THE EFFECT OF GELATIN ON CATHODE POLARIZATION DURING THE ELECTRODEPOSITION OF COPPER

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A

THESIS

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HISTORICAL REVIEW

INTRODUCTION

The purpose of this historical review is essentially to record the results of experimental investigations into the effect of addition agents on the electrodeposition of metals, particularly the effect of gelatine on the deposition of copper from acid copper sulphate solutions, since it is with this type of system that the majority of the recorded work has been concerned. The survey covers a period of approximately 40 years, during which time a large body of data has been accumulated and numerous theories advanced, both involving many contradictions.

It is no easy task to present a clear, comprehensive and well-organized discussion of the problem, since even the simplest case of electrodeposition, as, for example, a metal from an aqueous solution of one of its simple salts, involves many variables, the relations between which have not proven amenable to any general mathematical formulation. As a rule, each investigation has been restricted to the study of one or two variables over a comparatively narrow range of experimental conditions, followed either by an explanation of the results on the basis of available theories or, very frequently, by formulation of a new hypothesis. As a result, many of the published papers are restricted in scope and frequently conflicting. The task of welding the whole into one framework, to correlate the many data available, is comparable to the task of fitting together a jig-saw puzzle from which pieces are missing and in which apparently erroneous pieces have been included. It is hoped, nevertheless, that the present report might serve to trace in barest outline some of the stronger figures in the pattern, and thus perhaps to indicate some of its many aspects still to be constructed.

Before attempting any discussion of the effects of addition agents on the process of electrodeposition, it is obviously necessary to establish a basis of reference, which, equally obviously, is the nature of the process in the absence of addition agents. The survey, therefore, begins with a brief outline of relevant information on electrodeposition in simple systems, after which the added complexity arising from the presence of an addition agent is considered.

I. - ELECTRODEPOSITION WITHOUT ADDITION AGENTS

GENERAL PRINCIPLES

In its simplest conception, the process of electrodeposition involves the transport of an electrically charged body through a medium to an electrode where the charge is removed, with the subsequent deposition of the uncharged body on the electrode. This very general statement is applicable not only to deposition resulting from transport of ions, but also to deposition as a result of electrophoretic movement of colloid particles. Both of these enter into consideration of electrodeposition from a medium to which addition agent has been added.

Confining attention for the present to systems involving no addition agents, and also to system comprised of an aqueous solution containing anions and cations, there is little need to dwell upon the matter of ionic transport through the body of the solution, since this aspect has been brought to a reasonably satisfactory stage of development, particularly in relatively dilute solutions. The complications arising from this phase of the problem, as far as commercial electrodeposition is concerned, are, in general, the complications arising from the use of concentratrated solutions to which the theories of solution are not accurately applicable. Incomplete dissociation (1) hydration of the ions concerned, complex ion formation and other factors, conspire to make the Debye-Hückel Theory (2) quantitatively inapplicable. Qualitatively, however, the theory, by its postulate of an "ionic atmosphere", indicates that under the influence of an e.m.f. the motion of an ion in one direction will be retarded by motion in the opposite direction of the oppositely charged ions constituting its "atmosphere".

Tentative calculations and experimental observations show that dissociation may be far from complete in concentrated solutions (1). In general, uni-univalent salts (NaCl) tend to complete dissociation, bi-bivalent salts ($CuSO_4$) are weakly dissociated, while uni-bivalent salts ($CuCl_2$) occupy an intermediate position. A marked coordinating tendency of the anion depresses the dissociation, while solvation, by reducing the effect of the positive charge on the cation, tends to increase dissociation. The solvent molecules may exert an attractive force on an ion (3), the nature of this force being specific for a given ion and a given solvent. This may make the dissociation no longer simple, since the metal ion may appear alone, or be confined almost entirely to a complex cation, depending upon the relative affinities of cation and anion for the solvent.

While degree of dissociation, nature of the ions, hydration of ions, ionic transport, and other factors determined by the nature of the body of the electrolyte, may, under certain conditions, play a major role in the process of electrodeposition, their influence may, in general, be minimized by suitable choice of experimental conditions, or, alternatively, be experimentally assessed. The processes taking place in the immediate vicinity of the electrode, and finally on it, following transport of the ions, constitute a problem of much greater experimental and theoretical difficulty, and it is to this aspect of electrodeposition that attention has been increasingly directed in more recent years.

The problem to be solved may be stated in general terms: By what mechanism does the metal ion in solution change into the metal atom, and how does the metal atom so formed assume its place in the lattice structure of the electrode ?

Attempts have been made to simplify the problem by drawing an analogy with the process of crystallization from solution (4,5,6). Hughes (5), for example, assumed that the "metal atom concentration" at the surface of the cathode governed the deposition rate and crystal size. A similar viewpoint, modified to take cognizance of the influence of current density and polarization, has been postulated by other workers (7) . A direct analogy with crystallization seems to be untenable, however, particularly since crystallization from the molten state, which is generally considered more nearly analogous to electrodeposition than crystallization from solutions, is still quite different from electrodeposition (8).

In general, two main views of the mechanism of ion discharge and integration of the resulting atom into the electrode lattice have been postulated:

(1) An instantaneous process of ion discharge and crystallization;

(2) An intermediate state of the ion precedes crystallization.

The first suggestion has received its main support from the work of Blum & Rawdon (9), but has also been favoured by others (10). The basis of the argument is contained in the following statement from the paper of Blum and Rawdon (9):

> "The forces which cause the atomic orientation or crystalline structure must be attractive, and must, therefore, counteract the tendency of the metal to pass into solution as metal ions. In consequence, the solution pressure of a metal crystal must be less than that of a single metal atom".

On the basis of this statement, and since, according to the Nernst theory of electrode potential, the potential is a function of the solution pressure in a medium of constant osmotic pressure, the single potential of a metal would vary with the state of subdivision of the metal, being most negative for the finest state. Only unoriented atoms, or a mass of such unoriented atoms, may be expected to show a normal constant single potential.

According to their views, the single potential and solution pressure of a metal may, therefore, be regarded as the resultant of the "primary single potential" defined in terms of the solution pressure of a single unoriented atom (normal single potential), and the "oriented potential" which is a measure of the diminution in solution pressure, with corresponding algebraic increase in single potential, resulting from arrangement or orientation of adjacent metal atoms. The discharge potential, being a function of the solution pressure and the effective metal ion concentration in the solution adjacent to the electrode (osmotic pressure) must be higher to discharge an ion in a position unrelated to that of a previously discharged atom (i.e., to form a nucleus of high solution pressure), than to continue growth of an existing crystal. Similarly, the potential must be higher to discharge an ion upon a small crystal than upon a large one. Conversely, all factors tending to increase the potential difference between cathode and solution will favour nuclear formation. In other words, all changes in factors affecting electrodeposition leading to an increase in cathode polarization should give a finer-grained deposit. Now, it is reasonable to assume that an ion will be discharged at the point where the lowest discharge potential is required, which, according to Blum and Rawdon's theory, should be at a position corresponding to orientation in the crystal lattice already present. Hence, discharge of the ion and crystallization of the atom may be regarded as essentially one and the same process, according to Blum & Rawdon's views.

A considerable body of experimental evidence (11, 12, 13,14) seems to support Blum & Rawdon's theory, in particular, the fact that solid copper deposits were found invariably to show large deviations from their normal potential value, while spongy deposits showed very small deviations (15).

We must note that this evidence (11, 12, 13, 14, 15) has since then been criticized (8).

Although the soundness of the theoretical basis of the Blum-Rawdon Theory has often been questioned, it is undeniable that it proved very helpful in enabling the operator to predict correctly, in a qualitative way at least, the effect on crystal size of alteration of the variables governing electrodeposition. Blum & Rawdon showed, for example, that decrease of crystal size should accompany addition of a colloid, increased current density, or increased viscosity of the solution, while increase of crystal size should occur when the temperature is increased, the solution is agitated or the metal salt or metal ion concentration is increased. The authors further demonstrated that the apparently contradictory increase in crystal size at high current densities observed by a number of investigators (17,18,19) was due to formation of "trees" consisting of agglomerations of extremely fine, unoriented crystals, rather than groups of a few large crystals, as was previously thought. X-ray examination subsequently showed that typical powder photographs were obtained from such systems, demonstrating the correctness of Blum and Rawdon's contention.

Opposed to the above hypothesis of an unique process for both discharge and entry of the ion in the cathode lattice, the view that the ions assume an intermediate state prior to discharge and deposition has been suggested by Volmer and his co-workers (20,32,43). They assume that deposition takes place by layers of atoms. Until a given layer is complete, a certain percentage of the metal ions are supposed to be in a state intermediate between that in solution and that which they will assume in the lattice. Cathode polarization is attributed to this retarding effect by Volmer. Deposition in layers was observed during the growth of a single silver crystal from a solution of silver nitrate at low current density which confirms Volmer's views (33).

This theory was further developed (21) by assuming that the metal ions on entering the double layer are deprived of their water envelope, after which they seek convenient place in the lattice structure. For metals of the iron group at least, it has been further postulated (22, 23) that discharge occurs in a haphazard manner, and that the atoms so formed remain in a dispersed or adsorbed condition upon the cathode for some finite period, after which they orient themselves, to form the crystalline structure.

In its present stage of development, the theory of electrodeposition processes assumes that part of the cations in the cathode film constitute a double layer of the Helmholtz kind with the negatively charged electrode (24, 25), experimental evidence for which has been obtained (26). Between this double layer and the body of the solution must be present a diffusion layer. Alternative to improbable deposition from the double layer atom by atom, as would be postulated from Blum and Rawdon's Theory, accumulation of metal ions by adsorption, with preference to edges and corners, must be assumed. Electron transition (or the neutralization of an ion by an electron) is then assumed to occur, the necessary conditions for which have been quantum-mechanically stipulated by Gurney (27). When these necessary potential conditions have been fulfilled, the electrons are able to cross from the metal by equipotential lines to effect neutralization of the adsorbed cations (28). The neutral atoms are then incorporated into the already existing cathode surface, and become available for further adsorption of metal ions. There is disagreement concerning the size of the groups of cations deposited, although it seems fairly well established that deposition does not take place atom by atom: Hunt (29), who made a critical review of this question, believes that a continous lattice layer must be held over the face of any particular crystal before neutralization of this layer of cations may take place, while others (30) believe that neutralization may occur even if the layer is not complete.

Since it is now realized that the passage of electricity through a solution and the deposition of the metal on the cathode are both rate processes (31), the following steps can be recognized during the process of metal deposition :-

(1) the transport of the metal cations to the cathode film;

(2) the entry of the metal cations into the cathode double layer;

(3) the discharge of the metal cations by electrons;

(4) the entry of the metal atoms into the cathode metal lattice.

Volmer and his co-workers (20,32,43) consider that in general (4) is the slow step, and is, therefore, the essential cause of polarization. However, special cases have been noted where the polarization was ascribed to slow diffusion of the ions (step I) (70) or to the slowness of discharge of the metal ions (step 3) (95). It has been recently suggested that - at least for the electrolysis of aqueons solutions in which the overall reaction is the conversion of water into hydrogen and oxygen - the total electrode potential is operative across not one, but two double-layers, corresponding to two potential barriers (198,199,200). The outer -layer or "solution double-layer" is that at which the reversible hydrogen potenial operates, whereas the overvoltage is effective over the inner or "electrode double-layer". This concept as yet has been used only in the problem of the discharge of hydrogen ions.

The phenomenon of "periodicity" or deposition in cycles, seems to give more weight to the hypothesis that atoms are not deposited one by one.

This periodicity was first attributed to secondary reactions, at least in the case of the deposition of cadmium cyanide solutions (35). Glasstone, however, (36) showed that this was very unlikely to occur in electrodeposition. It was observed that as the temperature was increased, periodicity decreased, to finally disappear (8). It was also experimentally shown that periodicity increased with an increase in current density (35). It is logical, therefore, to conclude that periodicity is related to the metal ion concentration, the latter being large at high temperature or low current densities. As the region near the cathode gets depleted of metal ions, after deposition of a large layer (or part of a large layer) of atoms, the concentration of ions in the film must be replenished by diffusion before the cycle can be repeated. It is quite possible, as suggested by Hunt (8) that a discharge of hydrogen ions takes place immediately after the deposition of the group of atoms, the hydrogen thus evolved promoting diffusion and hastening the repetition of the cycle. Periodicity is favored by colloidal substances, possibly by isolation of the growing crystals from the supply of metal ions, as shown by the well-known deposits with alternate layers of copper and gelatine obtained by Grube and Reuss (37).

RELATION BETWEEN CRYSTAL SIZE AND CATHODE POLARIZATION

Blum and Rawdon emphasized the effect of cathode polarization upon the size of the crystals. In fact, their theory implies that similar crystal forms may be expected to be produced upon the same base metal with a given cathode potential. Conversely, increased polarization should result in decreased crystal size. The contrary has been noted, however, in certain cases (38,39,40,41) and it has been suggested that the apparent interdependence of cathode polarization and grain size is more of the nature of a parallel result of certain other operative factors. As already mentioned, the fundamental experimental evidence offered by Blum and Rawdon in support of their theory has also been attacked as erroneously interpreted (8). It is now realized that the solution pressure of a metal is a manifestation of both the "thermionic work function" and certain specific forces operating between metal and solvent. The "thermionic work function", also called "electron affinity", gives a measure of the work done in removing an electron from the metal surface in vacuo. There is found to be fairly close agreement between the electron affinity series of the elements and the electromotive series (29). Concerning the specific forces operating between metal and solvents, the evidence is controversial, although the action of specific attractive forces between metal ions and solvent molecules has been proven (42,43,44,45,46). Hunt believes that the potential difference is a surface phenomenon, dependent on the thermionic work function of the metal, the free energy of solvation of its ions, and the concentration of ions in the cathode film, and not on any solution pressure of the metal. The parallelism so often obtained between increase in cathode polarization and the reduction in grain size may be due to the compensating processes operating to supply metal ions to the cathode film: dissociation, migration, diffusion, and convection.

A mathematical expression correlating the two factors: polarization and grain size, has been attempted (47), but it is not established that there is a direct relation between the two. Results of recent experiments (48) seem to indicate a direct relation when using high current densities (from 5 to 40 amps/dm^2) with a rotating cathode (800 R.P.M.). Glasstone, however (49), in a review of this subject, concluded that the relation between the two factors was indirect, remarking that changes in cathode environment may influence the cathode potential. He agrees with Atens and Boerlaage (7) that current density influences the size of the crystals, and with Blum and Rawdon that small crystals should be deposited at a more negative reversible potential than large ones. He also mentions, however, that experimental evidence offered by Volmer (20) showed that zinc deposited from zinc sulfate solutions shows little cathode polarization when the cathode consists of small crystals of zinc, whereas it is appreciable when the surface is made up of large crystals, in contradiction with Blum and Rawdon's Theory. This was attributed by Volmer to a retardation phenomenon: when the surface crystals are small, the new atoms are rapidly accommodated, while when they are large, there may be a considerable delay. Glasstone also notes that changes in concentration, temperature, neutral salts concentration, which all affect the crystal size, may affect the cathode polarization in different ways. He concludes that it is evident that there must be some connection between the character of the deposit and the cathode polarization, but influences may work in opposite directions and the presence of many complicating factors make it rarely possible to determine the exact relationship.

NUCLEUS FORMATION

It is generally admitted that interference causes ions to form new nuclei rather than enter the already-existing lattice. This may be caused by water dipoles brought up by the metal ions, or particles of a colloidal nature, which have migrated electrophoretically to the cathode layer. Interference might be expected to be particularly marked when the current density is increased, the metal ion concentration in solution decreased or the temperature lowered. This was experimentally confirmed when it was shown that these changes invariably caused an increase in the number of nuclei, or, at least, of miscroscopically visible initial crystals (50,102).

CRYSTAL GROWTH

In ordinary crystallization, crystal growth takes place in all directions, ie, in all three planes. In electrodeposition, the growth is largely in a plane normal to the cathode, the relative velocities of growth, normal and parallel to the cathode surface depending largely on electrolysis conditions. Thus it was experimentally shown (51) that an increase in concentration resulted in a decreased rate of growth normal to the cathode surface (KGI) and an increased rate of growth over the surface (KG II), the rate of nucleus formation being decreased (KZ). An increase in current density resulted in an increase in all three factors (KG I), (KG II) and (KZ). The rate of growth parallel to the surface is always much smaller than that normal to the cathode. The rate of growth normal to the surface (or more exactly, that along the lines of current in the electrolyte) depends to a large extent on the base structure and the behaviour of the first lattice layers, as was first realized by Huntington in 1905 (52). The influence of the base metal on the structure of the deposit was the object of many investigations (53,54,55,56,57, 201,202). From examination of deposits made on annealed, cold-rolled and buffed copper sheets, cold-rolled copper rods, etc., it was at first assumed (53) that continuation in the deposit of the structure of the base metal depends not so much on cleaning as on the structure of the base metal proper. Thus cathodes with large crystals caused continuation of this structure in the deposit to a marked degree of penetration before the typical columnar structure of the deposit began (Note: this columnar structure was typical only because of the specific conditions under which the investigator worked). Without well-formed crystals in the base metal, continuation of the surface crystals was of small penetration.

It is now well established, however, that before the crystals of the base metal can be "reproduced" in the deposit, cleaning and etching, or pickling withan acid, are necessary. (54,57). Cleaning appears to give an electrically clean surface, but etching is apparently required to expose the grain structure. (54). To have perfect initial reproduction, a plentiful supply of metal ions must be close to the cathode, but even under these conditions, if the base metal is not favourable for reproduction, a fibrous structure, due to growth in the normal plane, will result. On the other hand, if the metal ions supply is restricted in the film (for instance, at higher current densities), nucleus formation will be pronounced, whatever the structure of the base, and the influence of the latter will be considerably minimized (57,201,202). Thus Wood (57) noticed that for copper the continuation of the base metal structure, after etching, disappeared with current densities between 1.2. and 1.5 Amps / dm^2. At lower current densities, the orientation persisted even in thick deposits, and was not eliminated by the addition of gelatin, although the latter reduced the grain size.

NATURE OF CRYSTAL BOUNDARIES

Here again an attempt was made to establish a parallelism with crystallization from the molten state by assuming that the spaces between adjacent crystals of a metal are filled by an amorphous film or layers. It was assumed that owing to opposing tendencies of crystalline forces, some metal atoms should remain in irregular arrangement characteristic of the liquid state (so-called inter-crystalline "cement"). (58,59). This view may be tenable for cooling from the molten state, but is difficult to reconcile with the slow process of electrodeposition, where the ions have ample time in which to arrange themselves in a position of minimum free energy.

Morever, crystals of cast and rolled metal can be caused to grow by deposition of further metal, and there is no detectable difference between the two parts of a crystal grown in this manner. A modification of the above view assumed that the spaces are occupied by a great number of very small "crystallites" (60).

Where nucleus formation is prominent, there is considerable evidence that the boundaries contain various inclusions which enter the deposit. (61). In 1935, MacNaughton and Hothersall (62) used the fact that annealing at high temperature induces grain growth and re-crystallization to confirm the presence of organic matter in a deposit. Thus copper, deposited from an acid copper sulfate solution, without addition agents, and heated at 900°C for four hours in vacuo, exhibited large crystals after this treatment. But another sample, deposited from a cyanide solution, upon a similar heat treatment, showed very small equiaxial grains and a quantity of non-metallic matter was visible in the grain boundaries.

THE CATHODE FILM

Essentially, the whole process of electrodeposition takes place in the cathode film, the importance of which is, therefore, at once evident. Yet this is the phase of the problem about which the least is known.

It has already been mentioned that an electrical double-layer next to the cathode, followed by a diffusion layer have been assumed present in the cathode film. The first attempt at a direct study of the diffusion layer was made in 1940 by Read and Graham (63) and by Brenner (205), this work being continued by both groups of investigators in 1941 (206, 207). Read and Graham obtained a sample of the cathode film by drawing the catholyte through a 1 mm. hole in the cathode at a very slow rate. There is, however, strong indications from some of their data that they did not draw samples corresponding to true film composition, but rather that some of the body solution was included. Brenner selected the freezing method and, alternatively, the "drainage" method. Their findings can be summarized as follows: the current density is higher near the edges, and increases continuously from the bottom to the top of the cathode (63). The effective thickness of the film is about .01" and is about the same at room temperature for electrolytes of widely different compositions, but is decreased by rotation (207). The metal concentration increases almost linearly with the distance from the cathode (207), while for acidified copper sulfate solutions, the metal concentration in the film decreases linearly with an increase in current density, and the acidity increases with the latter.

The following general conditions may be assumed to exist in the cathode film: travelling toward the cathode are metal ions, other cations (hydrogen ions, alkali metal ions, etc.), complex cations, water dipoles and colloidal bodies. At random in the film are undissociated molecules, and solvent or water molecules. Travelling away from the cathode are anions, complex anions, and water dipoles. To replenish the metal ion supply of the film, which is constantly drawn upon by deposition, four processes are operative: dissociation, migration, diffusion and convection, to which may be added possible agitation. At the critical current density, equilibrium will be established between deposition and these four factors. Below the critical current density, the four processes will supply ions at the same rate as deposition. Thus the velocity of the four compensating processes must increase with the velocity of the deposition. A relation connecting the speed of diffusion, the limiting current density and the concentration of the electrolyte has been derived by Glasstone (64). Increase in temperature will increase the rates of diffusion and convection, and also reduce the thickness of the diffusion layers, so favoring rapid equilibrium and increasing the limiting current density. Agitation produces a similar result. The importance of the concentration of the metal ion in the cathode film is obvious. The size and nature of the anions may also affect the structure of the deposit, the large anions tending to give coarser crystalline structure (208). Under certain conditions the anions may even enter the deposit (71, 72, 208, 209).

The dependence of the crystalline structure of the deposit on the ratio of the metal ion concentration in the cathode film to the concentrations of other constituents in the film has been considered by Hunt (8). According to his theory, if the ratio is high, there is little interference with the crystal growth and a coarsely crystalline structure rests. If it is low, however, owing to small degree of dissociation, complex ion formation, high hydration of metal ions, or presence of a colloidal matter that has migrated cataphoretically into the film, the reverse is true. In short, any change that restricts the supply of metal ions, the concentration of inert particles remaining constant, will give a decrease in crystal size.

These views have the merit of greatly simplifying the problem and of considerably reducing the number of variables to be considered in electrodeposition, while conforming to experimental observations. Possible variables include current density, concentration of metal salt supply, agitation, temperature, conductivity, metal ion concentration, pH of solution, concentration of addition agent (if any), nature of solvent and base metal structure. With the exception of the last one, all other factors may be expressed in terms of one: the metal ion concentration in the cathode film.

In other words, changes of current density, temperature, etc. should now be considered in terms of their effect on the metal ion concentration in the film. Even the structure of the base metal becomes ineffective if the metal ion concentration of the film is sufficiently low (57,201,202). It follows that any change which tends to reduce the metal ion concentration in the film should give finer-grained deposits, according to Hunt's views: this could be achieved by decreasing the temperature, increasing the current density, diminishing the concentration of metal ions in the solution, by using solutions of complexes, like cyanides, etc., increasing the acidity, using no agitation. All these changes will decrease the metal ion concentration in the film, and it is a well-known fact that they give rise to finer-grained deposits.

The influence of the solvent on deposition is readily apparent by considering the metals silver, thallium, cadmium, lead and tin. These metals are prone to yield coarse deposits from aqueous solutions. They all have high atomic numbers, and are very little hydrated, hence their deposition suffers very little interference from water dipoles in the cathode film. In solvents other than water, however, their deposits assume different characteristics. Thus silver from a nitrate solution in pyridine gives fine-grained deposits (65); similarly for lead, tin and zinc from nitrate solutions and chloride solutions in formamide (66), while smooth deposits of cadmium and tin are obtained from their chloride solutions in acetone (67). The use of liquid ammonia as a solvent was extensively studied and fine-grained deposits were obtained therefrom for lead and cadmium (68) and silver (69). The explanation probably lies in the attractive forces between the metal ions and the solvent molecules. It was shown (45) that molecules containing groups of an ammoniacal or nitrile character, such as pyridine, aniline and acetonitrile, have a greater affinity for silver than those containing hydroxylic or ketonic groups. Thus, solvation may be expected to occur to a considerable degree in these solvents, and deposits obtained from them will be of a finely crystalline structure because of interference with the development of the lattice caused by the presence of these solvent dipoles. It may be concluded that with the heavy metals (such as the above) in aqueous solutions, low hydration outweighs feeble dissociation and the consequent low metal ion consequent low metal ion concentration, resulting in a marked tendency towards coarsely crystalline deposits. With metals of lower atomic numbers, such as copper and zinc, which are more highly hydrated, fairly fine structure is obtained, despite the greater degree of dissociation.

It is interesting to note that copper deposited from acid copper solutions in the presence of gelatin gives a deposit in which water has been found, as well as gelatin and sulphate ions. (71, 72).

II. - ELECTRODEPOSITION WITH ADDITION AGENTS

DEFINITION AND NATURE OF ADDITION AGENTS

Addition agents may be broadly defined as materials which are added to electrolytic baths to modify the nature of the deposits, without affecting either the chemical composition, the degree of dissociation, or the conductivity of the solution.

The definite purpose of adding these agents to electrolytic solutions is to obtain a smooth, fine-grained, hard, adherent, bright deposit, of high tensile strength. Growth of needles or projections on the cathode of a commercial tank, which might eventually cause a short-circuit across the two electrodes is thus prevented. An excess of certain addition agents will, however, give a powdery, non-adherent deposit which, for purposes of powder metallurgy, may be advantageous.

The earliest mention of the influence of addition agents on metal deposition is in the production of a "bright" copper deposit, about 100 years ago. In 1886, Von Hubl observed that 0.1% of gelatin added to a copper sulfate bath profoundly modified the appearance of the deposit, and three years later, Foerster noticed the same results with traces of caoutchouc. These observations, however, attracted little attention and the use of addition agents in electrodeposition remained to be developed largely by Industry itself, and to a large extent without systematic study (73).

Two excellent, although not recent, reviews on the subject of addition agents have been written (74, 75), to which the reader may refer for additional information on the early development.

A great number of substances have been found to have a beneficial action on electrodeposition. Their action is often specific, inhibiting in certain cases, and causing characteristic growths in other. As an example of their specificity, glue, goulac (a by-product of the Sulfite Pulp Industry) and gum arabic, have all been reported as beneficial in copper deposition, but are ineffective in bismuth deposition, for which pyrogallol, resorcinol, hydroquinone and benzoic acid are particularly effective. Resorcinol, ineffective for copper, gives excellent deposits of zinc from its sulfate solution. Glue, which is excellent in lead fluosilicate baths, gives poor results in tin fluosilicate solutions.

Certain addition agents give characteristically striated deposits, some horizontally, some vertically. Others give peculiar-looking knob-like projections. Mathers and Overman (76) in an investigation of lead deposition, observed that the deposits with the same peculiar characteristics were always given by the same addition agent.

Common addition agents in the refining of copper are glue (essentially crude gelatin), and goulac (also called binderine, glutrin, encore, lignin-sulfite, sulfite-lignose, or lig inhibitor) (106). Glue and goulac may also be used together. When used alone, the consumption of glue is roughly ½ oz. per ton of refined copper. For copper electroplating, it is preferable to use urea or phenolsulfonic acid, which can be used in larger quantities and is, therefore, easier to control (77, 83). This is a good example of the fact that an addition agent which may prove excellent in the refineries where a high degree of scientific control can be maintained, may prove unsatisfactory in the plating shop, where technical control over many different baths, operating at irregular intervals, is very difficult.

By-products or waste products of various industries are now being extensively studied as potential addition agents. These include, for example, Steffen's waste (by-product of the sugar industry), concentrated "steep-water" (produced in the initial soaking of corn in the manufacture of starch) (78), and "glycerol-foots" (distillation residues in soap manufacturing) (210). Direct addition of sulfite liquor to the bath has been employed (211).

The effect of an addition agent is often governed by its previous history, mode of preparation, degree of purity, etc. Thus, four copper deposits, all of different appearance, were obtained by using four different brands of gelatin, all of the "pure" grade (79). It is known, moreover, that the iso-electric point of commercial gelatin may differ considerably (80), and also that aqueous solutions of gelatin may undergo a reversible change with time (81), both of which factors alter the protective power of the gelatin (82). Certain addition agents seem to be slow in producing their effects. Thus, urea in copper sulfate solutions becomes effective only after several hours of electrolysis, while phenol develops full effect only after a few days (83). This is very likely due, however, to anodic oxidation followed by cathodic reduction.

Of the large number of substances investigated during the past thirty years, few have the required commercial potentialities. For copper deposition, in particular, laboratory experiments have shown that gelatin and serum albumin appear to be the most effective, gum arabic and gum tragacanth have an average effectiveness, while dextrine and glycine are relatively ineffective. In general, the most effective ones are the most easily adsorbed (84, 85). Amines are now being extensively investigated by Brockman and his co-workers with varied success (86, 87, 88). From similar amine solutions, brighter and more adherent deposits of copper have been obtained by the addition of ammonia and ammonium sulfate (89). The better results thus obtained have been accounted for by the fact that copper-amines complexes are formed in these solutions. Without ammonia, brittle, off-color deposits are probably due to co-deposition of insoluble copper complexes along with the copper, whereas addition of ammonia and ammonium sulfate to the copper sulfate bath containing the amine prevents deposition of basic compounds by exerting a solubility effect in the cathode film. Investigation of these amines in zinc deposition led to the interesting generalization that the concentration of nitrogen in the solution for satisfactory zinc deposition is approximately the same for most amines investigated. It appears that it is the actual amount of nitrogen bound in the amine when used as addition agent that determines the appearance and ductility of the deposit. An amount of amine, equivalent to approximately 0.00006 gm/L. of N_2 gives satisfactory deposition (90).

CLASSIFICATION OF ADDITION AGENTS

Hughes (91) employs the following classification:-

A. - Colloidal substances.

B. - Crystalloidal substances.

C. - Inorganic Salts.

A. - Colloidal substances

As early as 1905, Snowdon (92) and Nussbaum (93) classed all addition agents as colloids. On the other hand, Betts (94) claimed that addition agents acted as reducing substances, and believed that oxidizing acids should be excluded from the baths. Mathers and Overman (76), in their extensive qualitative investigation on lead plating baths, also came to the conclusion that the addition agents owed their beneficial influence to their reducing properties. Phloridzin (a bark extract) and clove oil, two agents which gave the best results, were considered by these investigators to be definitely non-colloidal in nature. Moreover, they found no relation whatever between the action of the addition agents and their chemical structure, except for the meager fact that the latter invariably contained -OH groups. The assumption that all addition agents work solely through a reducing action is now regarded as untenable.

The views of Snowdon and Nussbaum, regarding the colloidal nature of the addition agent, have been verified in a great many investigations. Thus, it was shown that certain non-colloidal reducing agents, effective as addition agents, owed their effectiveness to secondary formation of colloidal substances (50, 96). It has also been pointed out (74) that many of the addition agents that are not regarded as colloids contain at least traces of colloids. For example, commercial glucose affects copper deposits, while pure dextrose has no effect, the different behaviours being due to the presence of dextrin in the glucose. Similarly, sulfuric acid and certain sulfates may owe their effects to traces of silica. It is also possible that colloids may be formed from crystalloids in the cathode film, where the pH and other factors undoubtedly differ from the conditions prevailing in the body of the solution. Blum also aptly points out (74) that even if complexes of metal ions and crystalloids (the presence of which has been verified many times) never reach colloidal dimensions, they are probably sufficiently large to form a natural transition from simple ions to true colloids.

B. - Crystalloidal Substances

Fuseya and his co-workers (97,98) conducted particularly interesting experiments with crystalloidal agents of organic nature. They found that certain substances which increase the weight of the deposit to a value slighly larger than the weight deposited in a copper coulometer in series (the "excess" weight), tend to reduce the size of the crystals, while those which do not change the crystal size, do not increase the weight of the deposit. They worked on both unacidified copper sulfate and silver nitrate solutions, investigating a variety of crystalloids. They showed that copper and silver formed complex ions with metaphosphoric acid (the only inorganic substance investigated), tartaric acid, glycocoll (an amino-acid) and various other oxy-and amino-acids, while sugars and higher alcohols, which did not form complex ions, did not affect the deposit in any way. From observations with the Seidentopf-Zsigmondy ultra-miscroscope, Fuseya concluded that no colloid particles were present in the solutions used, even after several months, and that any beneficial action observed was not due to colloidal particles. It should be recalled, however that according to Blum, such colloids may be formed in the cathode film.

Isgarischew (99), in 1921, had already shown the existence of gelatine and copper ion complexes, but while he believed that crystal growth is retarded by slow separation of free metallic ions from the complex, Fuseya from the above evidence concluded that complex formation is the explanation by itself, co-deposition, and not velocity of separation, being the cause of hindrance to crystal growth. Three years later, however, Fuseya found that glycocoll in lead and zinc solutions, although forming complex cations in the solution, did not affect the crystal size nor increase the weight of the deposit (203,204).

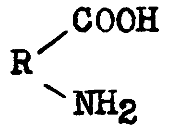
C. - Inorganic Salts

Certain inorganic salts have been noted to have a definitely beneficial action on electrodeposition from certain solutions. Among them may be mentioned sodium thyosulfate in copper deposition from cyanide baths (100), ammonium hydroxide in silver deposition from cyanide baths (101), cyanates in silver deposition from cyanide baths (41). All the above are believed by Taft (103) to act through an electrolytic reduction process. Unlike colloidal and crystalloidal addition agents, the above inorganic addition agents never increase the weight of, and are not found in, the deposits, from which it seems plausible to conclude that they act by a different mechanism. This conclusion is borne out by the fact that they decrease cathode polarization, instead of the usual increase observed with colloidal substances. However, certain inorganic salts may form colloidal particles near the cathode: this has been shown:selenium dioxide in copper baths. The beneficial action of this addition agent lies in the relatively narrow range of 0.05 to 0.15 mg./L., greater concentration leading to powdery deposits (112). Silicic acid is also used as addition agent and is added to certain zinc baths of low pH in the form of sodium silicate, and very likely appears in the bath in the colloidal form (130). Other inorganic colloids that have been studied are prussian blue, silver, ferric hydroxide and arsenic trisulfide in nickel solutions (131).

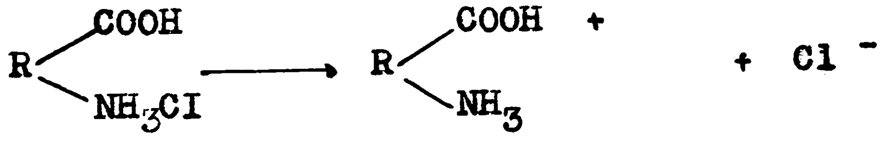
The effectiveness of certain other inorganic salts has been traced to an entirely different action. Thus aluminum salts have a marked beneficial action in zinc deposition from acid zinc sulfate solutions. Colloidal aluminum hydroxide begins to precipitate at pH 3-4, while the pH of the zinc cathode film was shown to be about 6.2 (104). It may be assumed, therefore, that aluminum salts are effective because of a buffer action, by which the cathode film is prevented from becoming less acid as long as aluminum salts are present to be hydrolyzed (105). This would indicate that the brightening action in this case is secured not by the aluminum absorbed, but by preventing hydroxides and basic salts of zinc from precipitating. It is known that many "burnt" deposits contain basic salts or hydroxides, (164), and evidence tends to show that they may be present in even merely dull deposits.

ACTION OF GELATIN ON COPPER DEPOSITION

Of the many systems involving addition agents that have been studied, the effect of gelatin on copper deposition has probably received greatest attention.

Gelatin in water gives a hydrophilic sol, which may be coagulated by relatively large amounts of electrolytes, or by an oppositely-charged hydrophilic sol. The stability of gelatin is a minimum at the iso-electric point (pH = 4.7), but coagulation does not occur until both charge and hydration layer are removed. Each particle consists of a great number of neutral gelatin molecules at the center, each associated with a certain number of water molecules. The surface may be regarded as consisting of a layer of macromolecules of amino-acids of formula:  $R\begin{smallmatrix}COOH\\ NH_2\end{smallmatrix}$.

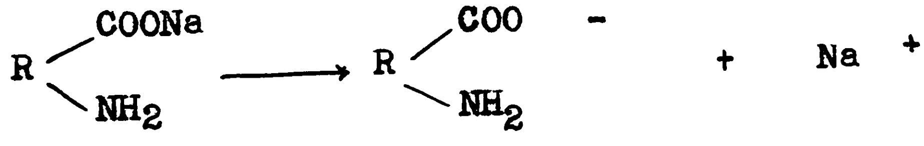
In hydrochloric acid, the dissociation may be represented by:-



$$R\begin{smallmatrix}COOH\\ NH_3Cl\end{smallmatrix} \longrightarrow R\begin{smallmatrix}COOH\\ NH_3\end{smallmatrix}^{+} + Cl^{-}$$

.... (a) .

Similarly, in sodium hydroxide, the dissociation may be represented by :-



$$R\begin{smallmatrix}COONa\\ NH_2\end{smallmatrix} \longrightarrow R\begin{smallmatrix}COO\\ NH_2\end{smallmatrix}^{-} + Na^{+}$$

.... (b).

As a protein, therefore, gelatin exhibits amphoteric behaviour. At the isoelectric point, no dissociation occurs.

In acid solution, gelatin behaves like a base, and, when submitted to an EMF, gelatin ions (a) move towards the cathode electrophoretically with a velocity of the same order as that of copper ions. Working in acid copper sulfate solutions, Frolich in 1924 (107) inferred the existence of a layer of gelatin on the cathode by observing the increase in size of the hydrogen bubbles liberated, and the difficulty with which they tore loose from the cathode, from which he concluded that there must be present a layer of high viscosity. At the iso-electric point, no migration occurs, while at greater pH values, gelatin ions (b) migrate and accumulate on the anode. It was shown as early as 1906 that gelatin in alkaline baths had no effect on the cathode deposit (108), but forms foam around the anode (212). On the other hand, the anode potential should be unaffected by the addition of gelatin in an acid bath, whereas the cathode potential is observed to rise. (109,110,111). Similarly, in a acid medium, anions will have a precipitating and cations a stabilizing effect on the gelatin particles.

In general, investigation into the effect of gelatin on copper on copper electrodeposition have consisted essentially of obtaining deposits under conditions such that different variables were controlled and measured, analysing the deposits, and measuring the gain in weight over that of a deposit obtained in a coulometer in series without addition agents ("excess weight"). The majority of the work used concentrations of addition agent greatly in excess of that used commercially. Thus for gelatin in copper sulfate solutions, the commercial concentration is about 2-3 mgs/L (or rather its equivalent in terms of glue), while investigators have generally used from .1 to 2 gms/L, or higher, with a marked preference for a concentration of .5 gm/L.

Marie and Buffat (7) showed that the copper deposits contained not only copper but gelatin, sulfate ions and water. The excess weight consisted of about 66% gelatin and 33% of copper sulfate, which they assumed to be present in its normal hydrated form. A plot of the excess weight S, expressed as percent of the deposited weight, against the concentration C of gelatin in the solution, expressed in gms/L, gave a smooth curve corresponding to the relation $S = K C^{\frac{1}{2}}$. No dependence on current density was observed. They concluded that this pointed to purely electrostatic absorption of the gelatin, in agreement with the results obtained by Audubert and Quintin (113).

Marie and Jacquet (115), the following year, attempted to find the degree of hydration of the copper sulfate included in the deposit, and concluded from a study of desiccation curves that the water appeared to be partly associated with the copper sulfate and partly with the gelatin.

Referring again to the relation $S = K C^{\frac{1}{2}}$ obtained by Marie and Buffat, since S was shown to consist not only of gelatin but also of copper sulfate, it must be assumed that gelatin forms a constant fraction of the excess weight. Working on the two crystalloids glycocoll and leucine in copper sulfate solations, it was found that glycocoll and copper sulfate in one case, and leucine and copper sulfate in the other, were present in fixed ratios in the deposit, these ratios being very close to the ratios of their molecular weights (114).

Marie and Claudel (116) in the same year studied the effect of the solution pH on the excess weight. First, they noticed that even with addition of copper carbonate, in a 12% solution of copper sulfate, the highest pH they could reach was 3.57, which is still far removed from the isoelectric point of gelatin. Additions of acetate, borate, fluoride salts all increased the pH, but gave erratic depositions. Using a fixed concentration of gelatin of 0.2%, and measuring the excess weight of the deposit for various pH values (from 0.88 to 3.57), determined with a quinhydrone electrode, they obtained a smooth curve of excess weight against pH, which passed through a maximum for pH = 3.2, and decreased again for higher pH levels. This is analogous to other properties of gelatin, such as viscosity, swelling, osmotic pressure, etc., which all pass through a maximum at pH 32-3.6, and through a minimum at the isoelectric point. It should be interesting to see if this excess weight would reach a minimum value, or even the value zero, at the isoelectric point, but it does not appear possible to increase the pH beyond about 3.6.

Taft and Messmore (79,117), following the above experimental procedure, have confirmed and extended the results of Marie and co-workers. They obtained a curve similar to that of Marie and Buffat's, but also made the following interesting observations (79) :-

(a) Up to .15% of gelatin, the deposits showed numerous raised points, scattered at random over the cathode surface. As the gelatin concentration was increased, these points or raised areas aligned themselves to form finally vertical striations. For concentration greater than 1.3% the striations were no longer evident.

(b) Miscroscopic examinations of the raised points and striae mentioned in (a) showed a finer-grained structure than the base metal.

(c) Various base metals (gold, platinum, silver and brass), with a given gelatin concentration, gave initial deposits of different appearance, which became of the same general type, however, after the lapse of ~~some~~ time.

(d) The excess weight due to CuO and $Cu(OH)_2$ was shown to be very small compared with that due to gelatin and hydrated copper sulfate.

(e) The relation between excess weight and the percentage gelatin in solution proved to be a function of the current density, contrary to the findings of Marie and Buffat.

(f) A curve showing the relation between cathode polarization and current density was obtained for a copper sulfate solution without sulfuric acid on a copper cathode, and another curve for the same solution to which 0.5% gelatin had been added. Much greater polarization was observed in the presence of gelatin and the corresponding curve showed a point of inflection at a current density of 0.8 amps/dm^2. Replacing the copper cathode by a platinum one gave slightly lower values of cathode polarization.

INFLUENCE OF ADDITION AGENTS ON PROPERTIES OF ELECTRODES AND SOLUTIONS

A. - CATHODE POLARIZATION

Cathode polarization may be defined as the difference between the dynamic potential (with current flowing) and the static potential. It may be readily measured in the very simple cell devised by Haring (118)

Sand, in his review (75), attempts to differentiate between polarization and "transfer resistance", or Gore's concept (119) introduced around 1885, according to which the difference between the electrode potentials with and without the passage of current is assumed to be brought about by an imaginary transfer resistance at the cathode surface. Investigations of transfer resistance carried out from 1910 to 1920 were controversial (120,121), but results of recent extensive investigations show that transfer resistance does not exist, and that additional surface resistance appears only when gases are evolved (122,123,124,125,126,127).

In general, addition agents increase the cathode polarization (74,94, 107,128,134) Von Hubl, during his very early work, had observed that addition of gelatin almost doubled the resistance of his solutions. This increase can, of course, be accounted for by polarization. There is considerable evidence that the addition of colloids such as gelatin to acid copper or zinc sulfate solutions produce little or no effect on the static equilibrium (129,109), but they change the dynamic potential and make it more negative. This change in cathode polarization at first increases with an increase in colloid concentration, and then tends to reach a maximum which is not sharply defined. Thus, in acid copper sulfate solutions, a maximum increase of about 0.1.v. was reported at 1.5 Amp./dm^2., when the gelatin concentration was from 15 to 20 mgs/L. (118,110). For zinc, results are conflicting (132,133). The anode polarization, on the other hand, is in generally very little, if at all, affected by addition agents (109,110, 111,141).

Frolich (107) explained the increase in cathode polarization in presence of gelatin by assuming that the layer of gelatin on the cathode increased resistance to the transport of cations. To substantiate his point, he mentions the excellent micrographs obtained by Grube and Reuss (129), showing distinct alternate layers of gelatin and copper, and published with a corresponding graph of the cathode polarization plotted against time, which exhibits roughly the shape of a sine curve, the time between two peaks being approximately 9 minutes. Frolich suggested that this was approximately the time required for copper deposits to grow out of a given gelatin layer, and for another layer of gelatin to form over the deposited copper.

Clark & Jones (47) have examined the effect of several addition agents on the cathode polarization. They investigated gelatin, dimethylaniline, grape sugar, lactic acid, starch, peptone and camphor, at a fixed concentration of 0.5 gm/L of all of them, except the last one. They found that the polarization was invariably increased by the addition agent, some of the curves being uniform, others exhibiting the peculiar inflection point noted by Taft and Messmore, and still others showing several such inflection points. The addition agents were found to reduce the grain size, or to increase the number of grains $\underline{n}$ / cm^2. If the current density is $\underline{C}$, the cathode polarization is $\underline{P}$, the ratio dP/dC will be the slope of the cathode polarization - current density curve at any point. No simple relation between the grain size $1/n$ and the cathode polarization P was observed, but $n/P(dP/dC)$ was found to be approximately constant, variations in this function being paralleled by variations in the conductivity $\underline{K}$. The relation $n = (f) KP(dP/dC)$ was suggested.

B. - CONDUCTIVITY

Contradictory evidence has been noted regarding the influence of addition agents on the conductivity. Thus Skowronski and Reinoso in 1927 (135) concluded that they caused very little change on the conductivity, even as much as 1 gm/L of glue (400 times the usual commercial concentration) changing the conductivity less than 1 part in a 1000, if at all. Clark and Jones (47), however reported that 0.5 gm/L of gelatin decreased the conductivity from .352 mhos per cu. cm. for the standard solutions of sulfate without gelatine to .3291 mhos/cm.^{3}, while dimethylaniline reduced it to .3045 mhos/cm^3.

C. -HYDROGEN OVERVOLTAGE

Addition agents increase the hydrogen overvoltage (136,142). It was also observed that the hydrogen overvoltage of metals is always increased by colloids, the greater increase being noted with metals normally possessing large values of the hydrogen overvoltage (137).

D. - CATHODE EFFICIENCY

Cathode efficiency may be regarded as a resultant of the respective tendencies for metal deposition and hydrogen evolution. Such tendencies, at least for the separate processes, may be expressed in terms of the cathode polarization curves and hydrogen discharge on that metal surface. Colloids generally increase the cathode polarization, and if this occurs without changing the hydrogen overvoltage, the cathode effiency will be decreased, i.e., the evolution of hydrogen will be made relatively easier. Most colloids, however, increase the hydrogen overvoltages and if this increase is greater than that of the metal polarization, the cathode efficiency will be increased. Thus an increase up to a limiting value, then a decrease has been found in certain cases (138). It was also observed (139) that gelatin in a zinc solution lowers the contact angle of hydrogen bubbles and thus facilitates their detachment from the cathode. The practical cathode efficiency is thereby increased, since there is a tendency for re-solution of zinc wherever hydrogen bubbles cling permanently.

E. - THROWING POWER

The throwing power, or ability to give a uniform deposit over a cathode surface, regardless of its shape, is improved by addition agents. Any increase of cathode polarization at a part of an electrode at which there is a high current density will tend to make electrolytic processes spread to parts with lesser current densities. It was found (100) that the throwing power of an acidified copper solution was very nearly doubled by the addition of 0.2 gm/L. of gelatin. It was also experimentally shown that the throwing power depends upon cathode polarization, conductivity and cathode efficiency (9, 100,140). For good throwing power, both conductivity and polarization should be high. The latter should be a large fraction of the total voltage drop in the bath, but not approach the point at which hydrogen is evolved. The slope of the cathode polarization-current density curve (dP/dC) should also be as large as possible (47). Since addition agents have only a small effect on the conductivity, but greatly increase the polarization, the throwing power is invariably improved when they are used.

F. - PH OF SOLUTION

The influence of PH of the solution on the excess weight has already been mentioned (116). Commercial concentrations of addition agents will have practically no effect on the pH of the body of the solution, but may be important in determining the pH of the cathode film, which it was realized quite early, may differ greatly from the pH of the body of the electrolyte (104,144). There is strong indication that this is true, from the results obtained (63) in the analyses of the cathode film.

INFLUENCE OF ADDITION AGENTS ON PHYSICAL APPEARANCE OF DEPOSITS

The effects of addition agents on the appearance of deposits are varied and often quite remarkable. From lead solutions containing gum arabic, loose conglomerations of very thin lead flakes have been obtained, (145), which when observed under the miscroscope, were seen to be embedded in a gelatinous mass and exhibited Brownian movement. From a copper sulfate solution to which 1/3 of 1% of gelatin was added, Bancroft and Briggs (146) obtained a pale brown copper deposit, which was capable of absorbing colloidal $Cu(OH)_2$ from a solution of cupric acetate, yielding a gelatinous mass of a beautiful blue color, which is now called "blue gelatin copper". Sieverts and Wippelman (128) observed that a very small amount of gelatin in a copper sulfate solution without agitation made the deposit brittle without visibly affecting the crystal structure, while larger additions caused a decrease in the crystal size and resulted in a structure consisting of reticular layers. Grube and Reuss (129) made miscrosections of such deposits and under 400 magnification, found that the bright copper deposits mentioned by Muller and Bahntje (108) consisted of so-called amorphous layers of gelatin and copper, the microscopic view showing straight streaks on the deposit from stationary electrolyte, while these streaks were undulated and displaced when agitation was used. From the above, several investigators (145,179) concluded that successive additions of colloids first produced fine-grained crystals and ultimately amorphous deposits. This word "amorphous" is now discredited: so-called "amorphous" deposits have been shown to consist of very small, unoriented crystals.

The tendency of certain addition agents to give characteristic deposits has already been mentioned. These may assume the form of knob-like projections, vertical bands, horizontal striae, raised areas, etc. It is generally believed that the tendency of certain colloids to give characteristic growths is associated with their selective adsorption on different crystal faces, similar to that so often observed in crystallization from solution.

Generally, large concentrations of addition agents cause first the appearance of numerous raised points, scattered at random on the surface of the deposit. For still greater concentrations, these points align themselves into well-developed striae in a vertical position, or, more exactly, in the direction of the convection currents which are always present when deposition takes place in an electrolyte. These convection currents flow up the cathode face (due to a decrease in density of the catholyte as deposition takes place) and down the anode face (due to an increase in density of the anolyte as the anode dissolves). Evidently, obstacles in the bath (supports, shields, etc) may deflect the convection currents, causing the striation to deviate from the vertical. These striations have been observed and studied for copper (79), silver (50), cadmium (213) and other metals. They finally disappear for still greater concentrations of the addition agent. The first appearance depends on the concentration of the addition agent, the current density, and other variables governing the deposition, all these factors being specific for each addition agent used. Taft and Bingham made a photographic study of the growth of striations in the presence of gum arabic (176) and a detailed discussion of the subject can be found in reference 148.

MECHANISM OF INCLUSION OF ADDITION AGENTS IN DEPOSITS

In explanation of the numerous instances where addition agents have been shown to enter the deposit, the following possibilities can be listed:

A. - Discharge of complex ions;

B. - Co-discharge of colloid particles and metal ions;

C. - Mechanical inclusion of the colloid;

D. - Adsorption of the colloid by the metallic cathode surface.

A. - Discharge of Complex Ions:-

Formation of complex ions with colloids and crystalloids: thus Isgarischew (99) in 1921 demonstrated the existence of gelatin-copper complexes, and the work of Fuseya and his co-workers on crystalloidal substances has shown the existence of crystalloidal complexes (97, 98). They could not, however, show that these complexes were discharged as such at the cathode to become part of the deposit. Further papers by these investigators showed that, although complex ions may be present in a solution, they may not enter the deposit, nor in any way affect its structure (203, 204).

Taft and Messmore (79) consider that the complex discharge theory is untenable as considerably less pure copper should be discharged in the cell containing the gelatin than in the copper coulometer in series (without gelatin) which is contrary to their experimental results. They recognize that complexes may be formed in the solution, but they suggest that the rupture of these complexes probably accounts for the inflection point obtained in their cathode polarization-current density curve, and also for the inflection points reported by Clark and Jones for other addition agents (47). These inflection points may be interpreted to mean that

some other additional processes, such as discharge of cuprous ions, (always present in a copper bath (143), or of complex ions, or of hydrogen ions, etc., might begin to take place. However, the experimental result obtained by Taft and Messmore show rather conclusively that the inflection point was due neither to an electrode nor to a mechanical process. Basing themselves on Cady and Groening's conclusions(150) that formation of complex ions would cause a change in the rate of increase of cathode polarization with current density, and also on the well-known fact that cells known to contain complex ions always exhibit a much greater cathode polarization than cells containing simple ions only, they conclude that for current densities below the inflection point, cupric ions alone play a role. Above this current density, the cupric ions supply is not sufficient to maintain the rate of discharge, and copper complexes must be broken, according to the equation:
$Cu^{++}(Gel.)_n \longrightarrow Cu^{++} - n\ Gel.$, for which a higher potential is required. These views are in conformity with those of Isgarischew's (99).

B.- Co-Discharge of Colloid Particles and Copper Ions:-

Taft and Messmore showed that co-discharge of colloid particles and copper ions was unlikely because the excess weight should increase continuously with increased gelatin content, which was not found to be the case. Such co-discharge should presumably give results similar to those obtained with alloys, as, for example, when copper and zinc are co-deposited from the same solution (151). If the copper content of the solution is maintained constant, an increase in the amount of zinc in solution results in an increased content of zinc in the deposit. Taft and Messmore (79) assumed that cataphoretic discharge could not play a large part in metal deposition, since it should lead to a decrease in the mass of copper deposited as the gelatin content is increased, which is not found experimentally.

C.- Mechanical Inclusion of Addition Agents in Deposits:-

Occlusion of addition agents in interstices of deposits is extremely unlikely, because the excess weight should increase continuously with increased gelatin content, and should become greater with increases in temperature, both of which are contrary to experimental results.

D.- Inclusion of Addition Agents Through Adsorption:

It is now generally accepted that addition agents are included in the deposit essentially as a result of adsorption. In many cases, the current probably assists in depositing the colloid on the cathode, but addition agents are generally adsorbed by solids independently of the current. Thus, in 1903, Schulz and Zsigmondy, while establishing the gold number of lyophylic colloids, ascribed the action of protective colloids to their adsorption on the gold micelles, and showed that a sheet of gold foil immersed in a gelatin solution will no longer amalgamate with mercury, even after the gold foil had been thoroughly washed with hot water (147).

Marc (153), in extensive investigations, showed that the rate of crystal growth in liquids is greatly diminished by colloids adsorbed by crystal faces. He particularly showed that the crystallization of sparingly soluble salts in the presence of a small amount of gelatin is generally restricted, and in some cases precipitation was entirely prevented, the salt remaining in colloidal form. These results have been applied to consideration of the structure of deposits (158, 159). Metals have been shown to adsorb various essential oils to varying extents (160), and in general, the most effective addition agents are those which are most easily adsorbed (85). Deposits obtained from a cathode previously dipped in protein solutions have been found to adhere poorly to the electrode, although deposits obtained on treated or untreated cathodes were physically alike (161). The adherence varied with the concentration of the colloidal solution, but was independent of the length of immersion. The poor adherence was attributed to the tenacious adsorption of the addition agent, even after extensive washings with boiling water. Further investigation (162) proved conclusively that the much greater influence of hydrophilic colloids, such as proteins and peptones, on the adherence of deposited copper is due to the much greater ease with which they are adsorbed, and this was experimentally shown by the fact that the structure of the deposited copper was the same whether it was deposited from a bath containing such colloids, or whether the cathode was alternately immersed in a solution of protein and then in the electrolyte, with thorough washing after each immersion. Adsorption is not restricted to colloidal matters: cadmium deposited from cadmium iodide solutions abnormally heavy due to the free adsorption of the salt by metallic cadmium (163). "Burnt" deposits containing basic oxides also offer another example of free adsorption: these "burnt" deposits occur when too high a current density is used. They were shown to contain about 20% of finely divided crystals of copper and about 80% of cupric oxide (164).

Taft and Messmore suggested that only adsorption could explain all of their results, especially the relation between excess weight S, expressed in percentage of the weight of the deposit, and the gelatin concentration, C, in gms/L, which they found to be of the form: $S = K C^{\frac{1}{2}}$. They also showed that the excess weight decreased with increased temperature, which is entirely in line with the view that adsorption is responsible for the excess weight. Experiments with gum arabic (which is essentially composed of calcium and magnesium arabate) showed that when acidity is low and the current density high, there is a deposition of an oxide which gives abnormal excess weights. From acid solutions, only gum arabic is adsorbed. (165). The use of gum arabic as an addition agent is particularly interesting since, the large arabate anion is negatively charged in acid solutions. The concentration used was rather high. This clearly shows that, although the colloidal particles move toward the anode, they still may enter the cathode deposit through adsorption when the concentration is suitable. Other investigators, using glycocoll as addition agent, also came to the conclusion that adsorption played the major role in the mechanism (166,167). Taft (103) and others (168) believe that, although cataphoretic discharge might take place, the major portion of the addition agent is included in the deposit through free adsorption. It must be noted, however, that the relation between adsorption and effectiveness is not always a simple one, so that adsorption may not be the sole determining factor (160). If it is assumed that adsorption is the main factor however, the decrease in size of the crystals could be explained by the decrease in interfacial tension at the solution-metal boundary, which results according to the equation of Gibbs (170).

CASES WHERE THE ADDITION AGENT IS NOT INCLUDED IN THE DEPOSIT:

Some cases are known where the addition agent is not adsorbed in the deposit. These agents may exert their effect through a reducing action at the cathode. It has been experimentally shown (171,172) that addition of ammonium nitrate in the electroanalysis of copper gives more adherent deposition of the metal, and that nitrates are reduced to ammonium compounds at a copper cathode (173). The extent of the reduction of nitrates depend, among other things, upon the nature of the cathode (174,175), ammonium salts being formed on copper surfaces, while hydroxylamine is the main product on a mercury surface. Since the reduction products of the nitrate ion are water-soluble salts, it may be that the finer-grained deposits obtained in the deposition of copper from solutions containing amonium nitrate (103) results from interference with the deposition. Very much higher current densities can be employed in acid copper baths without hydrogen being evolved, when ammonium or sodium nitrates are present (103) which means that the nitrate ion is preferentially reduced before the hydrogen ion. This might account for the observation regarding the adherence of deposits, since hydrogen evolution tends to reduce the adherence of the deposits.

A similar reducing action may be responsible for the effectiveness of certain inorganic salts as addition agents, among which may be mentioned sodium thyosulfate in copper from cyanide baths (100), ammonium hydroxide (101) and cyanates (41) in silver deposition from cyanide baths. The effectiveness of the brightener, carbon disulfide, commonly used in silver plating might be due to a reducing action also.

In addition to a possible cathode reduction of the addition agent, we might have anodic oxidation of the addition agent, followed by cathodic reduction. Such addition agents might be slow in their effects. It was shown that phenol developed full effect in copper baths only after a few days, and that oxidation products of phenol (hydroquinol and quinone) are, probably, the effective addition agents (83). The full effect of this addition agent was obtained much quicker when phenolsulfonic acid was introduced in the bath instead of phenol, showing that the first stage of the chemical change undergone by phenol was its conversion into phenolsulfonic acid. Urea has also been shown to be effective only after several hours' electrolysis (83). It must be noted that most of these addition agents seem to decrease the cathode polarization, and no good explanation has been offered for this behaviour.

GOLD NUMBER OF COLLOIDS IN RELATION TO THEIR EFFECTIVENESS AS ADDITION AGENTS:

It had been suggested as early as 1906 that there should be a simple relation between the gold number of the colloid, which is a measure of its protective action, and its effectiveness as an addition agent (82,108), but experiments carried out in 1912 (159) showed that this relation is not a simple one, and that a parallelism between the two cannot be claimed to exist. Later experiments, however, (177) indicate that the smaller the silver number (i.e., the greater the protective action) of the addition agent, the smaller were the grain sizes of electrolytic silver.

MECHANISM OF THE ACTION OF ADDITION AGENTS

This probably represents the most controversial and most difficult phase of the problem of addition agents. No clear, definite picture of the mechanism of their action has yet been offered.

One of the first attempts at an explanation was made in 1905 (93) when it was suggested that metal ions were first discharged in colloidal form and that the addition agent would act as a diaphragm, checking circulation and thus hindering the crystal growth. This explanation was further developed by Engelhardt (178) who suggested that colloid particles will deposit in increased number on the raised areas on the deposit, where maximum current prevails, and produce a sort of local diaphragm action. The diaphragm action is assumed to flash over continually to those spots of higher current density, resulting in a so-called "wandering diaphragm action" to hinder the crystal growth.

In 1924, Frolich (107) attempted to explain the action of gelatin on copper deposition by visualizing the latter as taking place in the intermicellar spaces of a porous, highly viscous layer of gelatin on the cathode. As deposition takes place, the deposit fills up the intermicellar spaces previously filled with electrolyte, and finally incorporates the gelatin layer as it builds up. A similar hypothesis was again offered recently (190).

Early experimental evidence was interpreted as indicating that the metal was first deposited in an unstable form (180). Other investigators (108) believed that the metal is first precipitated as colloidal metal in the neighborhood of the cathode, the addition agent acting as a protective colloid to determine the size of the crystals. The complex colloid is then assumed to be pressed to the cathode by electrophoresis. It has recently been experimentally shown (149) that when gold and platinum go into solution anodically, they pass through a colloidal stage. It was impossible to observe the reverse process (at the cathode) for both these and other metals, probably because the velocity of the transition from the ionized to the colloidal metal is smaller than that of the transition of colloidal to crystalline metal. This was taken to indicate that a colloidal transition may be fundamental in cathodic deposition. (It is interesting to note that as early as 1912 the ions were assumed to be discharged, not on the cathode, but at a slight distance from it (179).

Kohlschutter and his co-workers extensively studied the phenomenon of electrostriction (expansion or contraction of the deposits after their formation, thus exerting pressure or strains). For example, the tendency of nickel to contract during deposition is quite pronounced, and from results of studies with nickel deposited on platinum, they concluded (181) that an unstable, very dispersed form was initially deposited, which subsequently underwent spontaneous sintering or orientation. According to this view, the influence of addition agents resolves itself into predicting the form in which a metastable, very fine conglomerate of addition agent and metal will crystallize. Considerable support for such a mechanism is given by the micrographs of Grube and Reuss (129), which clearly show alternate layers of copper and gelatin, roughly horizontal for still solutions, but having an undulating, wavy arrangement for agitated solutions, suggesting the presence of a film prior to final orientation of sufficient mobility to be displaced by stirring.

In a very interesting experiment, Kohlschutter (182) showed that the initial stage of deposition determines the subsequent nature of the deposit. Silver from a double cyanide solution was deposited on a platinum cathode as an easily-removable, reddish to bluish-green film, the color of which closely resembled that of the sub-haloids or photohaloids of silver, obtained by coloring gels of silver chloride, etc., with colloidal silver. The cathode was then removed to a silver nitrate solution and the deposition continued when the further deposit, even after several hours, showed the appearance of one obtained from a double cyanide solution and not from a nitrate solution. The same thing occurred if, before the nitrate of silver treatment, all but the colored film referred to was removed by dipping in a mixture of ferric chloride and nitric acid. The determining role played by this film is obvious. From this evidence, it can be seen that the great dispersion of nuclei produced in the presence of colloids has profound influence on the subsequent structure of the deposit, causing, with small quantities of the addition agent, the fine-grained deposits of Seiverts and Wippelmann, with larger amounts, the apparently amorphous, but in reality microcrystalline alternate layers of Grube and Reuss.

Kohlschutter points out the complete parallelism between silver deposits obtained from solutions containing colloidal metal oxides, from solutions containing highly complex salts, cyanides for example (which have a low dissociation constant), and from solutions containing addition agents, and concludes that in all three cases colloidal substances are the determining factors. In many cases, the effect of colloids not intentionally added must be recognized: these may be present as impurities, or be produced by reduction reactions in the cathode film, and need not be absorbed in the deposit, as shown by the fact that zinc from zinc sulfate solutions in the presence of gelatin does not contain the latter. However, Frolich showed that the gelatin accumulated in the cathode film (104).

More recently, Glazunov and Drescher (183) have assumed that the process of metal separation is essentially a crystallization process in which velocity of crystallization and nuclear numbers are determined by many more factors than in ordinary crystallization from solutions. The addition of gelatin is assumed to cause a reduction in the crystallization velocity. For a definite electrolyte, the optimum amount of addition agent must lie in a relatively narrow range in which the crystallization velocity in the direction of the current is small and the nuclear number and crystallization velocity normal to the current direction are sufficiently large to form a deposit uniform in thickness, pore-free and coherent.

Muller and Bahntje (108) and others (179,181,182) suggested that in the electrodeposition of copper from copper sulfate solutions, in presence of gelatin, colloidal particles are first formed near the cathode in the cathode film (these particles consisting of metal particles surrounded by gelatin particles) which then serve as crystal nuclei for the deposited metal. It was attempted (184) to prove this theory by introducing colloidal copper (0.1 to 0.2 micron in size) into such a solution. Copper was also deposited from a similar solution, minus the colloidal copper. Micrographic analysis of the two deposits showed that the colloidal copper made no difference in the structure of the deposits.

It is generally admitted that in low concentration, the addition agent must migrate to the cathode. Of course, if concentration is fairly high (from .1 to 1gm/L for example), migration away from the cathode may take place, but the concentration around the cathode is still sufficient for beneficial action (165).

As a result of deposition, the metal ion concentration in the cathode film must always be smaller than in the body of the solution. Of the four compensating processes for ion replenishment, colloids may influence both diffusion and convection, the latter being reduced by the increased viscosity of the film, thus reducing the rate at which the ion concentration of the film is replenished.

From the experimental evidence so far obtained, the possible mechanisms of addition agent effects may now be summarized , keeping in mind that an addition agent does not necessarily have to decrease the crystal size of the deposit - although the majority do - but may exert its beneficial action by preventing detrimental oxides and basic salts from entering the deposit. It is quite possible that any addition agent exerts its influence on the deposit not through one, but several of the offered mechanisms:

<u>1)Direct Adsorption:-</u>

(a) <u>of the addition itself</u>: for example, gelatin, gum arabic, etc.

(b) <u>of a second substance, the formation of which is promoted by the presence of the addition agent.</u>

Such is probably the origin of the colloidal silver in a silver bath in presence of filter paper, the addition agent being probably furfural formed from the cellulose in the paper, and which was shown ~~to promote formatio~~n of colloidal silver. Theadsorbed colloidal silver acts as muclei on the cathode which result in a fine deposit (50). Such is probably also the action of chlorine in a copper bath, which results in the formation of cuprous chloride with the cuprous ions always present, this salt of very small solubility being adsorbed by the deposit, and its presence in the latter being easily detected.

2) Addition agents which have a chemical action on the film:

(a) buffers: these substances prevent the pH of the cathode film from increasing to a point where oxides or basic compounds are formed: such is the effect of boric acid in nickel deposition, or aluminum salts in zinc deposition from acid sulfate solutions.

(b) Reducing action : such compounds have been discussed previously. Their action is probably connected with the formation of a soluble compound in the cathode film which may hinder crystal growth, before being redissolved by the solution.

3) Addition agents which cause a change in the physical properties of the film:

(a) Wetting agents: all addition agents which are present in the cathode film decrease the surface tension to a certain extent, but wetting agents do so to a much greater extent. They are especially useful in nickel deposition, because they eliminate pitting by permitting the hydrogen bubbles to evolve, instead of remaining in the deposit (152). They may or may not decrease the crystal size at the same time (169).

(b) Agents which accumulate in the film and increase its viscosity: Beside increasing the viscosity of the cathode film, these agents will decrease the concentration in metal ions of the diffusion layer, and reduce the rate of replenishment by decreasing the rate of convection. The addition agent may or may not be subsequently adsorbed by the deposit. With gelatin in a zinc sulfate bath, for example, presence of a viscous film on the cathode has been shown. Although the gelatin reduces the grain size of the deposited zinc, none of it enters the deposit (104).

4) Formation of complex cations which may discharge at the cathode:

This mechanism is supported by the work of Glazunov and his co-workers (154, 155, 156, 157). Mathers also favours it (209). These complexes, upon being discharged may break down into other complexes, either stable or unstable (155). They may also migrate a certain distance from the point of discharge (156).

This phase of the problem is being extensively studied at the present time by Glazunov and other workers. Although the discharge of a complex cation and its effect on the grain size of a deposit has been observed for a few special cases, it is yet too early to generalize and apply this mechanism to all addition agents.

STUDY OF THE STRUCTURE OF DEPOSITS BY METALLURGICAL & PHYSICAL METHODS:

The smoothness and mechanical properties of deposited copper are affected by many factors, as may be illustrated by the following experiment, carried out by Hothersall in 1931 (56), on deposits obtained from acid copper sulfate solutions. He found that by increasing the current density from 15 to 200 amps/ft.^{2}, there was little change in the Brinell hardness (42 to 52). (Incidentally, the Brinell test is the best for this type of work, at least for a range of 100-400 in Brinell units which covers copper completely, but not chromium; however, a relatively thick deposit is needed to eliminate the effect of the base metal). By increasing both the current density and the acidity, slightly harder deposits were obtained. At 15 Amps/ft.^{2} , from neutral solutions, with the addition of ammonium sulfate (giving the common ion effect, hence, reduction in the concentration of metal ions in the cathode film), the hardness went up to 81. He similarly obtained hard, smooth and very brittle deposits from neutral copper sulfate solutions containing ammonium nitrate,(reducing action at cathode). The Brinell hardness went up from 42 to 83-93 by adding 2 ppm. of gelatin or peptone, and a concentration of 0.01 gms/l of gelatin raised the hardness to 128. Dextrin (up to 10 gms/L) had little effect in fresh copper solutions, but had some effect when "aged". Solutions containing up to 10 gms/L of phenol (added as phenolsulphonic acid) gave smoother deposits. As on continued electrolysis, the effect of the above three addition agents disappears, control over the concentration of these agents must obviously be maintained: gelatin (or glue) is difficult to control in such small concentrations. Phenol, used in larger quantities, can be detected analytically (83), although the presence of oxidation products makes it difficult to obtain analysis better than within 10 to 15%. Gulac, frequently used in copper refining, is also used in small concentrations, and control of its concentration in the solution is similarly difficult. Its effect on the deposit is slightly different from that of glue, making it less malleable and more brittle (109).

In recent years, lattice distortion and internal stresses in copper deposits have been the subject of many investigations. Jacquet, in particular, studied the stresses in copper deposited in presence of gelatin (186) and other colloids (187). During the last few years, these stresses were studied in conjunction with hardness and grain size and unsuccessful attempts were made to derive a relation between the three (188). Studies on nickel deposition show that no direct relation between hardness and stress appears to exist nor does there appear to be a relation between cathode polarization and hardness (189, 62). A definite relation between the crystal size of the deposit and the hardness was observed, however, the hardness increasing appreciably as the crystal size decreased slightly (62). The hardness of the nickel deposits has been attributed to interference with the crystal growth exerted by colloidal basic nickel compounds, which, due to the discharge of hydrogen (which plays an important role in nickel deposition) are precipitated in the film of solution next to the cathode. Thus potassium ions, which stabilize the colloids tend to harden the deposit, while chlorine ions, which exert a flocculating action, tend to soften it. Heat treatment induced grain growth and re-crystallization, and showed that non-metallic substances accumulated in the crystal boundaries after heat treatments (62)

METALS AS ADDITION AGENTS

Closely related to the effect of addition agents may be mentioned the addition of metals in very small concentrations to electrolytes, which may or may not already contain addition agents, with a view of obtaining still brighter deposits, as, for example, addition of zinc to nickel solutions (191, 192,193,194). Lead acetate and glycerin used together are a commercial brightener for nickel deposition (195).

In 1921, Blum (197) had already stated that ... "small amounts of foreign metals in deposited metal . . . . may exert profound effects upon the structure of electrodeposits". More recently, Meyer & Phillips (196) presented a photomicrographic study of copper deposited from cyanide solutions containing lead, thallium. silver, cadmium, tin, nickel, zinc and cobalt. Lead had the most brightening effect and silver the greatest roughening effect. Similarly, lead caused the most pronounced increase in cathode polarization, and silver the greatest decrease. The authors interpreted their results in terms of Hunt's Interference theory (8). Periodic deposition was observed and was shown to be coincident with potential-time variations.

EXPERIMENTAL PART

PART I

EFFECT OF SURFACE ON CATHODE POLARIZATION DURING THE ELECTRODEPOSITION OF COPPER.

INTRODUCTION

The use of addition agents during the electrodeposition of metals has been standard commercial practice for many years. Such agents include substances of widely different chemical constitution and behaviour, but have in common, when present in comparatively minute amounts in an electrolytic bath, the ability to impart acceptable characteristics to a metallic deposit which, in their absence, might be considered unsatisfactory. For example, a suitable concentration of an appropriate addition agent will permit of deposition at a higher current density than is possible in the absence of the agent, without deleterious effects on the structure, formation of "trees", etc. It is necessary, however, to control the concentration of addition agent within comparatively narrow limits, since optimum improvement of the deposit cannot be realized with too little of the agent, while an excess generally results in an unsatisfactory condition of the deposit and an excessive loss of power through increased polarization. Control of the effective concentration of addition agent is difficult, however, mainly because of the small concentration generally used. Chemical control of phenol as an addition agent in electrotyping solutions is possible (83) but such an analysis takes no cognizance of anodic oxidation and cathodic reduction and only gives, therefore, approximate results.

Estimation of the concentration of addition agent by measurement of the cathode polarization in a special electrolytic cell which bears his name has been suggested by Haring (118). The cell consists simply of a relatively long, narrow box, one end of which is covered with the anode, the other with the cathode. Two intermediate electrodes of copper gauze are 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. True values of the polarization are obtained only if the intermediate electrodes are not polarized, and if the lengths of all compartments are accurately the same for constant cross-section of the cell throughout its length.

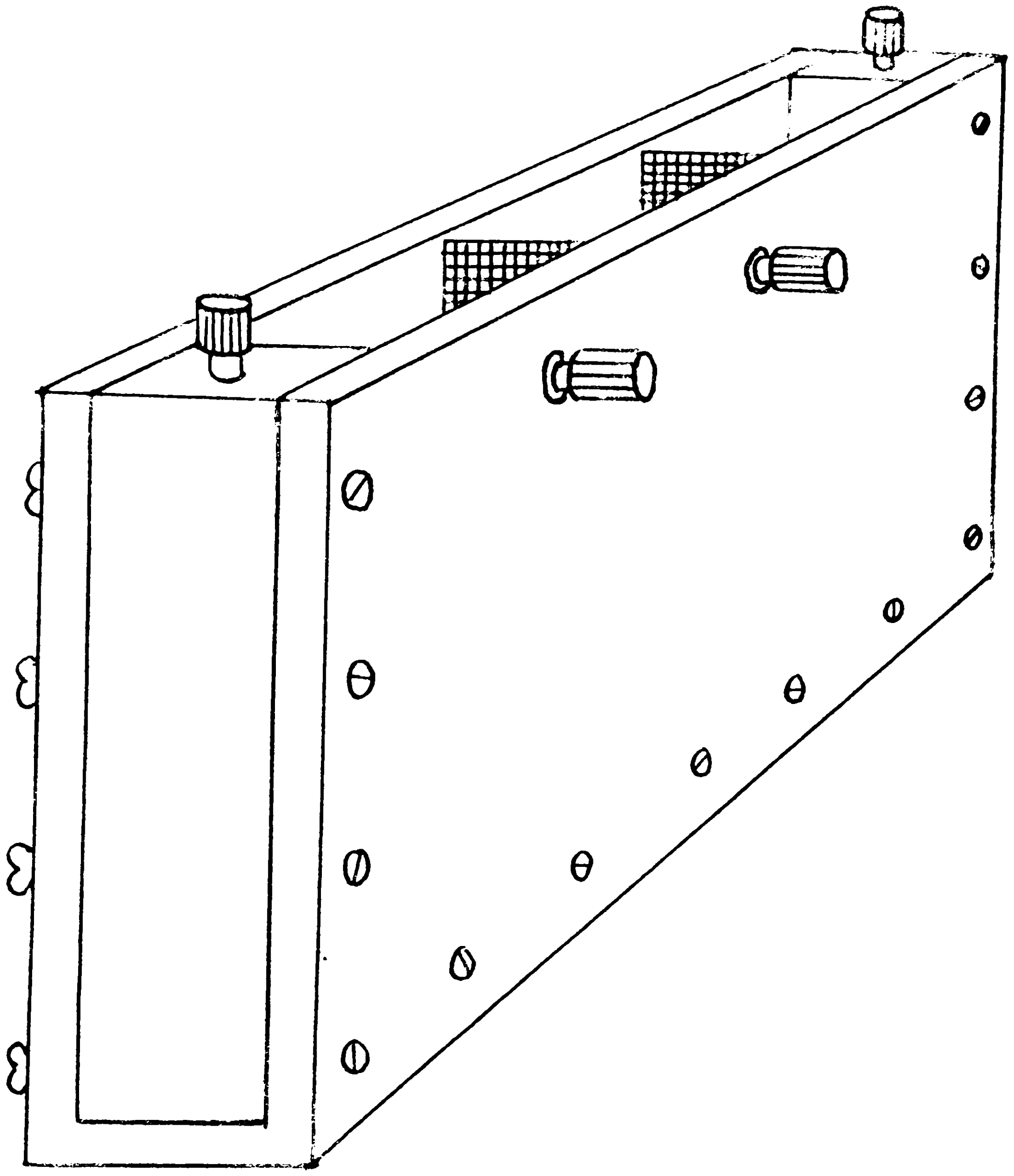
By this method, close control of the concentration of glue used as addition agent in copper and lead refining was claimed to be possible, but comparison of the results obtained with this cell by other workers shows very poor agreement between the recorded values (47, 55, 79,, 109, 110, 111, 118). Since there appears no reason to doubt the fundamental soundness of the Haring method, the lack of agreement between different investigators may be presumed to be due to inadequate attention to the variables that might influence the measurements. With this in mind, an investigation was undertaken, with a view to determining, if possible, the conditions under which reproducible cathode polarization measurements might be made with the Haring cell and, subsequently, to assess accurately its applicability to the problem of determining addition agent concentrations during copper electrodeposition. The present section is limited to discussing the development of a method whereby satisfactory reproducibility may be obtained with the cell.

EXPERIMENTAL

The electrolytic cell used in the present studies was a slightly modified form of the Haring cell, and is depicted in fig. 1, which is practically self-explanatory. Briefly, it consisted of two blocks of cast copper, used as anode and cathode respectively, inserted between the bakelite walls and bottom. The whole unit was assembled with 13 bolts and winged nuts, so that the electrodes could be rapidly removed for inspection and the whole cell re-assembled again. All parts were machined with precision, so that the cell was water tight when assembled with thin paper gaskets, lightly coated with paraffin. Two intermediate electrodes of 20-mesh copper gauze, with a coat of electrodeposited copper, were inserted in grooves made in the bakelite walls, and divided the cell in three equal compartments. These intermediate electrodes were held firmly in place and connected to the electrical circuit by copper clamps screwed to the two binding posts on the side of the cell, and which are not shown on fig. 1.

A 6-volt battery, with recharging circuit, constituted the current source. Potential differences between electrodes were measured with a type K Leeds and Northrup potentiometer, with the usual apparatus to complete the circuit. Currents from 250 milliamperes to 1.5 amperes were measured with a calibrated ammeter which could be read to one milliampere, while currents of less than 250 milliamperes were measured with a milliammeter with an error not greater than 0.1 milliampere.

The cell was carefully levelled to position in a thermostat controlled to within 0.05°C. All metallic parts of the cell were prevented from coming into contact with the thermostat liquid by a coating of high-melting paraffin. Since bakelite is a poor heat conductor, sufficient time was allowed to permit the cell to come to the thermostat temperature.



HARING CELL

Materials: walls and bottom: bakelite, 3/8" thick.
electrodes: solid cast copper, 21/32" thick.
intermediate electrodes: copper gauze, 20 mesh.

Dimensions: Height of electrodes: 8.6 cms.
Width of electrodes : 2.6 cms.
Inside length of cell : 15 cms.
Immersed area of electrodes : 10 cm^2.

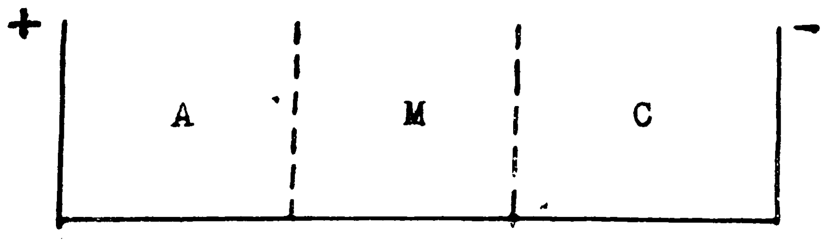


FIG. 1

THE HARING CELL

During this time, the solution to be investigated, contained in a flask immersed in the thermostat liquid, was also permitted to come to the bath temperature.

Prior to mounting in the cell, new electrodes were polished successively with No. 2, 1, 0 and 00 emery papers, following the procedure used in the preparation of a metallic sample for micrographic inspection, without carrying it down, however, to the last 3 "wheel" treatments (which could use, for example, tripoli, alumina and tin oxide as the polishing materials). The polished electrodes were then washed thoroughly in benzene, then rinsed in distilled water, after which they were etched in a solution containing 435 mls./L of concentrated sulphuric acid and 72 mls./L of concentrated nitric acid. A second method, used when the electrodes were not polished, consisted of immersion for 15 minutes in a boiling solution of sodium hydroxide (15 gms./L), sodium carbonate (60 gms./L) and sodium cyanide (7.5 gms./L). Thorough rinsing with distilled water followed either the acid etch or the alkaline cleaning treatment.

Since all potential measurements were made on a relative basis, it was not necessary to know exactly the apparent electrode area covered by the solution, but it was essential that the area covered should be reproducible in successive experiments. Solutions were therefore measured into the cell with a volumetric flask, calibrated to deliver sufficient solution to cover 10 sq. cms. of the electrode faces, as determined by measurement with a vernier caliper. Care was taken to have the solution wet the electrodes uniformly to the prescribed height, indicated by a slight scratch on the bakelite walls, close to the electrodes.

Correction was made from time to time for slight inequalities in the distances between the four electrodes in the cell. These inequalities even if not present initially, are introduced to an appreciable extent as deposition of metal on the cathode and solution of metal from the anode take place with prolonged use of the cell. Mechanical measurement of the inter-electrode distances was not found sufficiently accurate, and an alternative method was used, based on the observation that in an unacidified copper sulphate solution containing 125 gms./L of $CuSO_4.5H_2O$, the anode and cathode polarizations were found not to exceed 12 millivolts for apparent current densities of 0.3 to 1.0 Amp./dm^2. The determination of the correction is most readily understood by reference to the diagram of fig. 1. For a constant current I, the potential differences between D and E, and D and F are first measured, D being in both cases connected to the positive side of the source of current. Since the fall of potential between two electrodes is equal to the sum of the anode and cathode polarizations and the IR drop through the solution between them, the drop between D and E will be the sum of A_A (the anode polarization), IR_A (the drop through the solution in compartment A), and A_C (the cathode polarization), or:

Fall in potential between D & E $= A_A + IR_A + A_C$ ....(1)

Similarly, between points D and F, designating the cathode polarization by M_C, and the drop through the additional compartment by IR_M, we have

Fall in potential between D & F $= A_A + IR_A + IR_M + M_C$..(2).

M_C and A_C, the values of the cathode polarization at the two intermediate electrodes, are the same, because the same current I is used in both cases, and the two electrodes consist of the same material and have the same structure (essentially copper deposited under the same conditions), hence the value of IR_M will be obtained directly by subtracting (1) from (2).

If the same current I is then applied between E and F (E being connected to the positive side), and designating the anode polarization as M_A and the cathode polarization again as M_C, it can be written:-

Fall in potential between E & F $= M_A + IR_M + M_C$ ....(3)

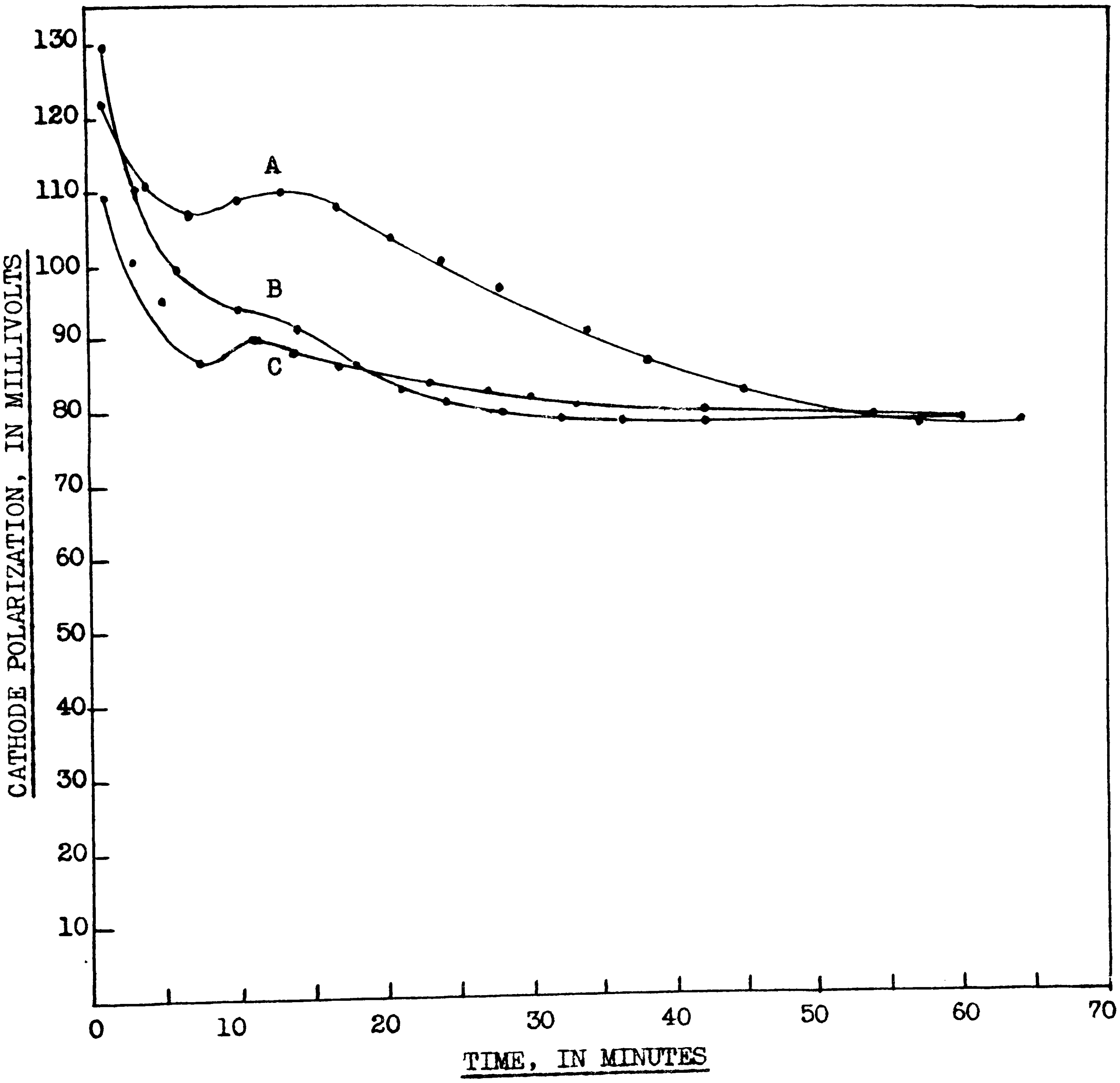
M_A and A_A will not be exactly the same, because, although the same current I is used, M_A represents the anode polarization at a gauze electrode, and A_A, that at a solid electrode, but since neither of them exceeds 12 millivolts, their difference will be small compared with the values of the IR drops in the various compartments which, at the current density used in these experiments (0.8 Amps/dm^2), were of the order of 1300 millivolts. This fact was further shown by reversing the polarity during the measurements, the new values agreeing within 3 to 4 millivolts with the previous ones. Hence the value of IR_A is given quite accurately by subtracting (3) from (2). The value of IR_C for the third compartment of the cell may be evaluated in exactly the same way. Since the cross-section of the cell is constant, the relative lengths of the three compartments are then calculated directly from the relative values of R_A, R_M and R_C.

RESULTS

Preliminary experiments were made, using polished electrodes in a solution containing 125 gms. reagent grade copper sulphate and 50 gms. concentrated sulphuric acid per litre. For future reference, this solution may be designated as the standard electrolyte (Solution No. 17). Measurements of the cathode polarization were not reproducible, variations as large as 100% being noted even when closely following the procedures outlined by other users of the Haring cell. A study of the change of cathode polarization with time was therefore made.

Using the standard electrolyte and electrode surfaces polished as described previously, it was found that the cathode polarization decreased during the first 30 to 90 minutes of the electrolysis. Typical curves, obtained at 24.8°C and an apparent current density of 2 $Amps/dm^2$ are shown in fig. 2. The initial values for a given current density at a given temperature were quite variable, but the final values were essentially the same (75.2 to 80.5 millivolts). In every case, an initial rapid decrease of the polarization from the original value occurred. This was followed, almost without exception, by a slight increase, generally after 10 to 12 minutes, after which the polarization decreased gradually to the final value. The general course of the curve representing the rate at which the final value was attained, and the time required to attain the final value, varied with different electrode specimens under otherwise comparable conditions.

The change in cathode polarization with time might be ascribed to slow attainment of equilibrium conditions in the electrolyte, particularly in the film in contact with the cathode. It has been demonstrated (207), however, that in nickel deposition from "still" solutions, a constant cathode film thickness and a constant concentration gradient across



Solution : No. 17.
Apparent Current Density : 2 Amps/dm^2.
Temperature : 24.8°C.
Initial Surface : Polished base metal.

FIG. 2

CHANGE OF CATHODE POLARIZATION WITH TIME ON POLISHED SURFACES

TABLE I

CHANGE OF CATHODE POLARIZATION WITH TIME ON POLISHED SURFACES

CURVE A

Time mins	Cathode Polar'n millivs
1	122.7
4	110.8
7	107.7
10	109.0
13	110.0
17	107.9
24	101.3
28	97.6
34	91.6
38	87.3
45	82.8
54	79.8
57	79.1
64	79.4

CURVE B

Time mins	Cathode Polar'n millivs
1	129.5
3½	111.0
6	99.8
10	94.1
14	92.2
18	86.2
21	83.6
24	82.1
28	80.2
32	79.8
36	79.4
42	79.4
60	79.5

CURVE C

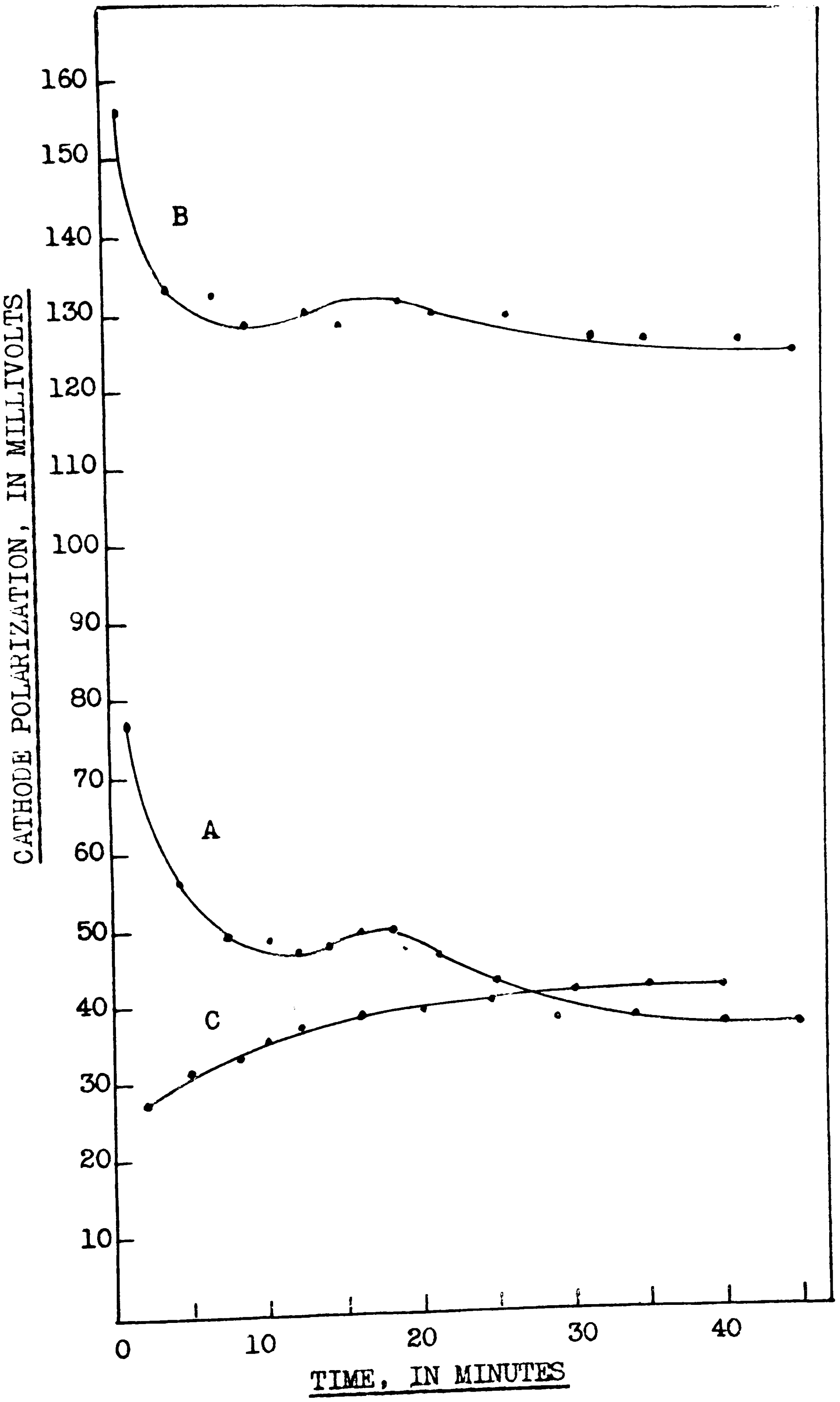
Time mins	Cathode Polar'n millivs
1	109.3
3	102.1
5	90.9
8	86.9
11	90.0
14	88.5
17	87.1
20	85.5
23	84.4
27	83.5
30	82.6
33	81.6
36	80.6
39	80.6
42	80.4
46½	79.9
60	80.0

the film, are fully established about two minutes after the start of the electrolysis. Since the current was maintained rigorously constant throughout the experiments, and that constancy of current, of cathode film thickness and of concentration gradient in the diffusion layer imply constant rates of migration, convection and diffusion, it seems very unlikely that the time factor involved in these studies is attributable to establishment of equilibrium conditions in the electrolyte. There remains the possibility that the electrode surface must attain a condition characteristic of deposition under given experimental conditions before a steady state in the over-all electrodeposition process can be completely established.

Numerous studies of hydrogen overvoltage, particularly the work of Bowden and Rideal (214), have shown that the amount of hydrogen which must be deposited on the cathode to raise its potential 100 millivolts is not a specific property of the metal atom, but depends only on the physical structure of the surface. Bowden and Rideal showed that this amount was very small for a mercury surface and much greater for a freshly etched silver surface of fine crystalline structure. Ageing of the latter somewhat reduced the amount of hydrogen needed, while polishing the same silver surface considerably reduced it. From these and numerous other observations, these investigators concluded that the accessible area of a mercury surface was considerably smaller than that of a silver one, the latter being reduced by polishing. Moreover, Foerster quotes some results showing that polishing increases the hydrogen overvoltage on cadmium (215), from which it can be inferred that polishing decreases the true area of the metal surface.

The changes in cathode polarization with time, depicted in fig.2, may be explained reasonably by assuming that deposition on a polished surface brings about an increase in true surface area of the electrode. The true current density then would be decreased for a constant current, and the cathode polarization correspondingly reduced, in accordance with the observed behaviour. Moreover, the lack of reproducibility in initial polarization values, and differences in shape of the curves between the initial and final values, are readily accounted for by failure to reproduce accurately, by polishing methods, the same surface characteristics for different electrode specimens. This, in turn, may be ascibed to the formation of a hardened skin - called Beilby layer - on the surface of the cathode during the process of polishing, which may or may not be completely removed by a subsequent etching. Portevin and Cymboliste (202) have made a thorough micrographic study of the effect of polishing on the structure of the deposit subsequently obtained on the polished surface, and showed that very small cavities, cracks, and irregularities may be caused by polishing, which cause considerable pertubation in the crystalline structure of the deposit.

On the other hand, final attainment of a surface of definite characteristics, representing an equilibrium condition corresponding to conditions prevailing in the electrolytic bath, would account for the definite value of the cathode polarization eventually obtained. Support for these views was obtained from an experiment, using standard electrolyte (Solution No. 17) at 25.0°C, the results of which are shown in fig.3. Curve A was obtained on a polished surface at an apparent current density of 0.875 Amps/dm^2. Such a relatively low apparent current density is conducive, as has been frequently reported, to formation of a comparatively coarse crystalline deposit. When the equilibrium polarization was attained, the current was switched off for 10 minutes, after which electrolysis was resumed at an apparent current density of 3.3 Amps/dm^2.



Solution : 17
Temperature : 25°C.
Apparent Current Density : for A: 0.875 Amps/dm^2
for B: 3.3 Amps/dm^2
for C: 0.875 Amps/dm^2

Initial Surface : for A: polished base metal.
for B: that at the end of A.
for C: that at the end of B.

FIG. 3
EFFECT OF CHANGE IN CURRENT DENSITY ON SURFACE

TABLE II

EFFECT OF CHANGE IN CURRENT DENSITY ON SURFACES

CURVE A

Time minutes	Cathode Polar'n millivs
1	76.9
4½	55.9
6	55.1
7½	49.6
9	49.6
10	48.6
12	47.2
14	47.7
16	49.4
18	49.8
21	46.9
23	44.2
25	43.0
27	43.0
29	37.9
32	38.3
34	37.8
37	37.2
40	36.9
45	37.9

CURVE B

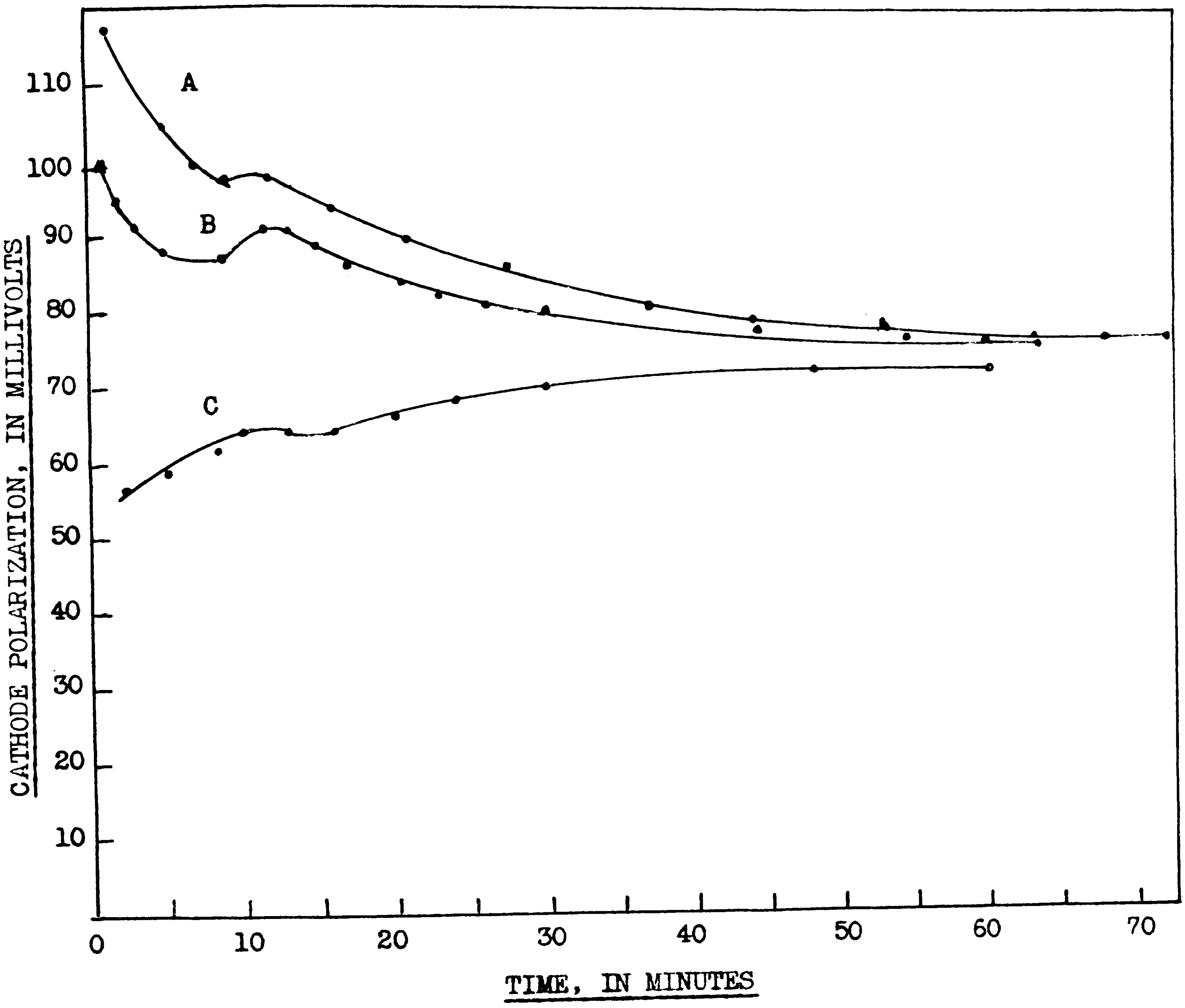
Time minutes	Cathode Polar'n millivs
1	156.1
4	133.5
7	133.6
9	129.1
11	128.9
13	130.6
15	129.1
17	130.0
19	132.0
21	130.5
23	130.1
27	130.0
29	129.0
31½	128.2
33	127.8
35	127.8
37	127.7
39	127.7
41	127.5
43	128.0

CURVE C

Time minutes	Cathode Polar'n millivs
2	27.4
3½	29.4
5	31.4
8	33.4
10	35.7
12	37.4
14	38.1
16	39.0
18	40.0
20	40.0
22	40.6
24½	40.9
27	41.4
30	42.3
32½	42.3
35	41.3
37	42.2
40	41.9

The lapse of 10 minutes before resumption of electrolysis should have been ample to allow complete dissipation of the cathode film created at the lower current density, since Brenner showed that the film was completely dissipated 3 minutes after interruption of the current (207). Electrolysis at an apparent current density of 3.3 Amps/dm^2 gave results shown by curve B. The higher current density is conducive to rapid nuclear formation, hence a finer crystalline deposit (50, 102), with accompanying increase in true cathode surface. The equilibrium polarization value is therefore less than the initial value on the coarse surface. Following a second interruption of 10 minutes, electrolysis was again resumed at the original apparent current density value of 0.875 Amps/dm^2. The results, shown in curve C, gave an initial cathode polarization lower than that corresponding to the equilibrium value for this current density, as might be expected for the finer crystalline structure of the surface, with its greater true area. As electrolysis proceeded, however, the cathode polarization increased to essentially the same equilibrium value as before.

Further confirmation that the cathode polarization should attain with time a definite equilibrium value under given conditions of electrolysis was sought by using cathodes having widely different initial surface characteristics, instead of the closely similar polished surfaces previously used. One cathode was given a very coarsely crystalline surface by deposition from the standard electrolyte at an apparent current density of 0.6 Amps/dm^2 and temperature of 26.4°C. The electrolyte was then renewed, and electrolysis continued at a current density of 2 Amps/dm^2. The cathode polarization-time curve is shown in fig. 4, curve A. A second cathode was given a comparatively fine-grained



Solution : No. 17.
Temperature : 26.4°C.
Apparent Current Density : 2 Amps/dm^2.
Initial Surface : for A: that obtained from the same solution, same conditions, but at an apparent C.D. of 0.6 A/dm^2.
for B: that obtained from Solution 33, Temperature of 26.4°C, and apparent C. D. of 3 Amps/dm^2.
for C: that obtained from Solution 17, at an apparent C.D. of 2 Amps/dm^2 and a Temperature of 2°C.

FIG. 4

ATTAINMENT OF EQUILIBRIUM POLARIZATION ON DIFFERENT SURFACES

TABLE III

ATTAINMENT OF EQUILIBRIUM POLARIZATION ON DIFFERENT SURFACES

CURVE A

Time minutes	Cathode Polar'n millivs
1	117.1
2½	116.9
5	104.6
7	99.4
9	97.6
12	97.7
13½	96.1
16	93.7
21	89.5
37	80.4
44	78.7
53	78.0
60	76.6
68	76.5
72	76.6

CURVE B

Time minutes	Cathode Polar'n millivs
1	94.4
2	91.0
3	87.9
5	86.9
7	86.5
9	90.8
11½	90.4
13	88.5
15	86.1
20½	83.7
23	82.1
26	80.8
28	80.3
30	80.1
32½	80.0
37	79.0
41	78.6
47	78.5
54	77.2
57	76.7
63	76.4

CURVE C

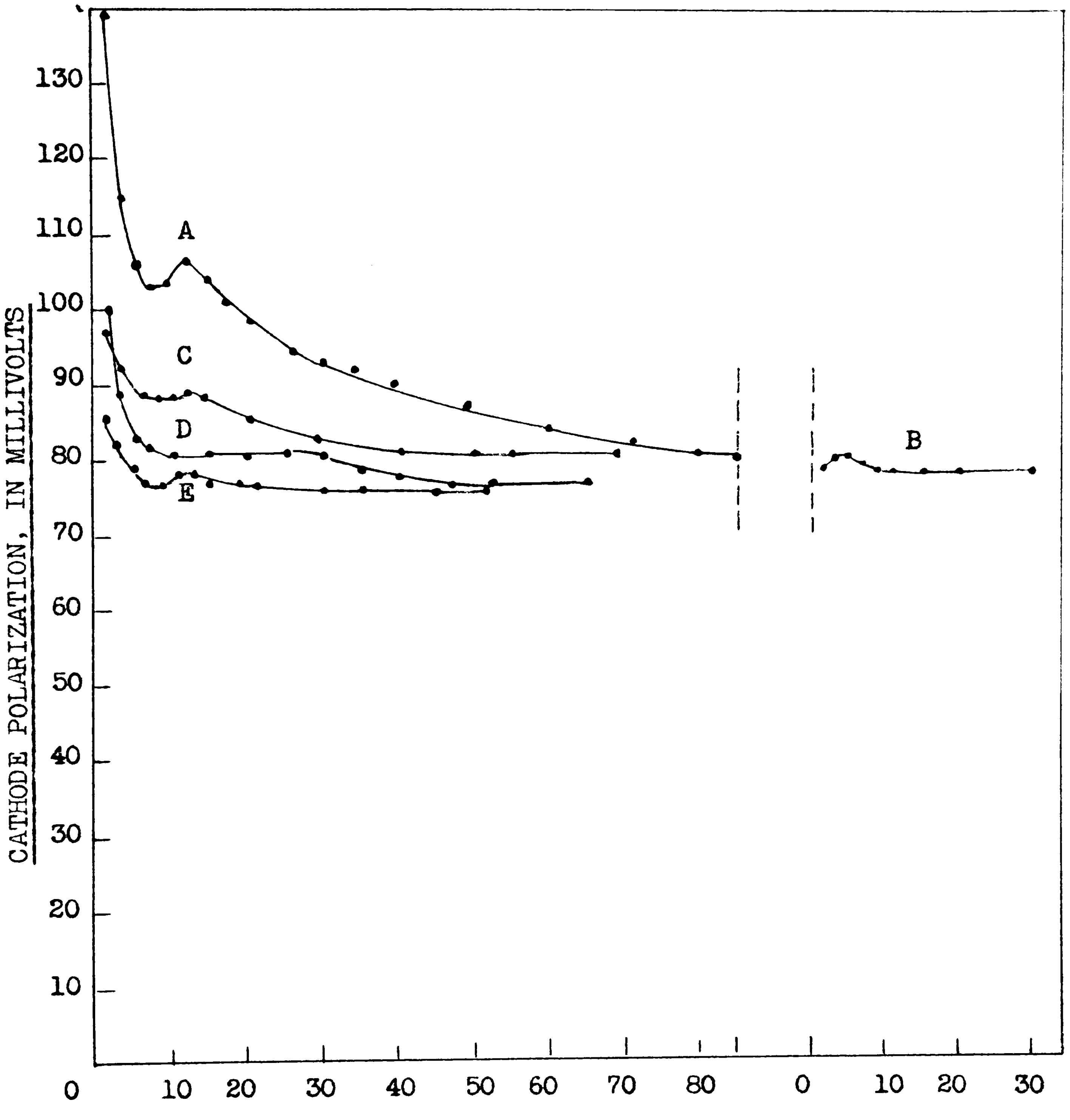
Time minutes	Cathode Polar'n millivs
2½	56.3
5	59.1
8	62.2
10	64.1
13½	64.0
16	63.8
20	66.2
24	68.1
30	69.9
48	71.9
60	72.0

surface structure by deposition from standard electrolyte at an apparent current density of 2 Amps/dm^2 and temperature of 2.0^{o}C. Electrolysis was then continued in renewed electrolyte at an apparent current density of 2 Amps/dm^2 and temperature of 26.4^{o}C. The corresponding cathode polarization - time curve is also shown in fig. 4, curve C. The changes in polarization with time can again be accounted for by an increase of true cathode area as a finer deposit is laid down (curveA), and a decrease in true area as a more coarsely crystalline surface is produced(curve C). Finally, a third initial surface was obtained by deposition from an entirely different electrolyte, containing 125 gms/L of copper sulfate and 150 gms of sulfuric acid (solution 33), at an apparent current density of 3 Amps/dm^2 and a temperature of 26.4^{o}C. Inspection showed that the surface was fairly coarse under these new conditions, and the change in cathode polarization with time - as shown by the cathode polarization - time curve obtained as before from our standard electrolyte at an apparent current density of 2 Amps/dm^2 (fig. 4, curve B) - can be accounted for by an increase of true cathode area. The important point, however, is that the final values of the cathode polarization (72.0, 76.6 and 76.4 millivolts) agree within the error of the experiment, and are, moreover, essentially the same as the values found previously for closely similar conditions of electrolysis when polished electrodes were used (75 to 80 millivolts).

It is a logical corollary of the behaviour with cathodes of diffe-initial surface characteristics, that no change in cathode polarization should be observed when the true electrode area is not allowed to change, providing other conditions of electrolysis remain the same. To investigate this point, the final value of the cathode polarization was established at 26.4 C in standard electrolyte at an apparent current density of 2 Amps/dm^2

on a polished electrode, fig. 5, curve A. Without otherwise disturbing the system, the current was then switched off for 10 minutes, after which electrolysis was resumed at the same current density: the result is shown in fig. 5, curve B. This curve was reproduced almost exactly with longer periods of interruption of the current. Obviously, the initial and final values of the polarization remain the same in curve B, but it is interesting to note that after 10-12 minutes a slight increase in polarization , similar to that noted previously, was observed, following resumption of electrolysis after each interruption of the current.

Following upon these experiments, the electrolyte was removed, the cell thoroughly rinsed with distilled water and dried. After 48 hours, electrolysis was resumed under the same conditions as before, but the cathode polarization values obtained at the beginning of this experiment showed a marked increase over the previous equilibrium value. As electrolysis was continued, however, the polarization diminished as shown in curve C, fig. 5, eventually attaining within 3 millivolts of the equilibrium value. The change in surface conditions of the electrode was ascribed, at first, to "ageing", as observed for the silver electrode by Bowden and Rideal (214). The cell was therefore emptied and again rinsed thoroughly with distilled water and dried. After one half-hour, electrolysis was recommenced, with the results shown in curve D, fig. 5. Apparently the change in surface conditions was not one involving a prolonged "ageing" effect, and it was therefore considered possible that even with comparatively short exposure to air some change, presumably oxidation, had occurred to an extent sufficient to alter the surface characteristics of the cathode rather seriously. In order to ascertain this fact, the cell was rinsed thoroughly with distilled water at the temperature of the bath before being used again, the electrodes given an "acid dip" for a few seconds, the cell rinsed thoroughly with distilled water as before,



Solution: No. 17.
Temperature : 26.4°C.
Initial Surface : for A: polished electrode,
for B: that at the end of A, and 10 minutes later.
for C: that at the end of B, and 48 hours later.
for D: that at the end of C, and 30 minutes later.
for E: that at the end of D, after acid etching.
Apparent Current Density : 2 Amps/dm^2.

FIG. 5

REPRODUCIBILITY OF EQUILIBRIUM POLARIZATION

TABLE IV

REPRODUCIBILITY OF EQUILIBRIUM POLARIZATION

CURVE A

Time minutes	Cathode Polar'n millivs.
1	139.3
3	114.8
5	105.8
7	102.7
9½	103.5
11½	106.6
14½	103.9
17	101.3
20	98.6
26	94.4
34	92.0
39½	90.1
49	86.8
56	85.3
60	84.1
71	82.3
80	80.7
85	80.5

CURVE B

Time minutes	Cathode Polar'n millivs
1½	78.6
3	80.0
5	80.7
7	77.4
9	78.5
11	78.3
13	78.1
15	78.4
20	78.2
30	78.3

CURVE C

Time minutes	Cathode Polar'n millivs
1	96.7
3	92.0
6	88.5
8	88.3
10	88.4
12	89.0
14	88.7
17	87.6
20	85.4
24½	83.5
29	82.8
40	81.2
45½	81.5
50	81.3
55	80.9
69	81.2

Curve D

Time minutes	Cathode Polar'n millivs
1	99.8
3	89.1
5	83.2
7	82.0
10	80.5
12	81.2
15	80.9
20	81.1
25	81.5
30	81.1
35	79.3
40	77.2
47	76.5
52	76.9
65	76.6

CURVE E

Time minutes	Cathode Polar'n millivs
1	85.5
2½	81.9
4½	78.7
6	77.0
8½	76.6
10½	78.0
12½	78.1
15	76.9
21	76.6
27	76.0
35	75.9
42	75.8
45	75.7
48½	75.9
52	76.3

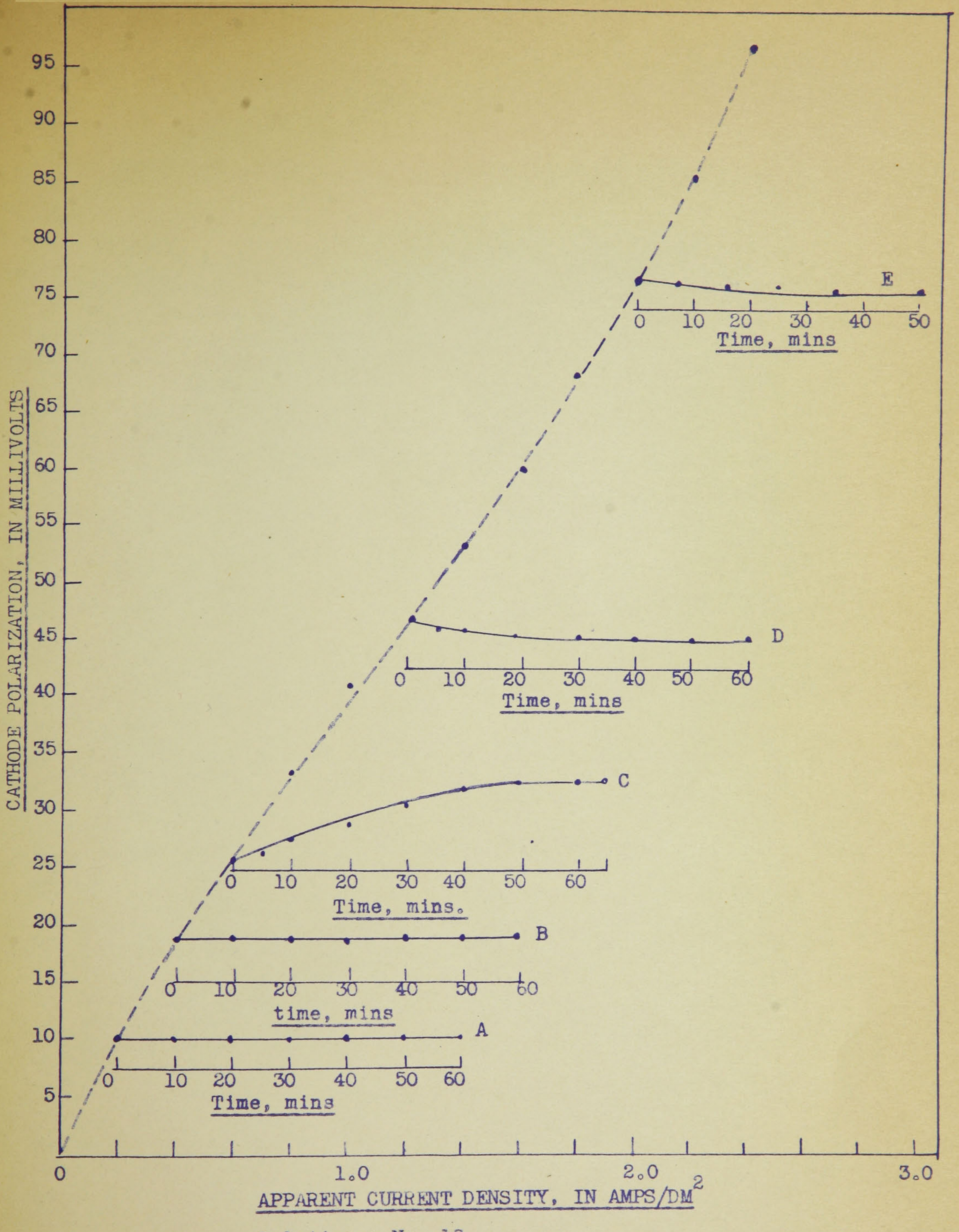
and electrolysis resumed immediately upon introducing the electrolyte, which had been kept at the temperature of the thermostat. The results obtained are shown in curve E, fig. 5. Obviously, the effect of exposing the surface to the atmosphere, though not entirely removed by the few seconds "acid dip", was largely reduced.

While the data so far presented demonstrate with some assurance that reproducible equilibrium values of the cathode polarization could be obtained at an apparent current density of 2 Amps/dm^2., it was of special interest for future purposes to determine the time required to attain equilibrium values at lower current densities, where the surface characteristics of the base metal may influence the nature of the deposit to a marked degree. Wood (57), in particular, has shown by X-Ray studies that at apparent current densities below 1.2-1.5 Amps/dm^2, the structure of the base metal was "continued" or reproduced in the deposit when the surface was chemically clean. It must be noted here that this critical range of the current density may be altered by different electrolyte compositions. Wood obtained his results in a solution containing 200 gms./L of copper sulphate and 100 gms./L of sulphuric acid.

To obtain the desired information, deposition on a polished cathode from the standard electrolyte at an apparent current density of 2 Amps/dm^2 was continued until the usual equilibrium polarization value was attained. The electrolyte was then renewed, after etching of the electrodes in the manner described for the last part of the previous experiment, and electrolysis was resumed at an apparent current density of 0.2 Amps/dm^2. At this low current density, the polarization assumed a constant value almost immediately after the current was adjusted. When the apparent current density was increased to 0.4 Amps/dm^2, the same behaviour was noted. At either value of the current density, no significant change in polarization occurred after as much as 60 minutes of electrolysis (fig. 6, curves A and B). This behaviour has been observed in many repetitions of the experiment. The explanation would seem to be that electrolysis at these low current densities perpetuates the surface structure of the base metal in the deposit.

When the apparent current density was increased to 0.6 Amps/dm^2 and maintained constant at this value, the cathode polarization increased slowly with time to an equilibrium value after approximately 50 minutes (fig. 6, curve C). The cell was then emptied and new electrolyte introduced, in order to minimize the change in copper sulfate concentration of the solution due to extensive deposition. The experiment was then resumed as follows: deposition was again obtained for 10 minutes at an apparent current density of 0.2 Amps/dm^2, then the current density was increased in steps of 0.2 Amps/dm^2 every 5 minutes, until an apparent current density of 1.2 Amps/dm^2 was reached, at which point the current was maintained constant, and polarization measurement taken against time, until equilibrium polarization was obtained (curve D, fig. 6). The electrolyte was then renewed, and exactly the same procedure repeated, i.e., the apparent current density was increased in steps of 0.2 Amp/dm^2 every 5 minutes, until a current density of 2 Amps/dm^2 was reached, at which point it was maintained constant until constant polarization values were attained (Fig. 6, curve E).

In fig. 6, showing the results of the complete experiment, the cathode polarization is plotted - as a dotted line - against the apparent current density to yield the curve for the experimental points representing the polarization values attained after 5 minutes electrolysis with successive increments of 0.2 Amp/dm^{2}in the apparent current density. In reality, 3 such curves were obtained, one from 0.2 to 0.6 Amp/dm^2, the next



Solution : No. 17.
Temperature : 25°C.
Initial Surface : Standard Base.

FIG. 6

DEVIATION OF POLARIZATION FROM EQUILIBRIUM VALUES

TABLE V

DEVIATION OF POLARIZATION FROM EQUILIBRIUM VALUES

CURVE A

Time minutes	Cathode Polar'n millivs
1	10.5
10	10.7
20	10.7
60	10.8

CURVE B

Time minutes	Cathode Polar'n millivs
1	18.2
10	18.3
20	18.6
60	18.6

CURVE C

Time minutes	Cathode Polar'n millivs
2	25.9
5	26.4
10	27.3
15	28.0
20	28.6
25	29.5
30	30.3
35	31.1
40	32.0
45	32.4
50	32.7
55	32.8
60	32.7
65	32.8

CURVE D

Time minutes	Cathode Polar'n millivs
2	48.9
5	48.6
10	48.4
16	47.9
24	47.6
32	47.8
40	47.7
52	47.7
60	47.7

CURVE E

Time minutes	Cathode Polar'n millivs
7	76.8
15	76.4
25	76.6
30	76.4
35	76.2
55	75.9
60	76.2

from 0.2 to 1.2 Amp/dm^2, and the third from 0.2 to 2 $Amps/dm^2$. However, the last one only has been plotted, as the agreement between the 3 curves was for all points better than 2.6 millivolts. Referring again to Fig. 6, it will be noticed that subsidiary time scales are placed immediately below each curve representing attainment of the equilibrium polarization. These time scales are adjusted so that the zero points correspond to the lapse of 5 minutes following adjustment of the current at each of the 5 current density values.

It is obvious from the figure that at an apparent current density of 0.6 Amp/dm^2, the equilibrium polarization is not attained in less than about 50 minutes, while at an apparent current density of 1 Amp/dm^2 or higher, the equilibrium polarization is attained within 5 minutes of adjusting the current. The influence of the base metal surface, at an apparent current density of 0.6 Amp/dm^2 is still readily discernable. For example, at this current density, the time curve shows an increase in cathode polarization to the equilibrium value. This corresponds to an increase in true current density, or to a decrease in true cathode surface area, which may be interpreted as a change from a finer to a coarser-grained cathode surface (compare with fig. 3, curve C, and fig. 4, curve C). Bearing in mind that the lower the current density, the more coarsely crystalline the deposit, it is evident that deposition at the apparent current density of 0.6 Amp/dm^2 did not take place on a surface representing equilibrium conditions at a lower current density - namely 0.4 Amp/dm^2 - but on a surface having the finer-grained characteristic of deposition at a higher current density. This, evidently, corresponds to the initial surface of the electrode, established at an apparent current density of 2 Amp/dm2, the nature of which was perpetuated in the deposits laid down at the lower current densities.

DISCUSSION

It is not difficult, on the basis of the results which have been presented, to account for the lack of agreement in cathode polarization values obtained by different workers using the Haring cell. Measurement of the polarization after an arbitrarily determined time, say 5 minutes following establishment of the current, a method that has been followed frequently in the past, obviously cannot lead to reproducible values, unless the time chosen is at least the minimum required to establish equilibrium conditions. Moreover, this minimum time will vary with the initial condition of the cathode surface and the current density used.

The slight increase in cathode polarization observed after approximately 10 minutes of electrolysis seems to be a general behaviour. On a few occasions, it was not observed, but this might mean simply that it occurred so rapidly that the time intervals between successive measurements were too long to allow it to be detected. No satisfactory explanation of this effect has been found yet. It is possible that it is associated with an oxidation-reduction reaction. A somewhat analogous behaviour has recently been reported (216) and ascribed to the influence of an oxide film, the formation of such film being assumed to be caused by the air present over the solution (217, 218). Obviously, more experimental information is required for a satisfactory explanation and a further study of this point is contemplated.

The results of the present study are in contradiction with the Blum and Rawdon Theory (9), according to which the change from a coarsely crystalline surface to a fine grained deposit should be associated with an increase in cathode polarization, and vice-versa. Curves B and C, fig. 3, and the three curves of fig. 4, show exactly the opposite effect. Instead of the assumption of a relation between cathode polarization and crystal size, it appears that the logical relation is one between crystal size and true current density: the smaller the crystal size, the smaller the true current density for a given apparent current density, hence the smaller the cathode polarization.

It is of interest to note that the present data give some indication of the probable rate-governing process in electrodeposition. The deposition of a cation may be regarded as occurring in four steps:-

(1) migration of the ion to the electrode by diffusion, convection and electrical transport;

(2) adsorption of the ion on the cathode;

(3) neutralization of the cation by an electron;

(4) entry of the atom into the crystal lattice.

Cathode polarization evidently has its origin in the retarding effect of one of these processes. It is generally conceded that migration of the cation to the cathode film (step 1) is not a rate-determining factor under normal conditions of electrodeposition. The results of the present study show that the greater the true area of the cathode <u>at a given apparent current density</u>, the smaller the polarization accompanying deposition. Of the four possible rate-governing processes mentioned, it seems probable that an increase of true cathode area should exert its main effect in expediting the adsorption of ions on the cathode face. In other words, it would appear that the rate-governing process is adsorption prior to entry of the neutralized ion into the crystal lattice (step 2).

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PART II

USE OF THE HARING CELL FOR MEASURING ADDITION AGENT CONCENTRATION IN ELECTROLYTIC BATHS

INTRODUCTION

A definite relation has been stated by Haring (118) to exist between cathode polarization and the concentration of glue used as addition agent in the electrodeposition of copper. The Haring cell was used subsequently by many investigators to make cathode polarization measurements, but the results recorded in the literature show marked disagreement. The apparent lack of agreement in certain cases might be attributable to failure of the investigators to report fully the conditions under which the measurements were made. Nevertheless, the information available does not seem to substantiate the original claim that use of the cell should enable the operator to maintain close control of the addition agent concentration.

Since the principle of the Haring method appeared to be sound enough, an investigation was made to determine the conditions under which satisfactorily reproducible cathode polarization measurements might be made. The results reported in Part I showed that the cathode polarizations, for carefully controlled conditions of electrolysis, were reproducible when sufficient time was permitted for equilibrium to be attained. On the basis of this information, the present study was made to assess the applicability of the Haring cell to the problem of determining the concentration of gelatin used as addition agent in copper electrodeposition. At the same time, a study was made of the effect of temperature and acid concentration on the cathode polarization in the presence of gelatin.

EXPERIMENTAL

The electrolytic cell and electrical equipment used were the same as described in Part I. The gelatin was Eastman purified, with a moisture content of 11.9% on a moist gelatin basis. All weights of the addition agent reported, are given on the moist basis. Sulphuric acid and copper sulphate were reagent grade.

Prior to making measurements of the cathode polarization at different apparent current densities, under given conditions of electrolysis, standard surface characteristics were imparted to the cathode by electrolyzing to the equilibrium polarization value at 26.4°C, with an a apparent current density of 2 Amps/dm^2 in an electrolyte containing 125 gms./L of copper sulphate pentahydrate, and 50 gms/L of concentratedsulphuric acid in distilled water (Solution No. 17). When the standard base metal surface had been established, the proper amount of electrolyte to be studied was placed in the cell, following the procedure described in Part I, the temperature of the thermostat adjusted to the desired value, and measurements of the cathode polarization made for a range of apparent current densities beginning with the value 0.2 Amp/dm^2. After attainment of the equilibrium polarization value at this current density, which only required a matter of a few minutes, the apparent current density was increased in successive increments of 0.2 Amp/dm^2, the polarization being measured after the lapse of 5 minutes from the time the current was adjusted after each increment. A previous experiment (see fig. 6) had shown, it is true, that at apparent current densities in the range from approximately 0.5 to 1.0 Amp/dm^2, equilibrium polarization values would not be attained after 5 minutes. Experience soon demonstrated, however, that reproducible relative polarization values, satisfactory for present purposes, could be obtained by this procedure, providing the standard base metal surface was always used as a starting point.

In Table VI, given below, are recorded the concentration and composition of the various electrolytes investigated, and also the numbers by which they are designated on the graphs.

TABLE VI

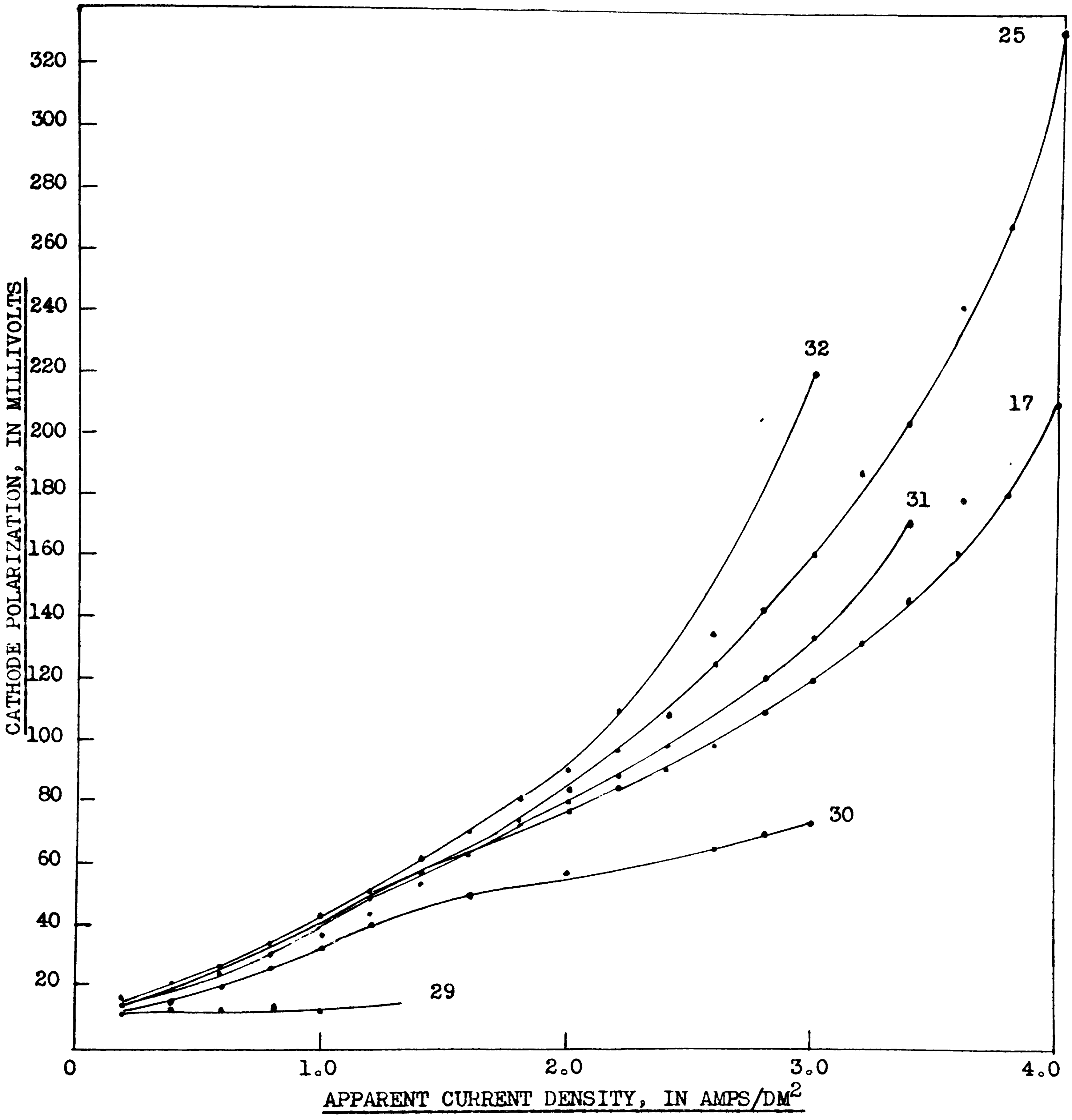
Solution Number	Copper Sulphate gms./L	Sulphuric Acid gms./L	Gelatin mgs./L
17	125	50	0
18	125	50	1
19	125	50	5
20	125	50	10
21	125	50	100
22	125	50	500
23	125	50	750
24	125	50	1000
25	125	150	0
26	125	150	1
27	125	150	5
28	125	150	10
29	125	0	0
30	125	25	0
31	125	100	0
32	125	225	0
33	62.5	150	0
34	62.5	150	0.5
35	62.5	150	1.0
36	62.5	150	2.5
37	125	150	2

RESULTS

Effect of Acid Concentration on Cathode Polarization

Measurements were first made to determine the effect of acidity on the cathode polarization, since there seems to be little agreement among different investigators on this point. It has been reported, for example, that an increase of acidity in copper sulphate baths results in: no effect on the polarization (109); a decrease in the polarization (118); an increase (110); an increase, followed by a decrease (55); and a large initial decrease, followed by steady values at higher acidities (111).

The results of the present study, made at 24.8°C, with electrolytes containing 125 gms. copper sulphate pentahydrate per litre of solution, are given in Table VII, and represented graphically in fig. 7. It was not possible to extend the measurements for the solution containing no acid (29), nor for that containing 25 gms/L of acid (30), owing to the low conductivities of these solutions, which rendered the current source and potentiometer used unsuitable at higher current densities. At apparent current densities less than 1.0 Amp/dm^2, there appears to be a marked increase in polarization with increase of acid concentration up to 50 gms/L. Above this concentration, the cathode polarization seems to suffer little change with further increase in acid content of the solution. At higher current densities, the rate at which the polarization increases with increasing apparent current density is generally greater the higher the acid concentration, although there are certain irregularities in the results that do not conform to this generalization. Most noteworthy are the consistently low polarization values for the solution containing 100 gms/L of acid (No. 31), over the apparent current density range 1.0 to 2.6 Amps/dm^2. It should not be surprising, perhaps, if a simple relation between cathode polarization and acid content of the solution does not exist, since the acidity of the cathode film appears to be a function



Temperature: 24.8°C.
Initial Surface : Standard Base.
Solutions: No. 29, no sulfuric acid.
No. 30, 25 gms/L of sulfuric acid.
No. 17, 50 gms/L of sulfuric acid.
No. 31, 100 gms/L of sulfuric acid.
No. 25, 150 gms/L of sulfuric acid.
No. 32, 225 gms/L of sulfuric acid.

FIG. 7

EFFECT OF ACIDITY ON CATHODE POLARIZATION

TABLE VII

EFFECT OF ACIDITY ON CATHODE POLARIZATION

Current Density Amp/dm^2	Cathode Polarization, in millivolts					
	Sol'n 29 No acid	Sol'n 30 25 gm/L	Sol'n 17 50 gm/L	Sol'n 31 100 gm/L	Sol'n 25 150 gm/L	Sol'n 32 225 gm/L
0.2	-------	10.5	14.0	14.9	10.9	17.1
0.4	13.9	15.6	20.4	21.0	17.0	21.8
0.6	10.5	21.6	25.4	25.6	23.7	26.9
0.8	11.5	27.0	32.9	30.8	30.0	34.8
1.0	11.9	33.2	41.8	36.8	37.5	43.6
1.2		41.5	49.0	43.8	44.1	52.2
1.4		----	57.6	50.1	53.9	62.7
1.6		49.7	64.1	55.9	63.8	72.3
1.8		----	71.9	60.3	74.7	82.2
2.0		58.5	78.2	----	84.7	92.4
2.2		----	85.7	----	98.7	110.7
2.4		----	93.0	----	109.8	-----
2.6		66.6	100.0	93.5	126.9	137.2
2.8		70.5	110.6	----	145.4	-----
3.0			121.3	135.9	162.8	223.2
3.2			134.8	----	190.3	-----
3.4			148.6	173.5	-----	-----
3.6			164.4	-----	244.8	-----
3.8			184.4	-----	272.6	-----
4.0			212.7	-----	334.5	-----

of both the acid content of the electrolyte (207) and the apparent current density (63).

The reason for the generally higher cathode polarization with higher acid concentration is not readily apparent. It has been suggested (74) that traces of silica in the copper sulphate and sulphuric acid might act as an addition agent. If this is true, an increased polarization at higher acid concentrations might be expected. A possible alternative explanation is, of course, that sulphuric acid is itself an addition agent. Both these explanations, however, seem incompatible with the relative constancy of the cathode polarization over a range of acid concentrations at lower current densities. A third explanation which would appear to be in better agreement with the observed behaviour,is that apparent current densities in excess of approximately 1.0 to 1.5 $Amps/dm^2$ give rise to slight, perhaps localized formation of hydrogen on the cathode. The minimum hydrogen overvoltage at a cathode appears to be essentially independent of the hydrogen ion concentration of the electrolyte over a wide range, e.g., from pH 0 to pH 12, (219), particularly at low current densities. At higher current densities, the overvoltage, at a mercury cathode at least, appears to increase somewhat with increased acid concentration (220). The available evidence, therefore, seems to be in accord with the suggested explanation of the behaviour observed in the present investigation.

Effect of Temperature on Cathode Polarization

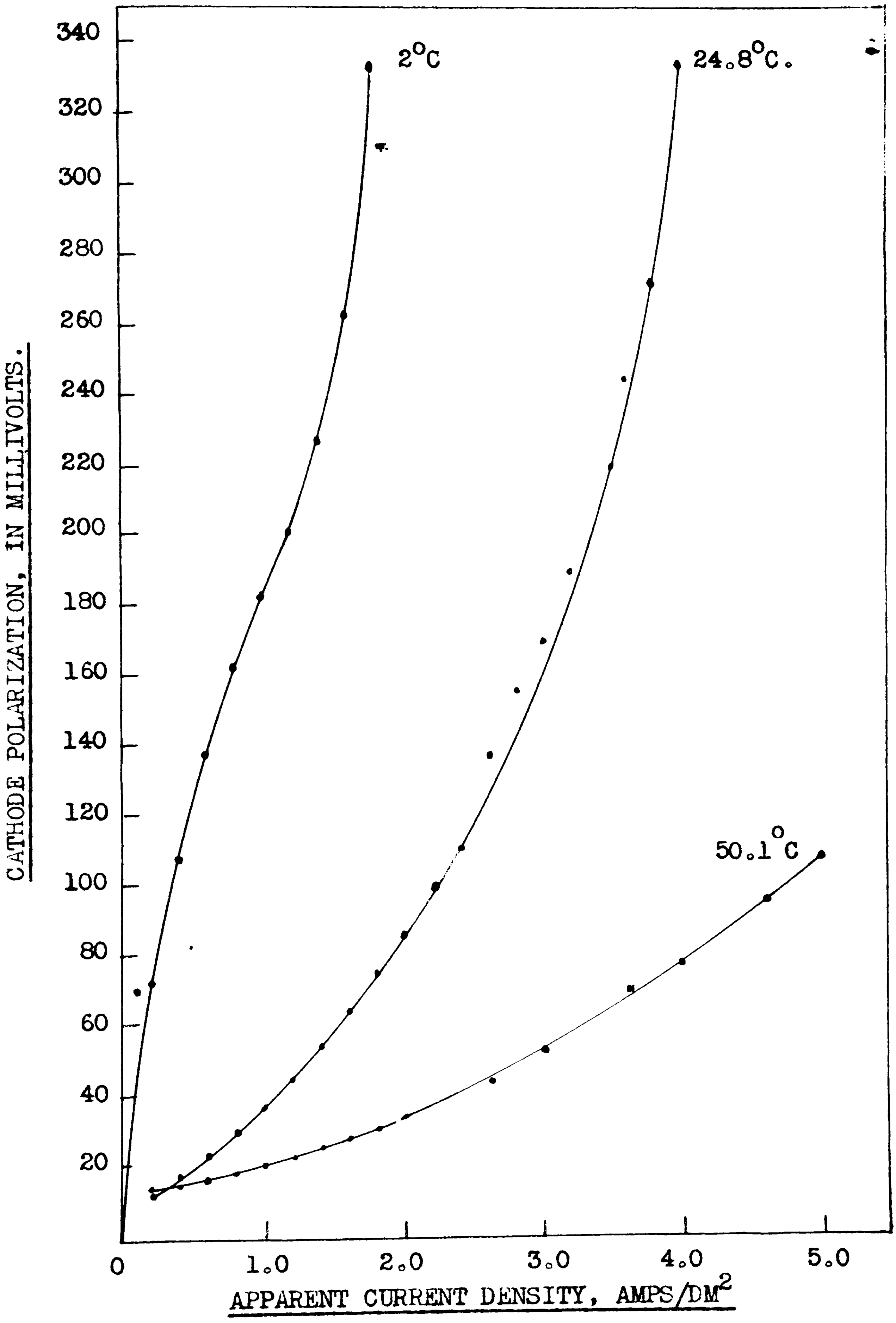
It has long been known that an increase of temperature decreases the cathode polarization. However, the nature of the relation between temperature and polarization has not been investigated in any detail. The cathode polarization has, therefore, been determined at 2°, 24.8° and 50.1°C for a range of apparent current densities, in an electrolyte containing

125 gms./L of copper sulphate pentahydrate and 150 gms/L of concentrated sulphuric acid (No. 25, see Table VI). As usual, the standard base metal surface was imparted to the cathode prior to electrolysis. The results are shown in fig. 8. Obviously, the relation between temperature and cathode polarization is functional with change in apparent current density.

Effect of gelatin concentration on cathode Polarization at 24.8°C, in weak acid electrolyte.

Experiments were made to determine the effect of increasing gelatin concentrations on the cathode polarization at 24.8°C, for a wide range of concentrations. The electrolyte used contained 125 gms/L of copper sulphate pentahydrate and 50 gms/L of concentrated sulphuric acid. The results are shown in fig. 9, each curve being the average of five with maximum deviation of ± 3 millivolts for apparent current densities below 1.5 Amp/dm^2, and ±4 millivolts for apparent current densities between 1.5 and 4 Amp/dm^2. Measurements at apparent current densities above the latter value were not reliable, possibly owing to localized attainment on the cathode of the hydrogen overvoltage. This assumption is quite logical, in view of the evidence recently presented by Read & Graham (63), who showed that the current density is not uniform over the whole immersed area of the cathode but increases from the bottom to the top of the cathode surface. It has also been shown that cathode polarization values vary somewhat over the face of the cathode (221). In other words, only average values of the cathode polarization for the whole cathode surface can be measured with the Haring cell, but that these average values are reproducible within close limits when obtained under closely controlled conditions is amply shown by the results obtained.

Measurements with 100 and 1000 mgs/L of gelatin also tended to be less precise than at lower gelatin concentrations, probably as a result of periodicity in the deposition (129).



Solution: No. 25 (all 3 curves).
Temperatures : 2°C, 24.8°C and 50.1°C.
Initial Surface : Standard Base.

FIG. 8

EFFECT OF TEMPERATURE ON CATHODE POLARIZATION

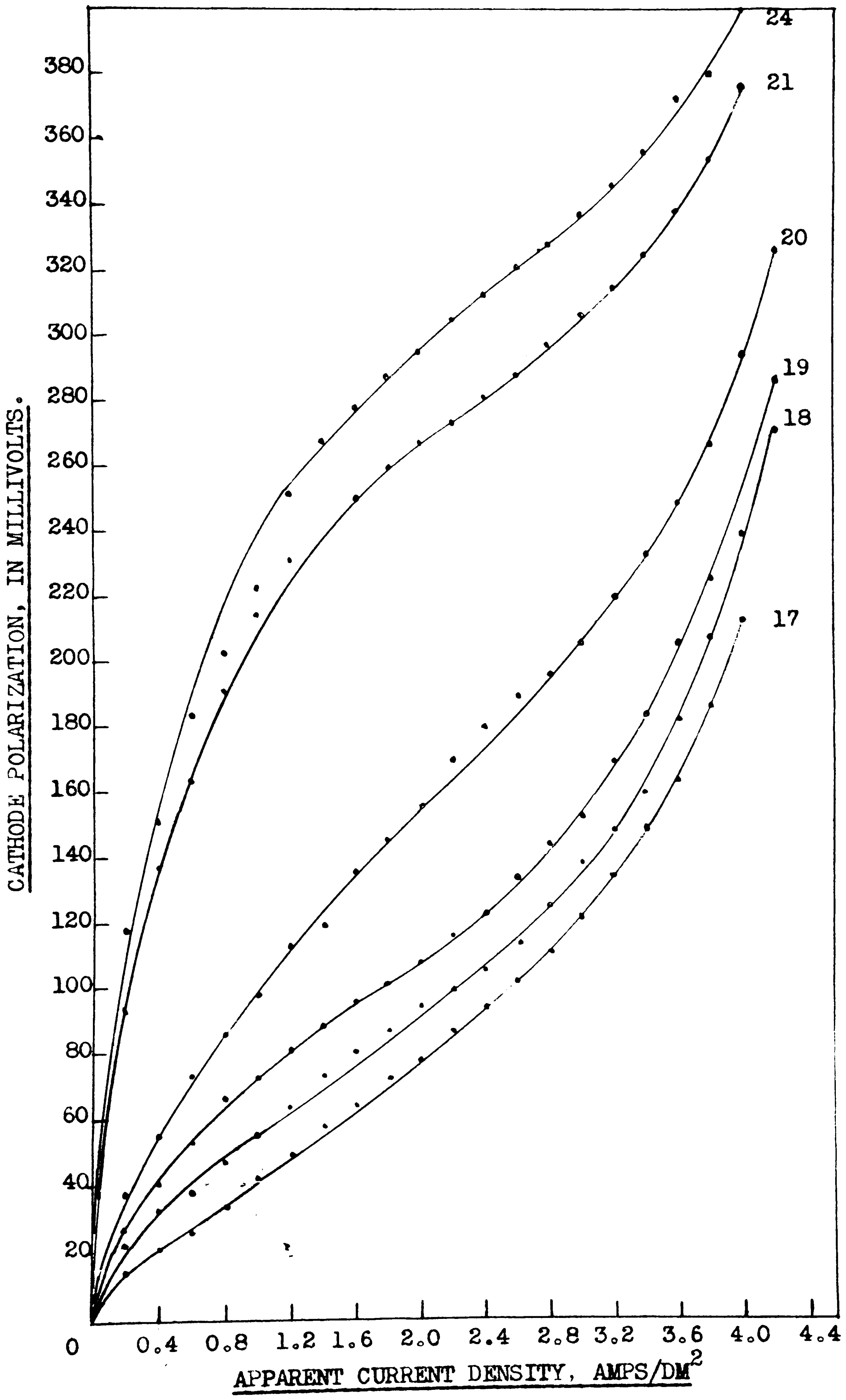
TABLE VIII

EFFECT OF TEMPERATURE ON CATHODE POLARIZATION

Solution No.25 (no gelatin)

Current Density Amp/dm^2	Cathode Polar'n, millivolts		
	2.0°C	24.8°C	50.1°C
0.2	72.1	10.9	13.9
0.4	108.4	16.8	15.1
0.6	136.7	23.3	16.5
0.8	162.2	29.7	18.4
1.0	181.6	37.3	20.6
1.2	201.2	44.6	22.9
1.4	226.9	53.9	25.1
1.6	263.1	63.8	27.6
1.8	332.0	74.7	30.0
2.0		84.7	33.5
2.2		98.7	----
2.4		109.8	----
2.6		126.9	43.1
2.8		145.9	----
3.0		162.8	57.1
3.2		190.3	----
3.4		-----	----
3.6		244.8	68.9
3.8		272.6	----
4.0		334.5	77.7
4.6			94.1
5.0			106.7

EFFECT OF GELATIN CONCENTRATION ON POLARIZATION AT 24.8°C (WEAK ACID SOLUTIONS)



Temperature : 24.8° C.
Solutions : No. 17 (No gelatin)
No. 18 (1 mg./L. of gelatin)
NO. 19 (5 mgs/L. of gelatin)
No. 20 (10 mgs/L. of gelatin)
No. 21 (100 mgs/L. of gelatin)
No. 24 (1000 mgs/L. of gelatin)

FIG. 9

TABLE IX

EFFECT OF GELATIN ON POLARIZATION (WEAK ACID ELECTROLYTE)

Current Density Amp/dm^2	Cathode Polarization, in millivolts										
	Sol'n No 17 (no gelatin)						18	19	20	21	24
	1	2	3	4	5	ave.	1mg/L	5mg/L	.01g/L	.1g/L	1gm/L
0.2	13.4	16.1	13.8	12.7	14.1	14.0	22.3	28.3	38.0	93.0	116.8
0.4	19.1	21.8	18.1	22.5	----	20.4	32.1	40.3	55.1	136.8	150.9
0.6	24.5	27.2	23.9	----	26.4	25.4	37.3	53.0	72.7	163.1	183.0
0.8	31.9	34.2	31.7	34.0	32.9	32.9	46.9	66.6	84.7	191.1	202.8
1.0	40.7	43.5	39.4	----	43.5	41.8	55.2	72.0	98.2	214.6	222.0
1.2	49.3	50.5	48.6	47.6	----	49.0	63.0	80.8	113.0	231.9	251.2
1.4	56.8	58.5	----	58.7	56.4	57.6	72.8	87.6	119.1	-----	268.6
1.6	63.6	----	63.2	65.8	63.9	64.1	81.4	98.8	136.3	249.4	279.5
1.8	70.2	74.1	----	72.9	70.6	71.9	85.8	103.6	145.2	259.4	287.8
2.0	77.6	79.7	76.1	79.3	----	78.2	93.9	111.1	156.7	267.4	295.5
2.2	84.3	88.2	83.1	85.4	87.3	85.7	99.6	115.9	170.0	274.9	304.1
2.4	92.0	96.5	92.2	92.0	93.3	93.0	104.7	121.7	179.9	282.2	311.6
2.6	99.9	103.8	101.5	97.1	97.4	100.0	113.0	134.1	189.8	288.5	320.9
2.8	108.7	115.7	109.9	109.5	109.0	110.6	125.5	143.6	197.1	297.9	327.8
3.0	118.4	124.1	121.8	122.9	119.5	121.3	138.5	150.70	206.5	307.3	336.7
3.2	131.2	135.9	135.4	136.2	135.5	134.8	144.3	169.7	211.4	314.6	345.8
3.4	146.8	147.0	151.1	146.1	151.8	148.6	159.1	184.0	232.7	327.0	357.1
3.6	167.3	161.2	168.2	160.9	-----	164.4	183.1	204.2	249.8	337.5	373.2
3.8	185.3	182.1	188.2	182.2	-----	184.4	208.0	226.2	268.0	353.5	380.4
4.0	215.4	208.4	216.8	210.1	-----	212.7	239.5	253.8	295.3	377.2	398.7
4.2							271.1	287.3			

Note: Blank spaces represent readings which could not be read within the time allotted.

The cathode polarization values are averages, except for Solution 17, where both the average values and the original readings are reported.

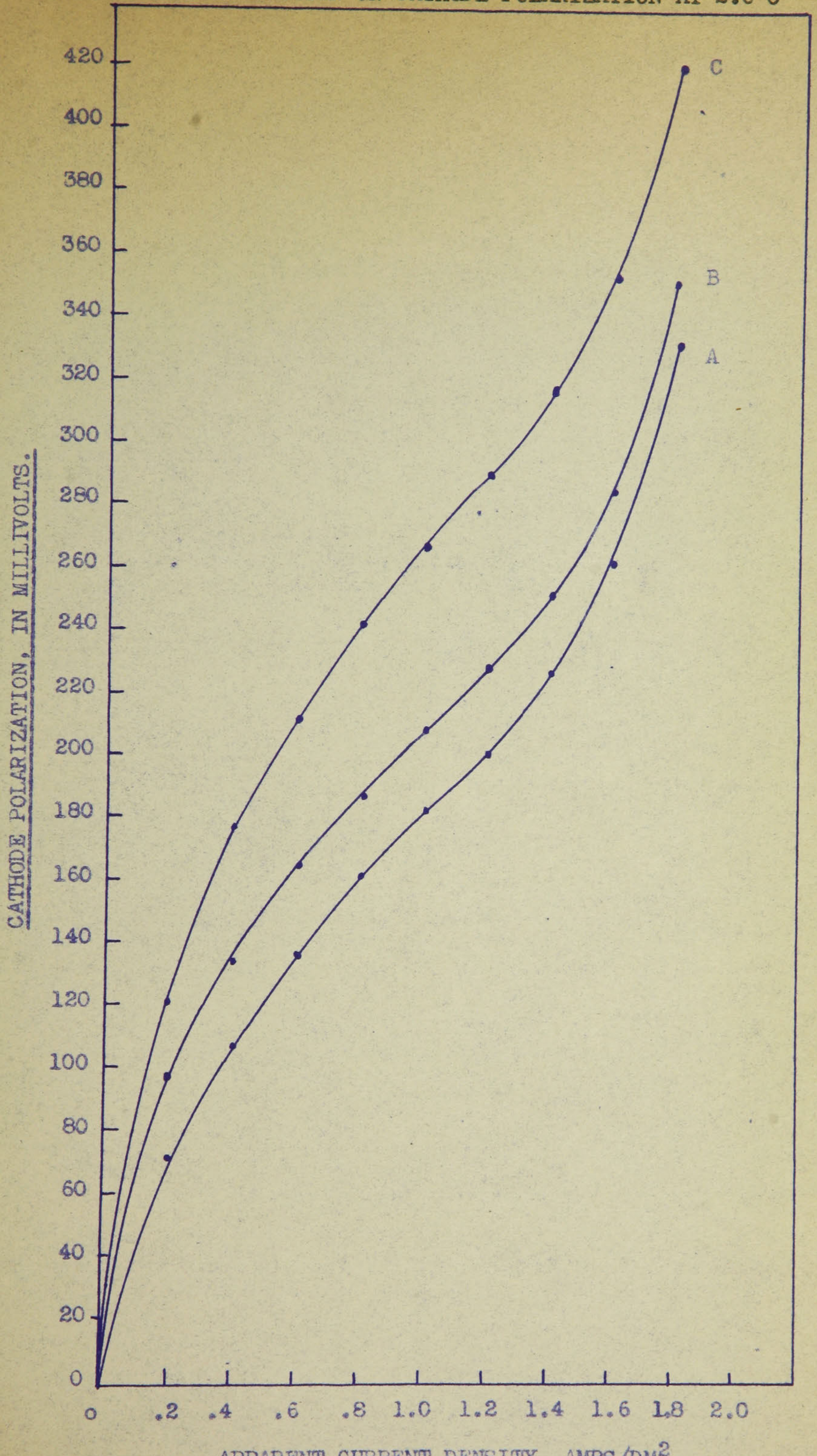
In commercial practice, however, concentrations of glue, expressed in terms of gelatin, rarely exceed 2 to 3 mgs/L, in which range the polarization measurements are considerably more reliable.

Effect of gelatin concentration on cathode polarization at different temperatures, in strongly acid electrolyte.

Commercial electrolytes generally contain concentrations of acid higher than that used in the preceding study. Studies were made, therefore, using electrolyte containing 125 gms./L copper sulphate pentahydrate and 150 gms./L concentrated sulphuric acid. The results obtained at 2°C, 24.8°C and 50.1°C are shown in figs. 10, 11, and 12. It may be noted, by comparison of figs. 9 and 11, that the increase of polarization at 24.8°C with increased gelatin content is not as large for the electrolyte containing 150 gms of acid per litre, as for the solution containing only 50 gms. of acid per litre. It is also evident that, contrary to a previous report (109), increase of temperature decreased, rather than increased, the effect of a given amount of gelatin on the cathode polarization at a given apparent current density. This effect is readily seen from fig. 13, in which the increase in cathode polarization due to the addition of various amounts of gelatin, at different apparent current densities and temperatures, are recorded. At 2°C, the effect of added gelatin was greatest, but a limiting current density was soon reached. It is interesting to note that measurements at this low temperature were somewhat more precise than at the higher temperatures, expecially at apparent current densities below about 1.6 Amp/dm^2.

For given gelatin concentration, the relation of temperature to cathode polarization is quite analogous to that in the absence of gelatin. Since decrease of temperautre corresponds to an increased effect of added gelatin on the cathode polarization at given apparent current density (fig.13)

EFFECT OF GELATIN ON CATHODE POLARIZATION AT 2.0°C



Temperature : 2°C.
Solutions : No. 25 (Curve A) no gelatin.
No. 26 (Curve B) 1 mg./L of gelatin
No. 27 (Curve C) 5 mgs./L of gelatin.

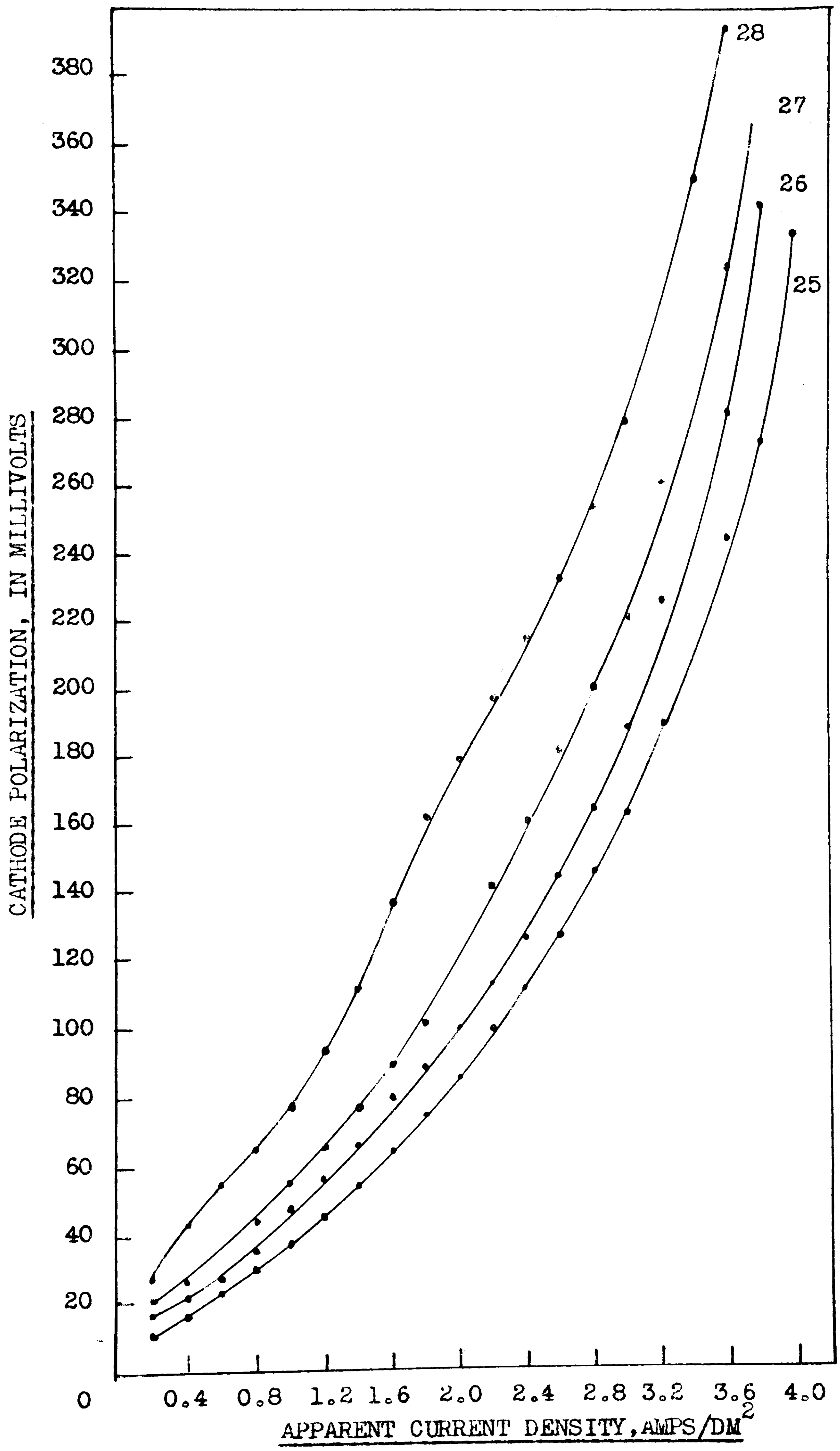
FIG. 10

TABLE X

EFFECT OF GELATIN ON CATHODE POLARIZATION AT 2.0°C

Current Density Amp/dm^2	Cathode Polarization, millivolts		
	Sol'n 25 no gel.	Sol'n 26 1 mgL	Sol'n 27 5 mg/L
0.2	72.1	99.4	124.8
0.4	108.4	134.4	174.2
0.6	136.7	164.5	210.2
0.8	162.2	186.8	241.3
1.0	181.6	209.3	265.2
1.2	201.2	228.0	289.9
1.4	226.9	251.8	317.5
1.6	263.1	284.8	353.0
1.8	332.0	352.3	421.0

EFFECT OF GELATIN CONCENTRATION ON CATHODE POLARIZATION AT 24.8°C



Temperature: 24.8°C.
Solutions : No. 25 (no gelatin)
No. 26 (1 mg./L of gelatin)
No. 27 (5 mgs/L of gelatin)
No. 28 (10 mgs/L of gelatin)
Initial Surface: Standard Base.

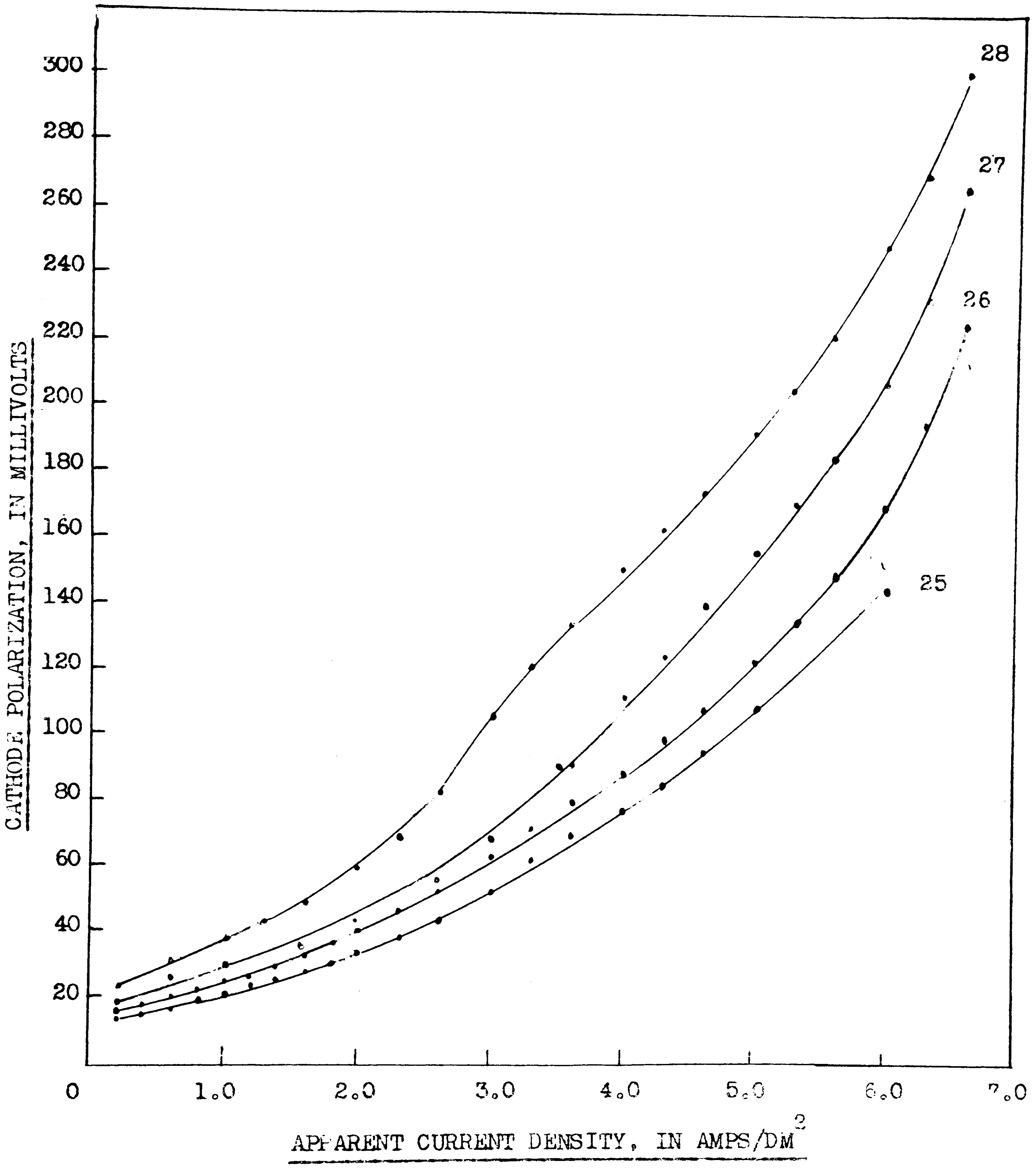
FIG. 11

TABLE XI

EFFECT OF GELATIN CONCENTRATION ON CATHODE POLARIZATION AT 24.8°C

Current Density Amps/dm^2	Cathode Polarization, millivolts Sol'n 25 no gel.	 Sol'n 26 1 mg/L	 Sol'n 27 5 mgs/L	 Sol'n 28 10 mgs/L
0.2	10.9	17.2	21.0	27.6
0.4	16.8	22.3	26.6	43.0
0.6	23.3	26.9	28.8	55.0
0.8	29.7	36.8	43.5	63.8
1.0	37.3	46.8	55.2	77.2
1.2	44.6	58.1	65.7	93.0
1.4	53.9	67.2	76.9	111.8
1.6	63.8	80.2	88.8	138.0
1.8	74.7	88.5	101.3	162.2
2.0	84.8	101.8	118.9	178.7
2.2	98.7	114.0	141.5	197.3
2.4	109.8	129.1	161.3	215.1
2.6	126.9	147.5	180.9	232.8
2.8	145.9	165.5	200.6	253.9
3.0	162.8	193.7	221.1	279.0
3.2	190.3	226.3	262.1	-----
3.4	-----	-----	-----	349.9
3.6	244.8	283.3	325.3	393.9
3.8	272.6	342.8	406.6	-----
4.0	334.5			

Note: Blank spaces indicatethat the measurements could not be made within the time allotted.



TEMPERATURE: 50.1°C.
SOLUTIONS : No. 25 (no gelatin)
No. 26 (1 mg./L of gelatin)
No. 27 (5 mgs/L of gelatin)
No. 28 (10 mgs/L of gelatin)
Initial Surface : Standard Base.

FIG. 12

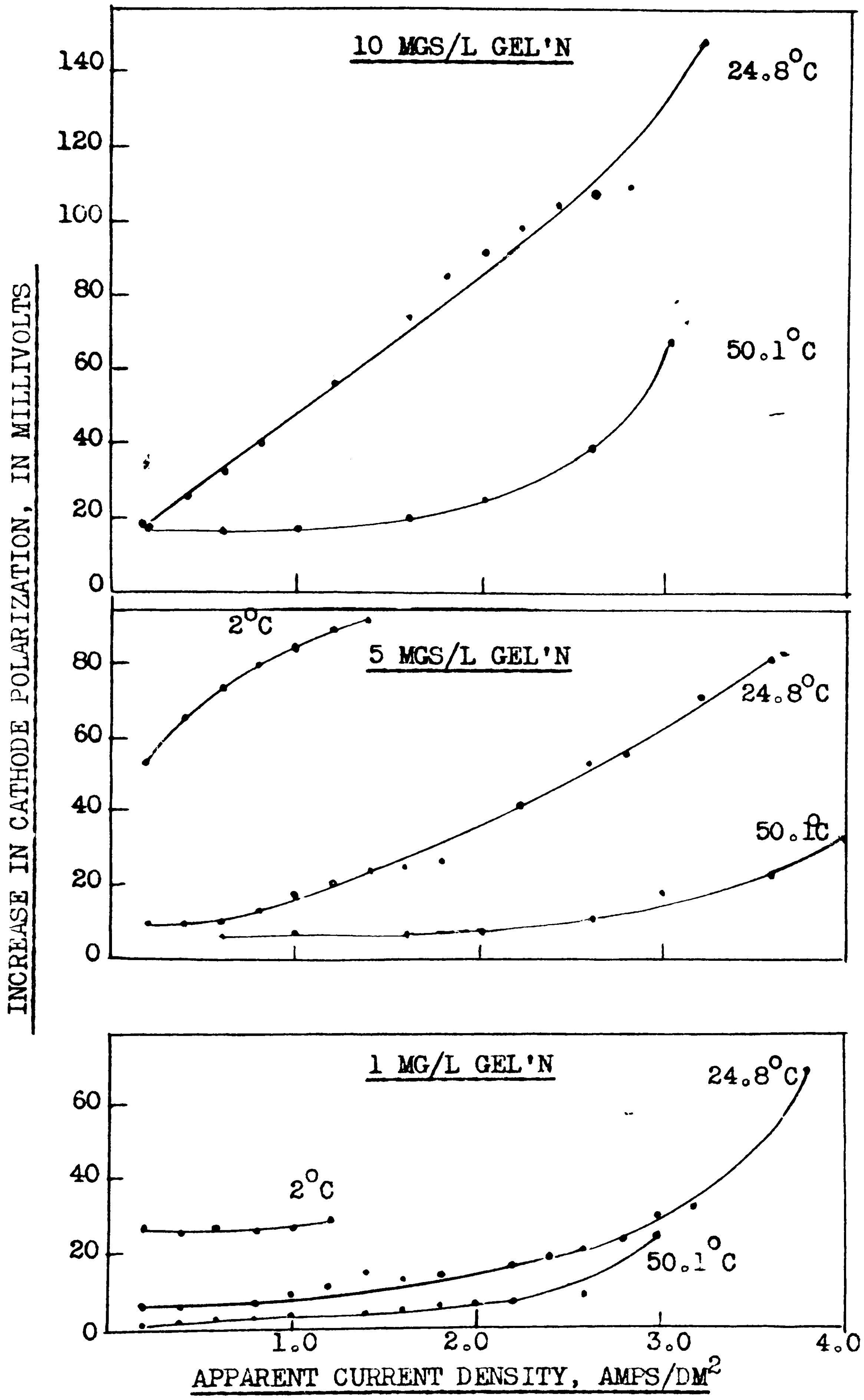
EFFECT OF GELATIN CONCENTRATION ON CHATODE POLARIZATION AT 50.1°C

TABLE XII

EFFECT OF GELATIN CONCENTRATION ON CATHODE POLARIZATION AT 50.1°C

Current Density Amp/dm^2	Cathode Polarization, millivolts			
	Sol'n 25 no gel.	Sol'n 26 1 mg/L	Sol'n 27 5 mgs/L	Sol'n 28 10 mg/L
0.2	13.9	14.6	-------	-----
0.4	15.1	17.3	20.2	28.1
0.6	16.5	20.1	25.7	32.4
0.8	18.4	21.5	27.2	35.8
1.0	20.6	24.5	28.6	37.6
1.2	23.9	24.6	29.9	41.5
1.4	25.1	29.3	----	----
1.6	27.6	32.2	34.5	48.4
1.8	30.0	36.0	38.2	----
2.0	33.5	40.0	40.3	59.4
2.3	38.3	46.1	45.9	68.8
2.6	43.1	52.4	53.8	82.4
3.0	37.1	62.5	67.5	106.0
3.3	60.5	70.8	79.0	120.0
3.6	68.9	79.0	91.3	132.6
4.0	77.7	87.1	110.9	149.8
4.3	85.3	97.9	123.4	162.3
4.6	94.1	106.8	139.7	173.9
5.0	106.7	122.4	156.1	191.9
5.3		134.5	170.2	204.7
5.6		149.3	184.8	220.7
6.0		170.0	208.2	249.1
6.3		195.2	232.9	270.2
6.6		225.5	267.0	300.6
7.0			340.2	

INCREASE IN CATHODE POLARIZATION DUE TO DIFFERENT CONCENTRATIONS OF GELATIN AT DIFFERENT TEMPERATURES



Increase in cathode polarization due to 3 concentrations of gelatin, at various current densities and temperatures.

Solutions : No. 25 (no gel'n, basis of comparison).
No. 26 (1 mg./L of gelatin)
No. 27 (5 mgs/L of gelatin)
No. 28 (10 mgs/L of gelatin)

FIG. 13

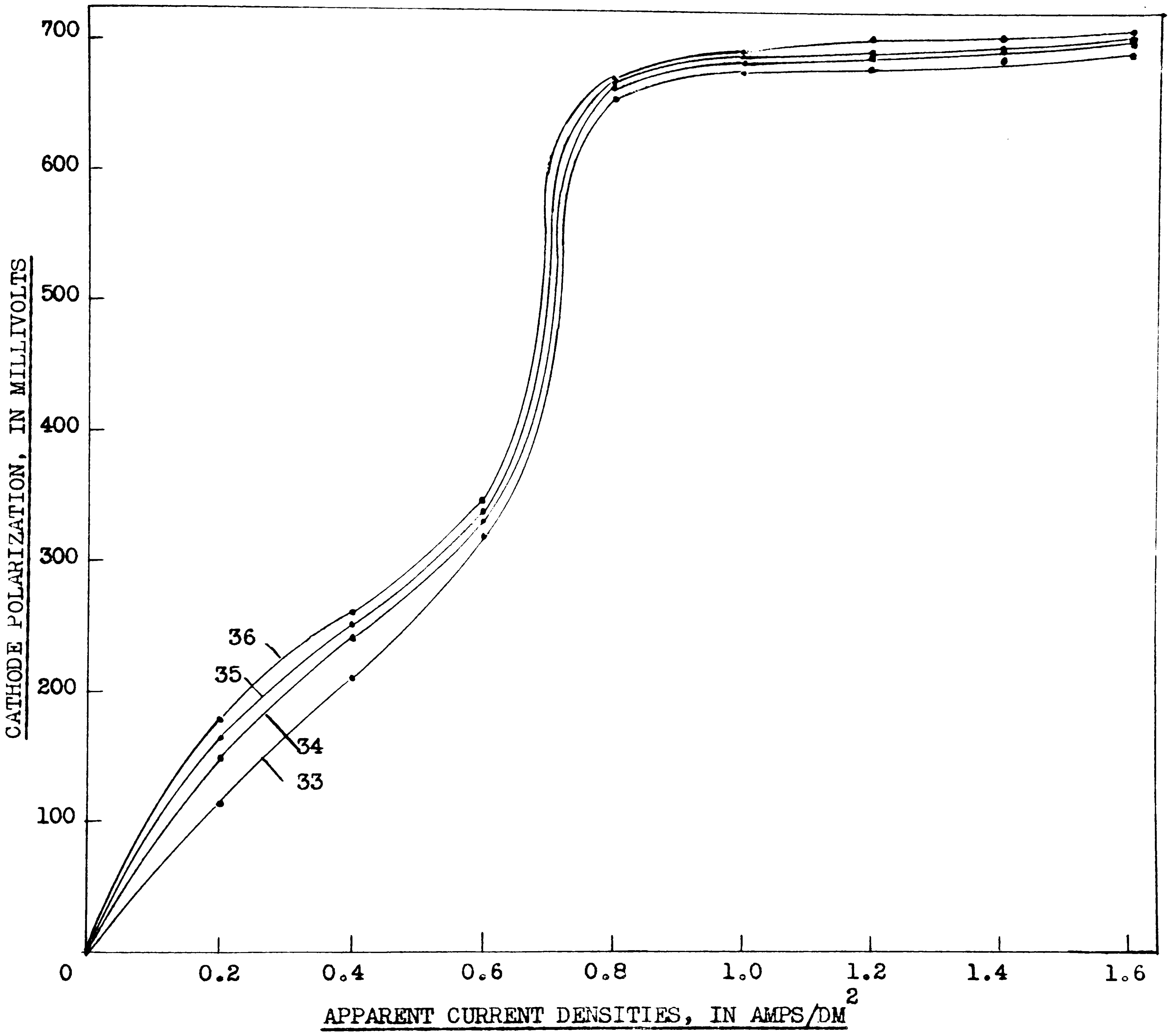
it was considered worth while to attempt measurements near the freezing point of the electrolyte. Temperatures were controlled within 0.3°C by adding dry ice to acetone as the thermostat liquid. Preliminary experiments showed that at a given temperature, the anode polarization increased enormously when a definite value of the apparent current density was attained. This "passivity" was soon traced to the precipitation of copper sulphate on the anode from the anode film. The relation between temperature and apparent current density at which precipitation occurred was determined approximately to be:

Temperature °C	Apparent C.D. at which precipitation occurred
-8.2	0.6 Amp/dm^2
-6.2	1.0 "
-4.0	1.4 "
-3.8	1.8 "

The behaviour is interesting in relation to the composition of the anode film, and a more detailed study of it is contemplated.

For purposes of the immediate investigation, difficulties arising from the precipitation of copper sulphate on the anode were circumvented by using an electrolyte containing only half the amount of copper sulphate pentahydrate used in the previous studies. The acid content was maintained at 150 gms/L, however, in order to have high conductivity, and also to depress the freezing point of the electrolyte. (Solutions No. 33, 34, 35 and 36. See Table VI).

Measurements were made at -4.2°C, with the results shown in fig.14. Hydrogen evolution invariably occurred at apparent current densities greater than 0.6 Amp/dm^2. This caused fluctuations in the cathode polarization values. It could be observed that, during formation of hydrogen bubbles on the cathode, the polarization increased 5-6 millivolts above a mean value,



Temperature : -4.2°C.
Initial Surface : Standard Base.
Solutions : No. 33 (no gelatin).
No. 34 (0.5 mg./L of gelatin)
No. 35 (1.0 mg./L of gelatin)
No. 36 (2.5 mgs/L of gelatin)

FIG. 14

EFFECT OF GELATIN ON CATHODE POLARIZATION AT -4.2°C

TABLE XIII

EFFECT OF GELATIN CONCENTRATION ON CATHODE POLARIZATION AT -4.2°C

Current Density Amp/dm^2	Cathode Polarization, millivolts			
	Sol'n 33 no gel.	Sol'n 34 0.5 mg/L	Sol'n 35 1.0 mg/L	Sol'n 36 2.5 mg/L
0.2	112.0	149.3	163.8	177.3
0.4	210.4	239.1	250.4	259.7
0.6	317.9	330.4	338.1	348.1
0.8	658.6	670.4	670.3	674.5
1.0	678.5	683.7	685.3	694.6
1.2	683.2	689.7	692.7	705.8
1.4	689.7	696.3	697.9	707.9
1.6	696.3	706.3	705.7	710.0
1.8	708.4			

followed by a decrease of similar amount when a sheet of hydrogen bubbles became detached from the electrode. The plotted polarization values for apparent current densities in excess of 0.6 Amp/dm^2, therefore, must be regarded as approximate only. The values for lower current densities were very reproducible, however, with no fluctuations detectable. The effect of added gelatin on the cathode polarization is slightly more pronounced at the temperature of this experiment than at the higher temperatures used in preceding experiments.

DISCUSSION

The main point of interest in the present study probably concerns the utility of the Haring cell as an instrument for determination of addition agent concentration in electrolytic baths. Obviously, it can be useful only when the addition agent produces a change in the cathode polarization. Where such an effect is observed, the accuracy with which addition agent concentration may be determined will, of course, depend upon the magnitude of the change in polarization with given amount of addition agent. The results which have been presented show that the concentration of gelatin in an electrolytic bath might be determined within 0.25 to 1 mg per litre, depending upon the temperature used.

It must be emphasized, however, that reproducibility of the polarization measurements appears to be contingent upon using a cathode to which standard surface conditions have been imparted (standard base), by electrolyzing in a standard electrolyte under definite conditions, until equilibrium polarization values are obtained.

From the results presented, it would appear that the sensitivity of the Haring cell as a method of control could be increased in two ways:

(a) by working at low temperatures;

(b) by diluting the solution.

Fig. 13, which gives the relative increase in cathode polarization resulting from addition of various amounts of gelatin, clearly shows that at any given current density and given gelatin concentration, these increments are considerably larger, the lower the temperature.

Figs. 9, 10, 11, 12 and especially 14, all clearly show that the relative increase in cathode polarization due to the addition of a small amount of gelatin to a solution containing none of it, is much greater than the increase noted when the same amount of gelatin is added to a solution already containing some of this addition agent. Since the experimental error - which, in the above studies, never exceeded ± 4 millivolts - must always be taken into account, it is obvious that diluting the solution will bring the concentration in addition agent within a range where the effect of the latter on the cathode polarization is considerably greater than the experimental error. This is essentially what was done when making measurements at -4.2°C.

From a commercial point of view, since glue, and not gelatin, is used as the addition agent, it will be necessary to re-determine the relations between cathode polarization and current density in terms of increasing concentrations of glue, and which may vary slightly from those reported for gelatin. It is quite possible that these relations may even vary for different makes of glue. It is interesting to note that slight variations in the Ni, As, Fe and Cl content of a commercial electrolyte should not affect the cathode polarization determination, as it was shown that small changes in their concentration have practically no effect on the latter. (110).

Another point of interest arising from the present study concerns the shape and equation of the cathode polarization curves. It was observed that the curve : log of the cathode polarization versus the log log of the current density, was linear over a considerable range of current densities. This applied to all the polarization curves, obtained in electrolytes containing gelatin as well as in electrolytes without addition agent. Allowing for the fact that the method followed did not permit attainment of equilibrium polarization values within the time allotted for a very few points of the polarization curves in the lower current density range, the range of linearity was noted to extend, for fig. 9, from .6 to 3 A/dm2; for fig. 10, from .2 to 1.2 Amp/dm^2; for fig. 11, from .2 to 2.4 Amps/dm^2; for fig. 12, from .2 to 5 Amps/dm^2; and for fig. 14, from .2 to .6 Amp/dm^2. Over the range in which this linear relation applied, the equation of the polarization curves conformed to the expression:

$$P = K_1 + K_2 (\log D)^n$$

where P is the cathode polarization, D is the apparent current density, K_1, K_2 and n are constants for any one curve.

Volmer showed that for the metals Zn, Cd, Ni, Pb, Bi, Cu and Ag, there was a linear relation between cathode polarization and current density, for very small values of the latter. From this relation, Volmer concluded that the rate at which the layers of metal spread from the corners and edges of a crystal over its faces, was the determining factor in the overall deposition process. (43). It can assumed, therefore, that - allowing for the presence of the concentration polarization values in the polarization values determined with the Haring cell - at some point in the low current density range, between a very low value of the apparent current density and the value .2 Amp/dm^2, a change in one of the deposition processes takes place, following which the two-dimensional growth of the nuclei postulated by Volmer is no longer the determining factor.

PART III

SURFACE EFFECTS IN THE PRESENCE OF GELATIN

INTRODUCTION

It was shown in Part I that the cathode polarization at different specimens of copper cathodes, polished in the same way, changed with time in a manner which differed with different specimens. It was found, however, that under closely controlled conditions of electrolysis, the polarization eventually assumed a constant or equilibrium value.

In the course of determining whether the same equilibrium value of the polarization would be attained under given conditions of electrolysis, regardless of the initial condition of the cathode surface, an experiment was made in which a very finely crystalline surface was imparted to the cathode by electrolyzing to equilibrium polarization in an electrolyte to which gelatin had been added. It was expected, in conformity with the behaviour shown in other experiments, that, using such a cathode, and electrolyzing under conditions that normally led to a more coarsely crystalline surface, would result in a gradual increase in polarization to the equilibrium value. However, a decrease, not an increase in polarization, was in fact observed. This observation prompted a more detailed study of the behaviour, the results of which are presented in this section.

EXPERIMENTAL

The apparatus and technique employed were similar, in all respects, to those described previously.

Prior to each experiment, the desired surface condition was imparted to the cathode by electrolyzing in appropriate electrolyte under controlled conditions of apparent current density and temperature, until equilibrium polarization was established. When the desired surface was thus obtained, the electrolyte used in obtaining this cathode specimen was replaced by the new solution investigated, and the cathode polarization determined as a function of time at a constant apparent current density.

RESULTS

Experiments were first made using cathodes to which definite surface characteristics were imparted by electrolyzing to equilibrium polarization, with gelatin in the electrolyte.

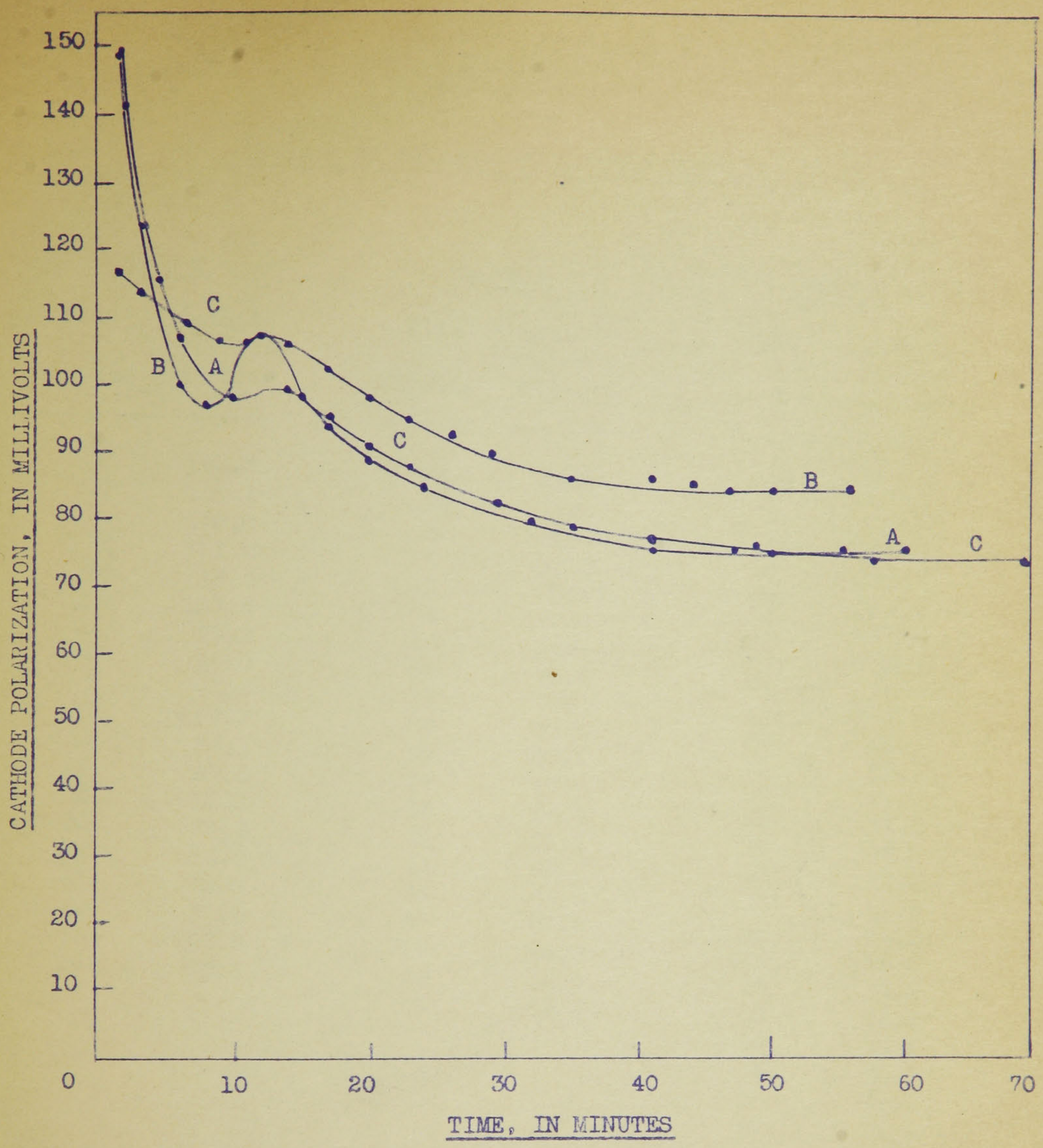
Two cathode types were prepared, using two different electrolytes, one containing 10 mgs/L of gelatin (Solution No. 20, see Table VI), the other containing 750 mgs/L of gelatin (Solution No. 23). The first was obtained at an apparent current density of 4.2 Amps/dm^2, and the other at 4.0 Amps/dm^2. A third specimen was prepared, using an electrolyte of higher acidity, but containing only 2 mgs/L of gelatin (Solution No. 37), at an apparent current density of 2 Amps/dm^2. These three different treatments gave cathodes, the surfaces of all of which were quite finely crystalline; the first two, however, seemed to be somewhat finer than the third, obtained with a lower gelatin concentration, while no difference could be detected between the first two, at least when examined under the microscope with x 50 magnification.

The cathodes so prepared were then used during electrolysis at 26.4oC with an apparent current density of 2 Amps/dm^2, in the standard electrolyte (Solution No. 17), containing no gelatin.

Data for the change in cathode polarization with time for the three surfaces are plotted in fig. 15, curves A, B and C, respectively. Two points of experimental interest may be noted: A slight increase, followed by a decrease in cathode polarization after approximately 12 minutes electrolysis began, a behaviour which has already been observed in Part I. Also, taking into account small differences in the temperatures at which the experiments were made, the equilibrium polarization values eventually attained (76 - 84 millivolts) are essentially the same as the equilibrium values previously recorded for electrolysis from the standard electrolyte under similar conditions of apparent current density and temperature. The final surfaces had the same characteristics as the standard base previously obtained in Part I.

The courses of the curves in attaining the equilibrium polarization were completely unexpected, and confirmation was sought by varying the experimental details. An experiment was made in which the cathode was first given a relatively fine crystalline surface condition by electrolyzing at an apparent current density of 2 Amps/dm^2 and temperature of 26.4°C, to equilibrium polarization in an electrolyte containing 2 mgs/L of gelatin (Solution No. 37). This fine surface was then used as the cathode in electrolysis to equilibrium polarization in the standard electrolyte (Solution No. 17), under the same conditions. The change of cathode polarization with time during the latter electrolysis is plotted in fig. 16, curve A. Again, the cathode polarization decreased with time, while visual observation easily revealed that the surface of the cathode had become considerably more coarsely crystalline and had acquired the surface characteristics of the standard base.

The electrolyte was then changed to one containing 10 mgs/L of gelatin (Solution No. 28), and electrolysis resumed at an apparent current



Solution No. 17.
Apparent Current Density: 2 Amps/dm^2.
for curve A: Temperature: 26.4°C.
Initial Surface: that obtained in Solution No. 20 (10 mgs/L of gelatin) at 4.2 Amps/dm^2
for curve B: Temperature: 25.3°C.
Initial Surface: that obtained in Solution No. 23 (750 mgs/L of gelatin) at 4 Amps/dm^2.
for curve C: Temperature: 26.4°C.
Initial Surface: that obtained in Solution No. 37 (2 mgs/L of gelatin) at 2 Amps/dm^2.

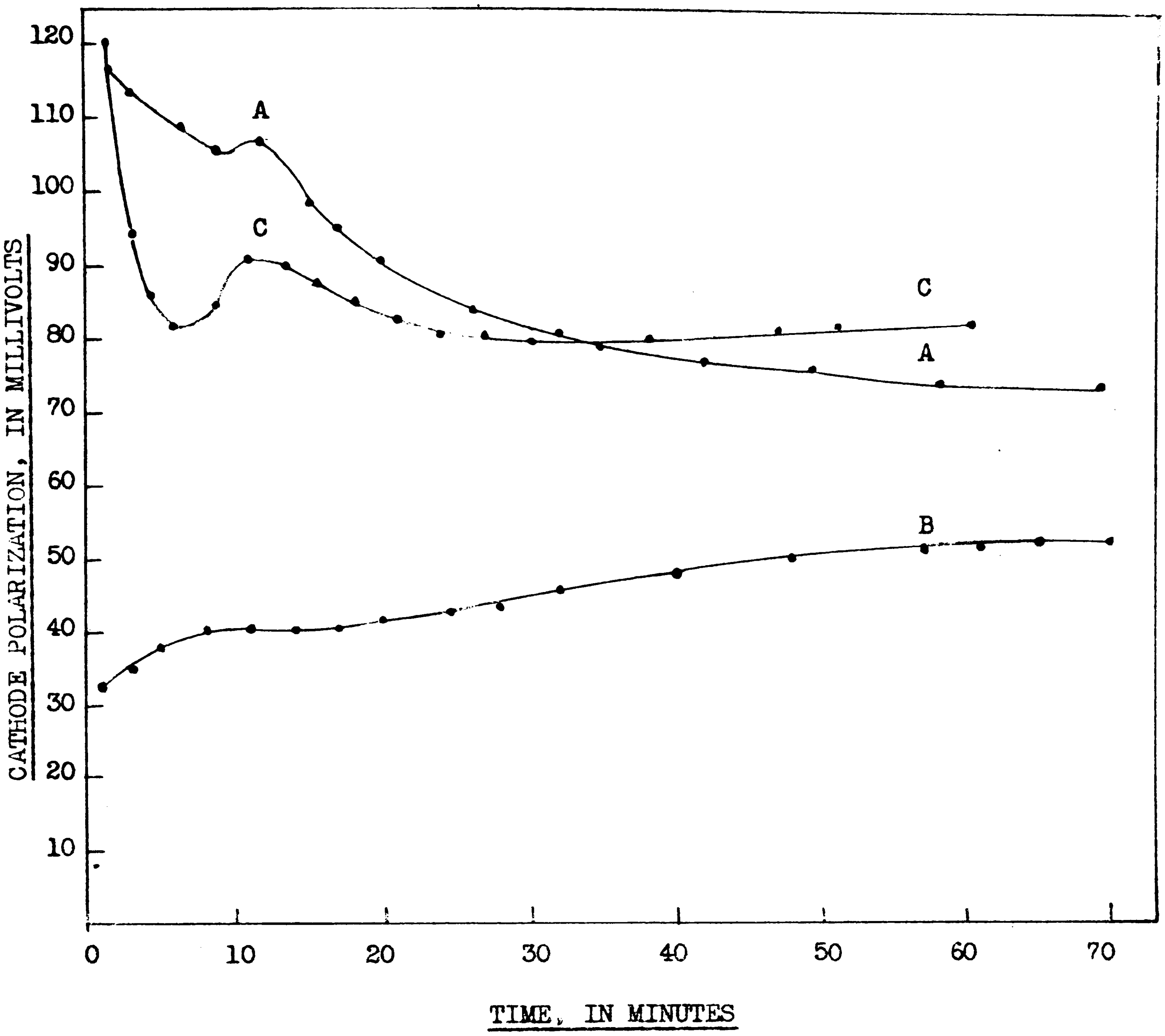
FIG. 15

EFFECT OF GELATIN ON CATHODE SURFACE

TABLE XIV

EFFECT OF GELATIN ON CATHODE SURFACE

CURVE A		CURVE B		CURVE C	
Time minutes	Cathode Polar'n millivs	Time minutes	Cathode Polar'n millivs	Time minutes	Cathode Polar'n millivs
½	168.7	1½	148.6	1½	117.0
1½	149.1	3½	123.9	3	113.8
2	140.8	6	100.3	6½	109.1
3½	123.5	8	97.3	9	106.0
4½	118.5	11	106.6	12	107.0
6	107.4	14	105.9	15	98.2
10	97.9	17	102.4	17	94.9
14	99.0	20	98.5	20	90.6
17	93.8	23	95.1	23	87.0
20	89.3	26	93.0	26	84.2
24	88.1	29	89.7	29	82.4
28	82.5	32	87.6	32	81.0
32	79.8	35	86.6	35	79.5
36	77.3	38	86.9	38	78.7
41	76.0	41	86.8	42	77.5
45	75.9	44	85.8	45	77.0
50	75.5	47	85.2	49	76.0
55½	75.9	50	85.6	55½	75.2
60	75.9	53	86.0	58	74.3
		56	85.4	63	73.9
				68	73.6
				74	73.5
				78	73.6
				90	74.6



Temperature: 26.4°C.
for Curve A: Solution 17.
Current Density: 2 Amps/dm^{2}
Initial Surface: that obtained after 62 mins. deposition from Solution No. 37 (2 mgs/L of gelatin)
for at an apparent current density of 2 Amps/dm^{2}.
for Curve B: Solution: No. 28 (10 mgs/L of gelatin)
Apparent Current Density: 0.5 Amp/dm^{2}
Initial Surface: Standard Base (obtained at the end of curve A).
for Curve C: Solution No. 17.
Apparent Current Density: 2 Amps/dm^{2}.
Initial Surface: that obtained at the end of curve B, above.

FIG. 16

EFFECT OF GELATIN ON CATHODE SURFACE

TABLE XV

EFFECT OF GELATIN ON CATHODE SURFACE

CURVE A

Time minutes	Cathode Polar'n millivs
1½	117.0
3	113.8
6½	109.1
9	106.0
12	107.0
15	98.2
17	74.9
20	90.6
23	87.0
26	84.2
29	82.4
32	81.0
35	79.5
38	78.7
42	77.5
45	77.0
49	76.0
55½	75.2
58	74.3
63	73.9
68	73.6
74	73.5
78	73.6
90	74.6

CURVE B

Time minutes	Cathode Polar'n millivs
1	33.1
2	34.2
3	35.0
5	37.9
8	40.3
11	40.6
14	40.2
17	40.6
20	41.4
24	42.7
28	44.4
32	45.9
36	47.3
40	48.3
44	49.5
48	50.0
53	50.8
57	51.6
61	52.2
65	52.8
70	52.7

CURVE C

Time minutes	Cathode Polar'n millivs
1½	120.2
3	94.6
4½	86.2
6	82.1
9	84.6
11½	90.8
13½	90.1
15½	88.0
18	85.0
21	82.8
24	81.2
27	80.2
30	79.8
34½	79.7
38	80.0
42	80.6
47	81.3
51	82.0
56	82.4
60½	82.4

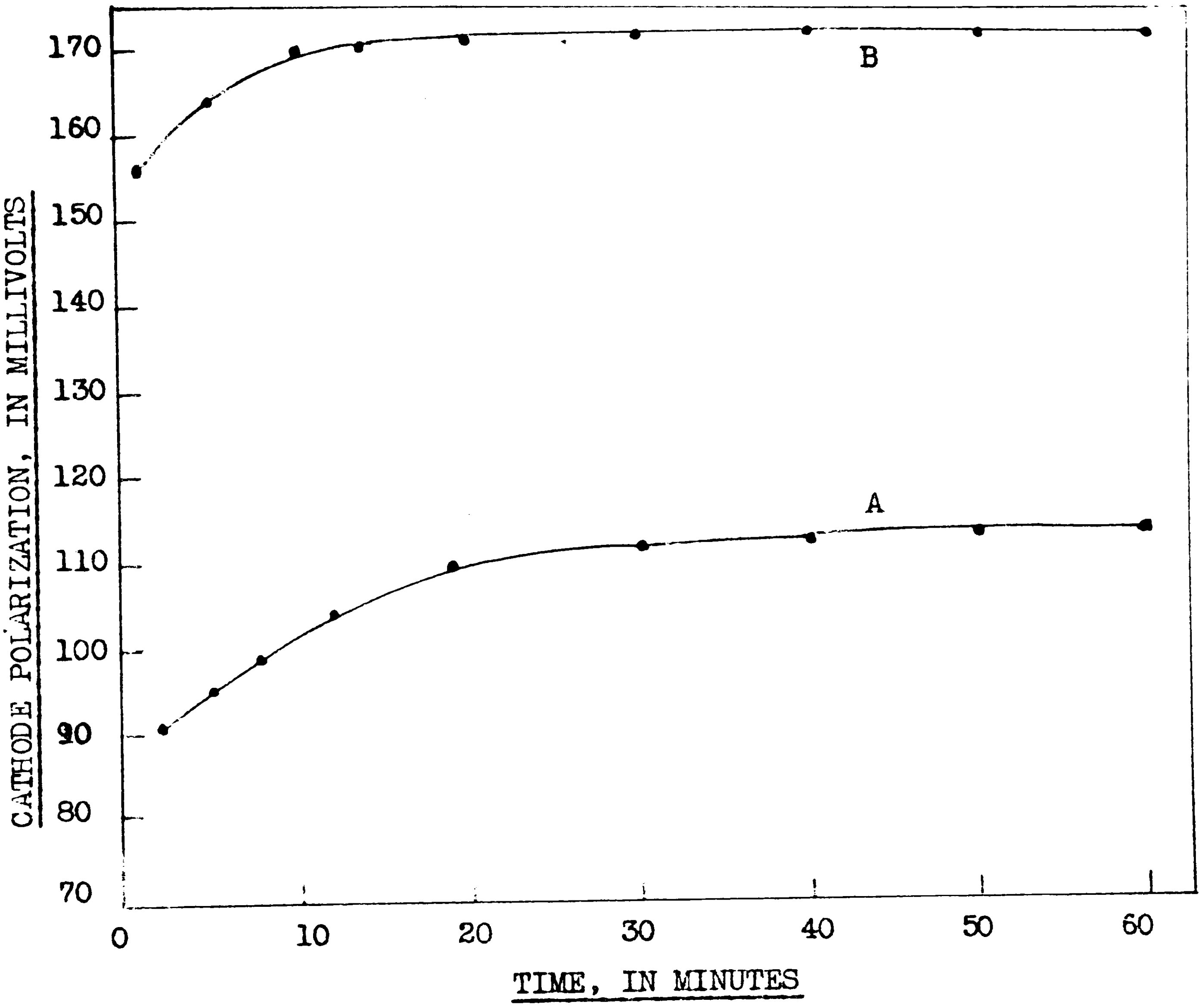
Note: Curve A of fig. 16 is the same as curve A of fig. 15

density of 0.5 Amp/dm^2, until equilibrium polarization was again reached. The cathode polarization now showed a marked increase with time, as indicated by Curve B, fig. 16. Inspection showed that surface condition had changed from the coarsely crystalline structure of the standard base, to a very finely crystalline surface.

The solution was then changed back to the standard electrolyte (Solution No. 17), containing no gelatin, and electrolysis continued at an apparent current density of 2 Amps/dm^2, until equilibrium polarization values were again obtained. The polarization again decreased with time, curve C, fig. 16, attaining essentially the equilibrium value generally found for electrolysis under standard conditions, and again the surface had changed to the more coarsely crystalline condition of the standard base.

Further information was obtained by working with solutions containing various amounts of gelatin. The surface of a cathode was conditioned by electrolyzing at an apparent current density of 2 Amp/dm^2 until equilibrium polarization was attained, using an electrolyte containing 1 mg/L of gelatin (Solution No. 26). On this visibly fine-grained surface, a deposit appearing even finer to the naked eye was obtained, using the same apparent current density, but with an electrolyte now containing 5 mgs/L of gelatin (Solution No. 27). The increase of cathode polarization with time during deposition of this finer deposit is shown in fig. 17, curve A. The gelatin content of the electrolyte was increased further to 10 mgs/L (Solution No. 28), other conditions remaining the same, and the cathode polarization increased with time, in accordance with curve B, of fig. 17. No change in fineness of surface structure was apparent following the last electrolysis, at least with x50 magnification.

Having observed the manner in which the presence of gelatin influenced



Temperature: 25°C.
Apparent Current Density: 2 Amps/dm^2
<u>for Curve A:</u> Solution No. 27 (5mgs/L of gelatin) Initial surface: that obtained after 60 mins. deposition from Solution 26 (1 mg/L of gelatin) under similar conditions.
<u>for Curve B:</u> Solution No. 28 (10 mgs/L of gelatin) Initial Surface: that obtained at the end of curve A, above.

FIG. 17

EFFECT OF GELATIN ON CATHODE SURFACE

TABLE XVI

EFFECT OF GELATIN ON CATHODE SURFACE

CURVE A

Time minutes	Cathode Polar'n millivs
2	90.7
5	94.9
8	98.8
12	103.8
19	109.7
30	111.9
40	113.2
50	114.3
60	114.0

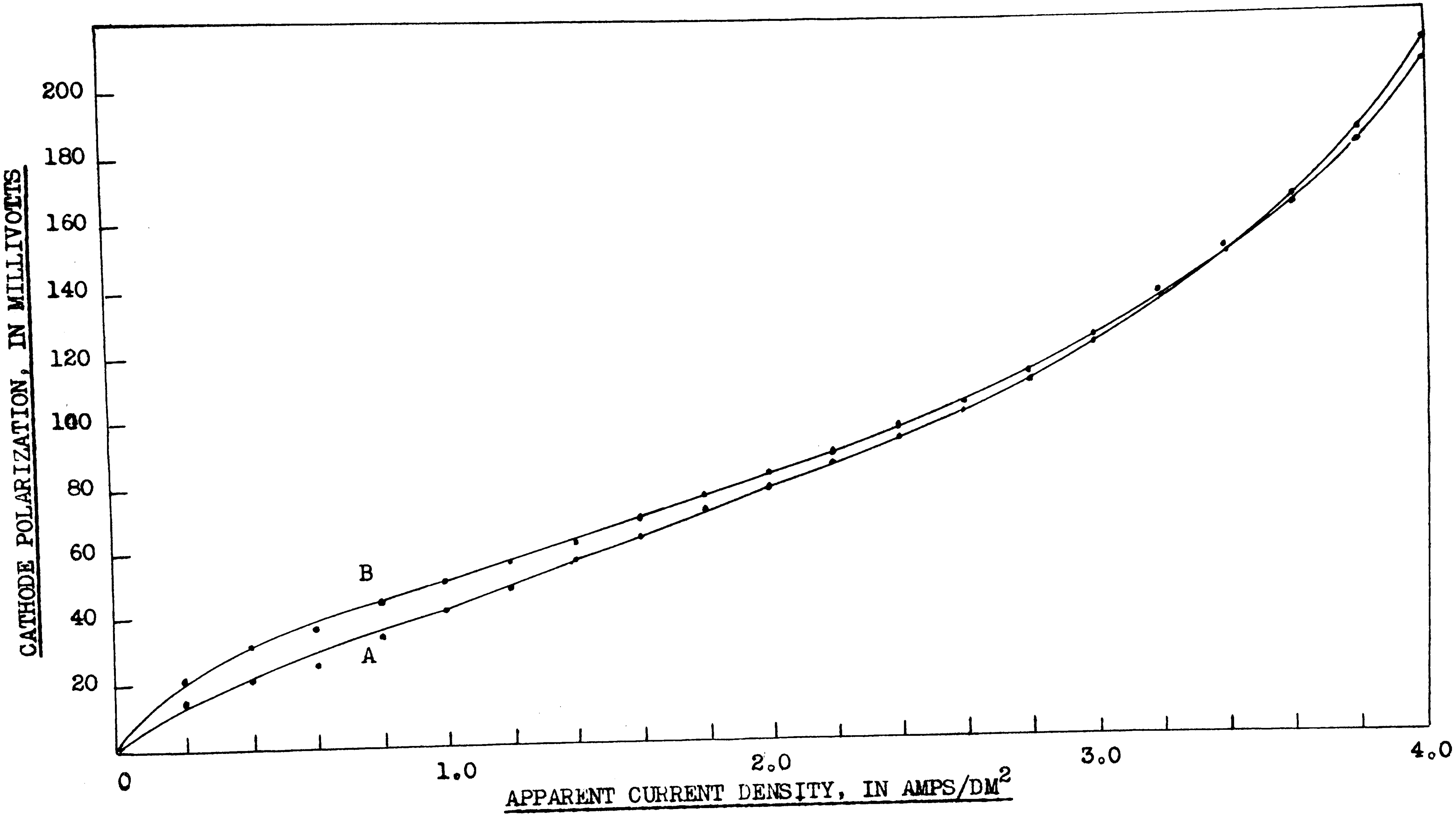
CURVE B

Time minutes	Cathode Polar'n millivs
1	155.9
5	163.8
10	170.2
14	170.0
20	171.1
30	171.9
40	172.0
50	172.3
60	172.3

the shape of the polarization - time curves under various conditions, it was of interest to determine how the behaviour might be reflected in the relation between cathode polarization and current density. The procedure for establishing this relation has been dealt with at the end of Part I (fig. 6) and followed throughout the experiments of Part II. One cathode was brought to standard surface condition, by electrolysis at an apparent current density of 2 Amps/dm^2 in the standard electrolyte (Solution No.17), until equilibrium polarization. A second cathode was given different, but again definite surface characteristics by electrolysis to equilibrium polarization at the same current density, using an electrolyte containing 2 mgs/L of gelatin (Solution No. 37), the final surface having assumed a fine crystalline structure. The relation between cathode polarization and apparent current density was then established for each cathode in the standard electrolyte, under standard conditions. The results are shown in fig. 18, curve A representing the cathode polarization - apparent current density curve, using the standard base as initial surface, and curve B, using the much finer-grained cathode as the initial surface. The interesting feature of the two curves is that the cathode polarization is considerably higher at lower current densities when deposition takes place on the surface laid down initially in the presence of gelatin, in spite of the fact that this surface was finer than the other. At higher current densities, the discrepancies disappear.

FIG. 18

EFFECT OF INITIAL SURFACE ON CATHODE POLARIZATION MEASUREMENTS



Temperature: 25°C.
Initial Surface: for (A) Standard Base.
for (B) Different Base.
Solution: No. 17 (for both curves).

TABLE XVII

EFFECT OF INITIAL SURFACE ON CATHODE POLARIZATION MEASUREMENTS

Current Density Amp/dm^2	Cathode Pol'n,mVs.	
	Curve A Std.Base	Curve B New Base
0.2	11.7	21.6
0.4	21.0	31.3
0.6	25.7	37.0
0.8	32.2	45.2
1.0	43.8	51.2
1.2	49.0	56.1
1.4	56.9	62.3
1.6	63.2	69.1
1.8	69.2	75.9
2.0	78.1	82.3
2.2	86.2	88.7
2.4	96.3	96.0
2.6	102.3	102.7
2.8	111.4	112.1
3.0	123.4	122.3
3.2	136.4	135.2
3.4	147.9	147.5
3.6	165.2	162.0
3.8	183.7	180.7
4.0	216.1	204.9

DISCUSSION

It was shown in Part I that a decrease in crystal size caused a decrease in cathode polarization values. This behaviour was logically attributed to an increase in the true area of the cathode, with a consequent decrease of the true current density at which deposition was actually taking place.

However, the experiments reported in this section, and made in the presence of gelatin show exactly the opposite effect, whether the decrease in grain size was from a coarsely crystalline surface to a fine one (fig. 16, curve B), or from a fined-grained surface to a still finer-grained one (fig. 17, curves A and B). The opposite change in surface, from a finely crystalline structure to a coarsely-grained one, normally accompanied by an increase in cathode polarization (see fig. 3, curve C), actually resulted in a decrease in cathode polarization in the presence of gelatin (figs 15 and 16, curves A and C). It is evident, therefore, that since a fine structure is always associated with a large true area (Part I), gelatin must be able to impart to such a fine-grained surface the characteristics normally associated with a coarser surface of smaller true area. The only explanation that can be advanced to reconcile the results obtained is that not all of the surface is active during deposition but only a certain fraction of it, which may be called the "active surface", and which is susceptible of being decreased by gelatin. It may be noted that Volmer, in 1931, (43) showed that deposition always starts from crystal corners, although it may sometimes start from an edge, but never from a crystal face. He called these corners "active centers".

From results obtained in Part I, it can be said that the active area increases with the true area, which is logical in view of the greater number of these "active centers", present in a finer-grained deposit. From the results presented in the present section of the thesis, however, it is obvious that, although gelatin increases the true area, the active area is considerably reduced. This will result in an increase in the true current density, accompanied by an increase in cathode polarization. The relation existing between cathode polarization and true current density is not affected by the new concept, but the true current density is now determined, not by the true area, but by the active area.

Since an increase in current density is always accompanied by an increased rate of nuclear formation (50, 102), the very large increase in current density caused by the reduction in active area in the presence of gelatin greatly increases the nuclear formation, and will cause a decrease in the crystal size, i. e. result in a finer structure. Reduction of the active area of a deposit by gelatin is probably best explained by adsorption. Since deposition has been shown to begin at corners, and adsorption, whether "chemisorption", "van der Waals", or purely electrostatic, will logically be greater at these points, it is seen that adsorption of gelatin on these active centers will prevent further deposition of copper, and will cause a large reduction in the active area. This explanation accounts for the very small amount of gelatin needed to exert a beneficial action on the deposit. As little as a fraction of a mg/L radically changes the appearance of the deposit. A large amount, on the other hand, should, according to these views, so reduce the active area, or area available for deposition, that the large number of nuclei formed are allowed to grow only to a very small extent before gelatin covers the active centers, and the presence of gelatin on almost all the available active ceters by which the new crystals first develop should considerably reduce the adherence, resulting finally in a powdery deposit. It is known, in fact, that a large amount of gelatin is conducive to formation of a powdery deposit.

The assumption that adsorption is responsible for the reduction in active area of a deposit gains considerable support from the observation, reported in Part II, that the relative increase in cathode polarization, due to the presence of a given amount of gelatin is considerably greater at low temperature, where adsorption is greater. Similarly, the fact that adsorption of gelatin tends toward a maximum for given conditions of electrolysis (71, 79) is also parallelled by a similar observation for the cathode polarization. This would account for the fact that the reduction in active area, resulting in an increased fineness of the deposit, at first very rapid for small gelatin concentrations, decreases rapidly with increased amount of the addition agent, making the visual appraisal of the degree of fineness of a deposit difficult for the higher concentrations of gelatin. This is substantiated by the visual observations reported for experiments fig. 15 and fig. 17, and also, in a qualitative manner at least, by the fact that curves A and B, of fig. 15, obtained on surfaces deposited in solutions containing 10 and 750 mgs/L of gelatin, respectively, exhibited much larger initial cathode polarization for the same current density than curve C, obtained on a surface deposited from a solution containing only 2 mgs/L of gelatin. The larger cathode polarization, implying larger true current density for a given current, associated with smaller active area, shows that the surface laid down in an electrolyte containing 2 mgs/L of gelatin,had a larger active area (i.e. was coarser-grained) than the other two electrodes, with surfaces characteristic of electrolytes containing higher concentrations of gelatin.

It is interesting to note that the mechanism offered does not postulate any fundamental change in any of the deposition processes, the essential change being, in fact, an increase in the true current density in the presence of the gelatin. A confirmation of the fact that no radical change in the deposition process takes place in the presence of gelatin is very well shown by the fact that all cathode polarization curves obtained in Part II conform within a wide range of current density to the same equation, this fact being true whether the solution contains, or does not contain gelatin.

The results depicted in fig. 18 show that cathode polarization values obtained, using a finely crystalline base deposited from a solution containing gelatin as initial surface, are as much as 50% greater at low current densities than those obtained on the relatively coarse standard base (obtained from solution No. 17, containing no gelatin) while they are the same for both initial surfaces at high current densities. Wood (57) showed that the influence of the base metal disappears at higher current densities, and the results obtained are in full agreement with his findings in the upper range of the curve. The discrepancy noted at low current density can be ascribed, therefore, to the influence of the initial surfaces on which deposition was started. To explain the relative position of the two curves, however, the concept of the active area seems to be essential. Since the active area of the initial surface, obtained in presence of gelatin, is considerably smaller than the active area of the standard base, the true current density will be greater, and will be associated with a greater cathode polarization.

SUMMARY

1- It was shown that for constant, given conditions of temperature, apparent current density, metal ion concentration, acidity, apparent area of the electrodes, during the deposition of copper from acidified copper sulfate electrolytes and in the absence of gelatin, there corresponded a definite equilibrium value of the cathode polarization presumably associated with a definite value of the true area of the cathode surface.

2- The Haring cell can be depended upon to give reproducible cathode polarization values only when the final equilibrium surface, corresponding to the conditions under which electrolysis is conducted, has been attained.

3- A procedure was developed for the study of cathode polarization - apparent current density relations at, or near, the equilibrium values.

4- Using the Haring cell and following the procedure developed, the effect of temperature on cathode polarization was studied, the results indicating that there is a large increase in cathode polarization with a decrease in temperature from 24.8°C to 2°C, while a smaller increase was noted for a decrease from 50.1 to 24.8°C.

5- A similar study of the effect of acidity showed that an increase in acidity had little effect at apparent current densities below about 2 Amps/dm^2, except for low acidities (0 to 50 gms/l of sulphuric acid), while at current densities greater than 2 Amps/dm^2, an increase in acidity resulted in an increase in cathode polarization.

6- The effect of increasing concentrations of gelatin on the cathode polarization curves were studied at -4.2°, 2°, 24.8° and 50.1°C, and were observed to increase the cathode polarization, the proportional increase being greater at lower temperature, and the relative increase in cathode polarization being greater at smaller gelatin concentrations. From these data, it was concluded that the accuracy and sensitiveness of the Haring cell - used as a method of control of gelatin or glue concentration in an electrolyte - will be considerably increased by making the cathode polarization measurements at low temperatures and in dilute solutions.

7- The true current density under which electrolysis was actually conducted, as opposed to the apparent current density, was shown to increase in the presence of gelatin, with decrease in the active area of the cathode surface, this active area decreasing with increasing concentrations of gelatin in the electrolyte, presumably owing to adsorption of the addition agent. This was assumed to be the main factor in causing a decrease in the grain size and an increase in the rate of nuclear formation. In the absence of gelatin, the "true area" is directly proportional to the "active area", a decrease in grain size being invariably accompanied by an increase in true area when no addition agent is present.

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