the polarization-chloride concentration curve obtained in the absence of arsenic or antimony did not shift to different chloride concentrations or appreciably different polarizations by the addition of either metal to the electrolyte. In addition, the structure

TABLE IX

Effect of Chloride on Cathode Polarization in the Presence
of Gelatin and Different Arsenic Concentrations

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$

$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

As conc. 0 g./l.		As conc. 0.8 g./l.		As conc. 1.6 g./l.	
Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)
0	244	0	248	0	232
0.4	225	1	195	1	177
1	186	2	170	2	170
2	162	4	204	2	165
3	180	6	261	3	181
5	235	8	263	5	236
7	256			7	267
10	256			9	265

Figure 9

Effect of Chloride on Cathode Polarization
at Different Arsenic Concentrations, in the Presence
of 25 mg./l. Gelatin.

(Current Density = 2 amp. per dm.²)

Figure 9

of the deposits obtained from the electrolytes containing arsenic, antimony or neither metal were all quite similar.

The effect of chloride in the presence of bismuth (1.0 g. per litre), with gelatin at a level of 25 mg. per litre was investigated next, and the results are recorded in Table X and plotted in Figure 10. When both bismuth and gelatin were present, the decrease in polarization with increased chloride concentration was virtually absent. This was perhaps a reflection of the large decrease in polarization brought about by the bismuth itself in the presence of gelatin (Figure 5). However, the appearance of the deposits passed through stages essentially similar to those observed in the presence of gelatin and chloride.

Experiments were also made to determine if the presence of arsenic and antimony together would modify the effect of chloride and gelatin (25 mg. per litre) on cathode polarization observed for electrolytes containing one or neither of the metals. The results are recorded in Table XI and plotted in Figure 11. Again, polarization-chloride ion concentration curves, with the characteristic minima, were obtained. The polarizations, at different chloride concentrations, were not unlike those obtained in the absence of the cations.

TABLE X

Effect of Chloride on Cathode Polarization
in the Presence of Bismuth and Gelatin

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Bi = 1.0 g./l.

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Cl ⁻ Conc. (mg./l.)	Polarization (millivolts)
0	151
0	142
1	142
2	148
3	165
4	201
6	242
7	256
9	264

Figure 10

Effect of Chloride on Cathode Polarization
in the Presence of Bismuth and 25 mg./l. Gelatin
(Current Density = 2 amp. per dm.²)

Figure 10

TABLE XI

Effect of Chloride on Cathode Polarization
in the Presence of Antimony-Arsenic Mixtures and Gelatin

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Sb = 200 mg./lb. As = 0.8 g./l.		Sb = 200 mg./l. As = 1.6 g./l.		Sb = 50 mg./l. As = 1.6 g./l.	
Cl ⁻ Conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)
0	233	0	232	0	242
1	202	1	189	1	194
2	175	2	169	2	176
4	208	4	215	4	213
6	256	6	258	6	265
9	270	9	272	9	279

Figure 11

Effect of Chloride on Cathode Polarization in
the Presence of Antimony-Arsenic Mixtures and 25 mg./l.

Gelatin

(Current Density = 2 amp. per dm.²)

Figure 11

EFFECT OF CHLORIDE ON CATHODE POLARIZATION IN THE PRESENCE
OF ANTIMONY, ARSENIC AND DIFFERENT GELATIN CONCENTRATIONS

The effects of chloride ions on the steady state polarization for depositions at different gelatin concentrations (5, 50, 100, 200 and 400 mg. per litre) and in the presence of antimony (200 mg. per litre) are shown in Tables XII and XIII. The effect of chloride ion at the gelatin concentration of 25 mg. per litre has been recorded previously in Table VII. The polarization-chloride concentration curves, plotted in Figure 12, have the characteristic minima, which shift to higher polarizations and higher chloride concentrations with an increase in gelatin concentration (with the exception of the minimum for the electrolyte containing 200 mg. per litre of gelatin). The shift of the minima by changes in gelatin concentration when antimony is present is similar to the corresponding shift observed in the absence of the cation (66).

The effect of chloride ion on polarization, in the presence of arsenic (1.6 g. per litre) and different gelatin concentrations (5 and 25 mg. per litre), was also investigated. The results are plotted in Figure 13, and recorded in Tables XIV (and Table IX for the electrolyte containing 25 mg. per litre of gelatin). As with antimony, the minimum of the polarization-chloride concentration shifted to a higher

TABLE XII

Effect of Chloride on Cathode Polarization in
the Presence of Antimony and Different Gelatin Con-
centrations

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Sb = 200 mg./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Gelatin 5 mg./l.		Gelatin 50 mg./l.		Gelatin 100 mg./l.	
Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)
0	202	0	233	0	230
0.5	157	1	206	1	216
1	145	2	191	2	208
2	177	3	180	3	209
4	226	4	187	4	210
6	253	6	205	6	214
9	255	7	237	9	235
12	247	8	257	11	261
15	243	9	261	12	274
		12	259	15	276
		15	258		

TABLE XIII

Effect of Chloride on Cathode Polarization in
the Presence of Antimony and Different Gelatin Con-
centrations.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.
 H_2SO_4 = 100 g./l.
 Sb = 200 mg./l.
 Current Density = 2 amp. /dm.²
 Temperature = 24.5°C.

Gelatin 200 mg./l.		Gelatin 400 mg./l.	
Cl ⁻ concn. (mg./l.)	Polarization (millivolts)	Cl ⁻ concn. (mg./l.)	Polarization (millivolts)
0	237	0	232
1	231	2	219
2	219	5	218
4	206	7	220
5	199	9	225
6	199	12	259
7	207	15	264
9	230		
11	239		
13	246		
15	255		

Figure 12

Effect of Chloride on Cathode Polarization
at Different Gelatin Concentrations, in the Presence
of 200 mg./l. Antimony.

(Current Density = 2 amp. per dm.²)

Figure 12

TABLE XIV

Effect of Chloride on Cathode Polarization in the
Presence of Arsenic and Gelatin

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Gelatin = 5 mg./l.

As = 1.6 g./l.

Current Density = 2 amp./dm.²

Temperature = 24.5°C.

Cl^- conc. (mg./l.)	Polarization (millivolts)
0	214
1	136
2	188
4	238
7	245

Figure 13

Effect of Chloride on Cathode Polarization
at Different Gelatin Concentrations, in the
Presence of 1.6 g./l. Arsenic.

(Current Density = 2 amp. per dm.²)

Figure 13

polarization and higher chloride concentration with an increase in gelatin concentration.

EFFECT OF CHLORIDE ON CATHODE POLARIZATION AT DIFFERENT TEMPERATURES IN THE PRESENCE OF ANTIMONY AND GELATIN

An experiment was made to determine the effect of temperature on the polarization curves previously studied. The electrolyte contained 200 mg. per litre of antimony, 25 mg. per litre of gelatin and the standard amounts of copper sulphate and sulphuric acid. It was kept at 41.0°C . during the determinations. The results are recorded in Table XV, and are depicted graphically in Figure 14 along with the corresponding curve at 24.5°C .

By comparison with the results obtained at 24.5°C ., an increase in temperature caused the minimum in the cathode polarization-chloride concentration curve to be shifted toward lower cathode polarization and lower chloride concentration. The shift of the minimum is similar to the corresponding shift observed for electrolytes containing no antimony (66). With successive increases in chloride concentration, the appearance of the deposit, obtained at 41.5°C ., passed through stages essentially similar to those observed at 25°C .

Effect of Chloride on Cathode Polarization at Different Temperatures in the Presence of Antimony and Gelatin.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.
 H_2SO_4 = 100 g./l.
 Sb = 200 mg./l.
 Gelatin = 25 mg./l.
 Current Density = 2 amp./dm.²

Temperature 24.5°C.		Temperature 41.0°C.	
Cl ⁻ conc. (mg./l.)	Polarization (millivolts)	Cl ⁻ conc. (mg./l.)	Polarization (millivolts)
0	215	0	134
0	213	0.5	112
0.4	208	1	104
0.4	205	1.5	128
1	188	2	160
2	162	3	182
3	182	4	204
4	201	5	206
6	250	7	203
9	265	10	205
12	259	15	189
15	259		

Figure 14

Effect of Chloride on Cathode Polarization
at Different Temperatures, in the Presence of
200 mg./l. Antimony and 25 mg./l. Gelatin
(Current Density = 2 amp. per dm.²)

Figure 14

EFFECT OF CHLORIDE ON CATHODE POLARIZATION AT DIFFERENT
CURRENT DENSITIES, IN THE PRESENCE OF ANTIMONY AND GELATIN

Experiments were made to investigate the effect of chloride on polarization at different current densities (0.5, 1.0 and 3.0 amp. per dm.²), and in the presence of antimony (200 mg. per litre) and gelatin (25 mg. per litre). The results are recorded in Table XVI and are plotted in Figure 15 along with the corresponding curve at 2 amp. per dm.².

The shifts of the minimum in the polarization-chloride concentration curves for electrolytes containing antimony are similar to the corresponding shifts observed in the absence of antimony (66). That is, the minimum was shifted to a low polarization and lower chloride concentration with a decrease in current density. Thus, such a shift was observed with a decrease in gelatin concentration, an increase in temperature, and a decrease in current density.

As with depositions at 2 amp. per dm.², the deposits (from electrolytes containing antimony) at the different current densities were silver-pink, and with successive increases in chloride concentration, passed through the stages described above.

TABLE XVI

Effect of Chloride on Cathode Polarization at Different
Current Densities, in the Presence of Antimony and Gelatin

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 125 g./l.

H_2SO_4 = 100 g./l.

Sb = 200 mg./l.

Gelatin = 25 mg./l.

Temperature = 24.5°C.

Current Density 0.5 amp./dm. ²		Current Density 1.0 amp./dm. ²		Current Density 3.0 amp./dm. ²	
Cl ⁻ conc. (mg./l.)	Polarization (milli-volts)	Cl ⁻ ion (mg./l.)	Polarization (milli-volts)	Cl ⁻ ion (mg./l.)	Polarization (milli-volts)
0	80	0	164	0	269
0	79	0.5	144	1	242
0.5	121	1	139	2	220
1	144	2	171	3	202
2	182	3	200	4	208
4	189	4	224	5	247
6	187	6	225	7	273
9	184	10	221	9	296
12	173	12	209	12	302
15	170	15	218	15	300

Figure 15

Effect of Chloride on Cathode Polarization
at Different Current Densities, in the Presence
of 200 mg./l. Antimony and 25 mg./l. Gelatin

Figure 15

EXCESS WEIGHT DETERMINATIONS

The difference in weight between a deposit obtained in the presence of a foreign substance (such as gelatin, antimony or arsenic) and that obtained in a coulometer in series is called the excess weight.

It is well known that deposition from an electrolyte containing gelatin results in considerable excess weight in the cathode. In an effort to gain some information about how, and to what extent, antimony and arsenic might influence the excess weight of copper deposits in the absence and presence of gelatin, experiments were made to determine the effect on excess weight of adding different amounts of antimony and arsenic to electrolytes containing 0 and 25 mg. per litre of gelatin.

Five electrolytic cells, consisting of battery jars of about 10 X 10 X 20 cm.³ (interior dimensions), were operated in series. Each anode consisted of two rectangular strips of 1/16 in. thick rolled copper (10 X 20 cm.²) placed against opposite walls of a cell. Each cathode, consisting of a piece of copper foil (.004 in. thick), 5 X 7.5 cm.², was submerged in 900 ml. of electrolyte and was suspended from a horizontal glass rod by a fine flexible copper wire.

Before each experiment, the anodes and cathodes were given a preliminary cleaning and etching with 40 per cent nitric acid, and then washed thoroughly with distilled water. The cathodes were rinsed further with hot water, and, finally, acetone. They were dried quickly by wafting gently in air. The clean cathodes were allowed to remain in a desiccator for two hours before they were weighed.

The electrodeposition was interrupted after about 4.5 g. of copper was deposited on each cathode, at a current density of 2 amp. per dm.². The cathodes were then raised from the cells and rinsed with hot water. After dipping in acetone, they were dried in a desiccator and weighed.

Four series of experiments were made where the effects on excess weight of adding the following were determined:

1. 25, 75, 150 and 300 mg. per litre of antimony in the absence of gelatin.
2. 25, 75, 150 and 288 mg. per litre of antimony in the presence of 25 mg. per litre of gelatin.
3. 0.25, 0.50, 1.00 and 2.00 g. per litre of arsenic in the absence of gelatin.
4. 0.25, 0.50, 1.00 and 1.92 g. per litre of arsenic in the presence of 25 mg. per litre of gelatin.

In series 2 and 4, the electrolyte in the coulometer contained 25 mg. per litre of gelatin.

Excess weights were calculated by taking the difference between the gain in weight of the cathodes from electrolytes containing arsenic or antimony and the gain in weight of the cathode in the coulometer, in which the electrolyte contained neither metal. The excess weights were expressed as percentage of cathode deposit. The results of the experiments are recorded in Tables XVII, XVIII, XIX and XX, and plotted in Figures 16 and 17.

An approximately linear excess weight-antimony concentration relation existed for electrolytes containing 0 and 25 mg. per litre of gelatin. Moreover, the presence of gelatin increased appreciably the excess weights attributed to antimony. The indication is that antimony is co-deposited with copper to a considerable extent. On the other hand, only very limited amounts of arsenic appeared to be adsorbed or co-deposited. The excess weights due to the presence of arsenic, alone or with gelatin, are very low.

TABLE XVII

Effect of Antimony on Excess Weight of
Copper Deposits

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$

$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$

Current Density = 2 amp./dm.²

(No gelatin present)

Sb conc. (mg./l.)	Expt.1 % excess weight	Expt.2 % excess weight	Expt.3 % excess weight	Aver. % excess weight
25	-.02	.00	.01	.00
75	.01	.03	.01	.02
150	.05	.04	.06	.05
300	.12	.13	.15	.13

TABLE XVIII

Effect of Antimony on Excess Weight
of Copper Deposits

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$

$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

Sb conc. (mg./l.)	Expt.1 % excess weight	Expt.2 % excess weight	Expt.3 % excess weight	Average % excess weight
25	.05	.02	.03	.03
75	.07	.10	.10	.09
150	.12	.14	.13	.13
288	.23	.24	.25	.24

Figure 16

Effect of Antimony on Excess Weight of Copper Deposits

Figure 16

TABLE XIX

Effect of Arsenic on Excess Weight
of Copper Deposits

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$

$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$

Current Density = 2 amp./dm.²

(No gelatin present)

As conc. (g./l.)	Expt.1 % excess weight	Expt.2 % excess weight	Average % excess weight
.25	.02	.01	.02
.50	-.01	.01	.00
1.00	.02	.00	.01
2.00	.01	-.03	-.01

TABLE XX

Effect of Arsenic on Excess Weight
of Copper Deposits

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 125 \text{ g./l.}$

$\text{H}_2\text{SO}_4 = 100 \text{ g./l.}$

Gelatin = 25 mg./l.

Current Density = 2 amp./dm.²

As conc. (g./l.)	Expt.1 % excess weight	Expt.2 % excess weight	Average % excess weight
.25	-.03	-.04	-.04
.50	.02	.04	.03
1.00	-.03	-.01	-.02
1.92	-.02	-.03	-.03

Figure 17

Effect of Arsenic on Excess Weight of Copper Deposits

Figure 17

DISCUSSION

The present study is an outgrowth of previous investigations which have been undertaken in this laboratory in an attempt to explain the effect of addition agents on the electrodeposition of copper. Although the results of these earlier studies have been outlined earlier, it seems desirable to summarize them again very briefly, to indicate the sequence of development that has occurred, and orient discussion of the results previously presented.

About twelve years ago, Gauvin and Winkler (43,44,47) investigated the behaviour of gelatin when gelatin alone was added to the electrolyte. After establishing the concept of the steady state cathode polarization, they found that these steady state values were markedly increased by the addition of very small quantities of gelatin to the electrolyte and that smooth fine-grained deposits were obtained. It was also observed that a change from a coarsely grained surface to a finely crystalline deposit, obtained by the addition of gelatin to the electrolyte, was accompanied by an increase in polarization, while exactly the opposite effect was

obtained for a similar change in the cathode surface in the absence of gelatin.

These studies on the effect of gelatin on the electro-deposition of copper were followed by investigations into the combined effect of chloride ions and gelatin in the electrolyte. Although the addition of chloride to acidified copper sulphate electrolytes in refineries has been well established, little information was available in the literature on the effect of chloride ion in the presence of the addition agent. The only results that had been reported were those of Yao to which reference has been made previously. It was hoped that the investigations would not only yield data of a practical value but also help in gaining a clearer understanding of the role played by gelatin.

Working with electrolytes containing gelatin and 10 mg. per litre or more of chloride ion (added as sodium chloride), Gauvin and Winkler (65) found that the addition of the halide, up to concentrations as high as 100 mg. per litre, did not affect the reflectivity and hardness of the fine-grained deposits or the cathode polarization. However, since the concentration of chloride used in conjunction

with gelatin is often less than 10 mg. per litre, these investigations were recently extended by Mandelcorn, McConnel, Gauvin and Winkler (66) to include the lower chloride concentrations. They found that successive increases of chloride ion concentration, in the presence of 25 mg. per litre of gelatin and at a current density of 2 amp. per dm.², first decreased the polarization and then increased it, thereby yielding a polarization-chloride concentration curve with a minimum. The minimum corresponded to a chloride ion concentration of about 2 mg. per litre. The polarization-chloride curve was altered by changes in current density, gelatin concentration, and temperature, as previously indicated. Thus, the minimum in the curve shifted to higher chloride concentrations and higher polarizations with increased gelatin concentration (from 25 to 100 mg. per litre) or increased current density (from 1 to 3 amp. per dm.²). With a temperature change from 25° to 40°C., the minimum shifted to a lower chloride ion concentration and a lower polarization.

Mandelcorn et al. also observed that the structure of the deposits, obtained in the presence of gelatin and chloride, depended upon the chloride concentration. With the addition of chloride to the electrolyte, the deposits became increasingly bright until the chloride concentration

corresponding to the minimum polarization was reached. With increase of chloride concentration, the deposits became progressively more striated, and had passive areas where apparently no deposition occurred. At higher chloride concentrations, where the polarization was greater than that observed in the absence of chloride, the deposits again became uniform but dull in appearance.

A logical extension of the earlier studies in this laboratory was to investigate the effects of gelatin alone, and in the presence of chloride, when the electrolyte more closely simulated the composition found in practical operations. In particular, it was of interest to determine whether these effects would be significantly different during electrodeposition from acidified copper sulphate electrolytes containing arsenic, antimony and bismuth. It seemed not improbable, to say the least, that the presence of these metals might alter the position of, or perhaps eliminate completely, chloride ion concentration relations observed at low chloride ion concentrations in the presence of gelatin. Although it seemed inevitable that the study of such complex systems might present difficulties in interpretation of the observations, it was felt that these

difficulties should not discourage their examination. Not only are such studies of possible practical significance, but the information so gained must be integrated into any comprehensive understanding of the effect of addition agents in electrodeposition.

The results of the present study make it abundantly clear that, for comparable conditions of electrolysis, the presence of arsenic, antimony or a mixture of the two, leaves unaltered to a remarkable degree the minimum observed with chloride in the presence of gelatin. An analogous though not identical effect is observed when bismuth is present. The most astonishing aspect of the results, however, is not the qualitative similarity of behaviour in the presence and absence of the metals, but the general quantitative agreement. For example, with chloride and gelatin (25 mg. per litre), but no foreign metal present, the polarization value decreased from 240 mv. to about 160 mv., when the chloride concentration was increased to 2 mg. per litre. In the presence of even quite high concentrations of arsenic, antimony or mixtures of the two, essentially the same minimum polarization values, at the same low chloride ion concentration was

observed.

The quantitative agreement between the behaviour observed by Mandelcorn et al., in the absence of the Group V metal ions, and the results obtained in their presence is further emphasized when shifts in the polarization with changes of operating conditions are considered. In summary, it may be stated that, whether these metal ions be present or not, the minima in the polarization curves shift towards higher chloride concentration, and higher polarization values, with increase of current density or gelatin concentration, and with decrease of temperature. To give an example of the remarkable similarity of the shifts, the minimum corresponding to a polarization of 150 - 165 mv. and 2 mg. per litre of chloride ion was shifted to a position corresponding to a polarization of about 130 mv. and 1 mg. per litre of chloride ion when the current density was changed from 2 to 1 amp. per dm.², whether the electrolyte contained antimony or not.

The quite similar structural changes in the deposit, as the chloride ion concentration is increased in the presence of gelatin, with or without added metal ions, is just further demonstration, if one were needed, of the relative ineffectiveness of the metal ions to alter the

pattern of behaviour dictated by the presence of gelatin and chloride in the electrolyte.

In view of the qualitative and quantitative similarities, indicated above, the conclusion seems inevitable that the mechanism by which gelatin and chloride together exert their effect as addition agents remains fundamentally the same when the metal ions are present. This in turn, appears to imply relatively secondary and independent action of the metal ions in those circumstances where they do introduce modifications into the polarization pattern given by the gelatin-chloride combination alone. Paranthetically, it seems appropriate to remark that the present results point up sharply the fascination and importance of determining the mechanism by which chloride ion, in such low concentrations, can so profoundly, and in a seemingly unique manner, influence the effect of gelatin.

If, as indicated above, the mechanism by which gelatin and chloride alone influence the polarization is essentially the same as that which operates when the metal ions provide an added complication, an explanation of the results when all are present reverts essentially to consideration of a system containing no metal ions. An interpretation of the polarization behaviour in such systems has been given by Mandelcorn et al. This has been outlined in the introduction to the

thesis and need be recapitulated here only in its most significant features.

In agreement with Erdey-Gruz and Volmer (22), Fischer (51,52) and others (50,53,54), Gauvin and Winkler (47) concluded from their studies that adsorption of gelatin resulted in a decrease of active electrode area, hence an increase of true (as opposed to apparent) current density, and concomitantly an increase of polarization. This view was extended by Mandelcorn et al. to account for the effect of chloride on the polarization, in the presence of gelatin, by assuming that two independent processes are simultaneously operative when both gelatin and chloride are present. One of these processes was adsorption of gelatin on the active centres of the surface, the other was attack by chloride ion on the less active portions not covered with gelatin. Such attack was visualized to cause lattice imperfections, corresponding to an increase in true surface area, hence a decrease in true current density, and a decrease in polarization. This decrease in polarization was limited, however, to low chloride concentrations. At higher chloride concentrations, the formation and adsorption of cuprous chloride was assumed to become a predominant factor. An addition agent effect due to cuprous chloride was postulated to cause the observed

minimum. The type of mechanism so envisaged permitted a reasonable interpretation of the observed shifts of the minimum polarization with change of current density, gelatin concentration and temperature.

The assumptions set forth in the above explanation would seem to receive some support from work recently done in this laboratory by Parsons (83). With an oscillograph, he made a study of the changes in polarization, in the presence and absence of addition agents, immediately after closing the electrodeposition circuit. In the presence, but not in the absence of gelatin, he observed a maximum in the polarization curve, after times of the order of a few seconds up to a minute. This maximum increased to higher polarization values with increased length of time the electrode was allowed to remain in the electrolyte prior to closing the circuit (for convenience, designated the immersion time). After sufficiently long immersion time, generally of the order of 60 to 75 minutes, the observed maximum attained a steady value. Attainment of this steady value of the maximum must be ascribed to processes that go on during immersion and before current flow is begun. Presumably these processes are corrosion and adsorption. In the presence of both gelatin and chloride the immersion time to attain a steady value of the maximum is drastically shortened, and the maximum value for given immersion time is

increased some 30 mv. On the other hand, the maximum value is essentially independent of chloride concentration, while the steady state polarization, measured in the present study, passed through the minimum value noted previously at 2 mg. per litre chloride ion concentration.

These observations of Parsons are readily explained by assuming attack of the chloride ion during immersion, to form cuprous chloride on portions of the electrode surface. This would act as an addition agent to increase the polarization immediately after current flow was begun, i.e., to increase the maximum in the polarization-time curve. However, as soon as convection currents were set up in the system, this accumulated cuprous chloride might be swept away, to leave active centres and cause the polarization after longer periods of time (the steady state value) to pass through the observed minimum with chloride ion concentration.

While the explanation suggested for the polarization behaviour in the absence of added metal ions can be carried forward to explain the similar type of behaviour when arsenic, antimony and bismuth are present in addition to gelatin and chloride, it cannot be denied that these metal ions are capable of exerting influences of their own. This is amply testified by examination of the data when these added metals are present alone, or with gelatin, or with chloride. An

explanation of their behaviour in detail is perhaps beyond our present comprehension of the effects of addition agents. However, some indications of their possible mode of action would seem to be possible.

It is well known that the Group V elements, arsenic, antimony and bismuth, present a transition from non-metallic to metallic character, since in arsenic non-metallic properties, and in bismuth, metallic properties predominate. Salts of all three elements are susceptible to hydrolysis. Bismuth, however, shows a marked difference from the other two elements in the much more pronounced basic character of its oxides. For example, bismuthous oxide is much more basic than antimonious oxide, and indeed possesses no perceptibly acid properties. Thus, due to the predominantly non-metallic character of arsenic, oxysalts first appear with antimony, and extensively with bismuth. Trivalent arsenic cation is almost non-existent, antimony is sufficiently metallic to form trivalent antimony ion, while trivalent bismuth ion is the most stable (82). Therefore, it may be assumed that in deposition from electrolytes containing arsenic, and to a lesser extent antimony, there is probably a greater tendency for adsorption of oxides of the two elements than codeposition of their ions. With bismuth, and to some extent antimony, codeposition of the metal may well occur. Local cell action would be expected

to occur at centres of codeposition, and oxides, especially of antimony, may be formed to some extent by such local cell action.

As with gelatin, the adsorption or formation of oxides of arsenic and antimony at active centres would result in a decrease of active area. On the other hand, corrosion due to local cell action would tend to increase the active area. The corresponding increase or decrease, respectively, of true current density would then account for the increase in polarization occasioned by the presence of arsenic and antimony (Figures 3 and 4) and the decrease in polarization due to the presence of bismuth (Figure 5), when only these metal ions are added to the electrolyte.

In the presence of gelatin, which may be assumed to cover existing active centres very effectively, bismuth and antimony in particular would be expected to increase the active area by corrosion at the relatively inactive portions of the surface. The decrease in polarization brought about by these substances in the presence of gelatin may be accounted for in this way (Figures 4 and 5). The subsequent increase in polarization at higher antimony concentrations may be ascribed to increased formation and adsorption of its oxides or oxysalts. The small effect of arsenic on polarization in the presence of gelatin is, from these views, a reflection of the non-metallic character of this element (Figure 3).

With electrolytes containing chloride and the metals, an increase in active area by corrosion, as a result of chloride ion attack and local cell action, may be predominant over the decrease in active area from adsorption of oxides of the metals (Figures 6 and 7). Since the small increase in polarization due to the presence of arsenic alone in the electrolyte suggested virtually ineffective adsorption of oxides (Figure 3), it may be assumed that corrosion by chloride ion attack caused a large increase in active area accompanied by a marked decrease in polarization.

It will be recalled that there is a linear increase of excess weight with antimony concentration in the electrolyte, in the presence and absence of gelatin, while very low excess weights were obtained for deposits from electrolytes containing arsenic and gelatin or arsenic alone (Figures 16 and 17). These excess weight measurements support the view that antimony is codeposited to a large extent, but that arsenic, owing to its non-metallic character, is not similarly deposited. Adsorption may result in a small inclusion of arsenic.

An attempt was made to estimate the antimony and arsenic contents of the deposits. Owing to the limited amount of material available from the small electrodes used,

such estimation has proven difficult. However, it has been established qualitatively that appreciable amounts of antimony are contained in deposits from electrolytes containing the metal. Similar information for the deposits from electrolytes containing arsenic is not yet sufficiently definitive to draw any conclusions concerning the contamination of these deposits by arsenic.

The foregoing remarks are intended primarily to indicate a line of thought and possible investigation, rather than a pretense of detailed explanation. The important point would seem to be that at least a considerable proportion of the behaviour, even in the relatively complex systems studied, lends itself to apparently reasonable interpretation on the basis of competing processes. It is freely admitted that the nature of these competing processes must, to a large extent, be a matter of conjecture at the present time. However, more extensive investigations of similar type, with different addition agents, and a more extensive application of oscillographic examination of the polarization changes with various conditions and addition agents should do much to test the validity of, and indicate the modifications necessary to, the views that have been suggested.

While the results of the present study have been of great interest in relation to the results of earlier studies, it would seem that at least one more complication must be introduced. In all the investigations made so far in this laboratory, no agitation of the electrolyte has been used. This has not been from ignorance of its importance. Rather, preliminary experiments by several workers in the laboratory have indicated serious difficulty in obtaining reproducible data when agitation is introduced, and that considerable work will be necessary to solve this problem. Moreover, it was desirable, even essential, to have data with unstirred systems as a reference for the behaviour of agitated systems. It is planned to study, in the immediate future, the polarization behaviour with different electrolyte compositions in the presence of agitation.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE.

1. In the absence of gelatin, increasing the concentration of arsenic (0 to 2 g. per litre) or antimony (0 to about 400 mg. per litre) in the electrolyte brought about an increase in cathode polarization, while increasing bismuth concentration (0 to 1.5 g. per litre) resulted in a decrease in polarization.

2. In the presence of 25 mg. per litre of gelatin, increasing the concentration of arsenic (0 to about 2 g. per litre) in the electrolyte had little effect on the polarization. However, at the higher arsenic concentrations there was a slight decrease in polarization. Antimony (0 to 385 mg. per litre), with gelatin, first decreased the polarization and then increased it, yielding a polarization-antimony concentration curve with a minimum. Increasing the concentration of bismuth, in the presence of gelatin, markedly decreased the polarization.

3. In the absence of gelatin, increasing the concentration of chloride in electrolytes containing antimony, arsenic or bismuth decreased the polarization. In the presence of arsenic or bismuth coarse, crystalline deposits were obtained. Electrolytes containing antimony-arsenic and

bismuth-arsenic mixtures yielded similar results.

4. In the presence of antimony and gelatin, the effect of chloride ion (0 to 10 mg. per litre) on polarization at different current densities, temperatures, and gelatin concentrations was quite analogous to that observed by Mandelcorn et al. (66) with electrolytes containing no antimony. Also, similar results were obtained with electrolytes containing arsenic and arsenic-antimony mixtures.

5. In the presence of 1.0 g. per litre of bismuth and 25 mg. per litre of gelatin, the effect of chloride ion (0 to 9 mg. per litre) on polarization was analogous to that observed in the absence of the foreign metal. However, at low chloride concentrations (0 to about 2 mg. per litre) the polarization was less pronounced in the presence of bismuth.

6. Excess weight was found to be related linearly to antimony concentration, in the presence and absence of gelatin.

7. Very low excess weights were obtained for depositions from electrolytes containing arsenic and gelatin, and arsenic alone.

8. The various observations have been explained on the basis of formation of crystal imperfections on the cathode by corrosion as a result of local cell action (due to presence of arsenic, antimony or bismuth) or chloride ion attack, in conjunction with addition agent effects of gelatin, cuprous chloride and oxides of arsenic, antimony and bismuth.

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