A Study of The Cathode Polarisation Potential

Of Silver In Silver Nitrate Solutions.

A Thesis submitted to the University of London
for the Degree of Doctor of Philosophy.

by

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The cathode polarisation potential of silver in aqueous silver nitrate solutions under varying conditions of concentration; current density; and agitation has been studied. It has been shown that, for the system under consideration, the half-cell method leads to the most reproducible results. Various types of addition agent (organic and inorganic) have been examined, both with regard to their effect on the polarisation, and also on the nature of the deposit. These addition agents may be divided into two classes, on a basis of their effect on the deposit. The first class, which consisted of glucose; thiourea; thioglycollic acid; the wetting agents; and the inorganic cations, had practically no effect on the deposit, while the second class (citric, tartaric and aminoacetic acids and gelatine) all caused a marked decrease in the grain size of the deposit. As a development of this, bright deposits of silver were obtained from solutions of silver nitrate by the addition of large quantities of aminoacetic acid, and traces of other addition agents, under carefully controlled experimental conditions.

An investigation has been made of the effect of different planes of a silver single crystal on the polarisation and nature of the deposit, when only one
crystal plane was available for deposition. The deposits obtained have been examined by X-ray diffraction methods, and it has been shown that there are no significant structural differences between smooth and bright deposits.

Finally, it has been shown that the adsorption theory of electrodeposition provides the most comprehensive qualitative explanation of the observed experimental results. It is considered that the quantitative treatment of polarisation phenomena will not be possible until a more detailed knowledge of the adsorption processes occurring at metal/solution interfaces is available.
In the event of any dispute arising in the execution of the provisions of this agreement, the parties hereby agree to submit such dispute to the decision of the Court or of the arbitrator chosen by the parties, and the decision shall be final and binding upon both parties.

This agreement is made and executed in the City of New York, New York State, this of the year .
The work described in this thesis was carried out in the laboratories of the Department of Metallurgy under the supervision of Dr. L.L. Shreir. The author would like to express his gratitude to Dr. Shreir for the valuable advice he has given, and the interest he has shown throughout the work.

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DEFINITIONS

AND

GLOSSARY OF SYMBOLS
The nomenclature employed in the study of cathode polarisation potentials by various authors, has been a matter of individual choice to a very large extent. To avoid confusion, a list of the more important terms used in the present work is given below, together with the definitions of the terms as applied in the work.

**Polarisation Potential:** The difference between the equilibrium potential of an electrode, and its potential when a current is passing. All polarisation potentials are referred to a particular apparent current density, and will be taken as positive in all cases.

**Overvoltage:** The polarisation of an electrode in which the process occurring is the liberation of a gas. Also taken as positive in all cases.

**Constant State Polarisation:** An arbitrary constant state attained by the system in any given determination, in which the polarisation does not change by more than a fixed amount in a given time.

**Electrolytic Stability:** A solution is taken to have attained electrolytic stability, when, under a given set of conditions, a reproducible constant state polarisation is obtained.

**Apparent Current Density:** The ratio of the current passing through an electrode, to the area of the
electrode presented to the electrolyte.

**True Current Density:** The ratio of the current passing through an electrode, to the actual growing area of that electrode.

**Activation Overpotential:** That part of the total polarisation due to some slow process in the electrode reaction.

**Concentration Polarisation:** That part of the total polarisation due to concentration differences between the cathode layer and the bulk of the electrolyte.

**Coarse Deposit:** A deposit in which separate crystals can be seen with the naked eye.

**Smooth Deposit:** A deposit in which no crystals can be distinguished with the naked eye.

**Bright Deposit:** A smooth deposit which exhibits a definite mirror-like reflection of light.

**Symbols.**

The symbols used in this work, are in general those recommended by the Symbols Committee of the Royal Society in their report published in 1931. However, in a few cases it has proved more convenient for typing purposes to use symbols other than those recommended, and therefore the following list of symbols used in this
work is given:-

\( n \) = Total polarisation potential.

\( n_a \) = Activation overpotential.

\( n_c \) = Concentration polarisation potential.

\( n_1 \) = Total polarisation potential in the first run etc.


c.s.p. = Constant state polarisation.

E.S. = Electrolytic Stability.

F.A.B. = Fully Annealed (Cathode) Base.

G.R.B. = Cold Rolled (Cathode) Base.

A. = Ampere.

mA. = Milliampere.

V. = Volt.

mV. = Millivolt.

E. = Electromotive Force, and Electrode Potential.

t. = Time (in minutes).

M. = Molality (gram molecules per litre).

s\( \text{q.m.} \) = Square Decimetre.

ml. = Millilitre.

I. = Current.
SECTION I.

HISTORICAL SURVEY.
It is a well known fact that almost all commercial silver electroplating utilises the complex silver cyanide bath. As a result of this, the cyanide plating solution has receive a considerable amount of attention, directed chiefly at improving the quality of the deposit. Conversely, silver nitrate solutions are seldom used except in electrefining when the nature of the structure of the deposit is unimportant. However, it seemed that the simplicity of the silver nitrate solution makes it a better means of approach to a more fundamental investigation of cathode polarisation phenomena, than the complex cyanide solution.

Also, this work was originally undertaken with another idea in mind, namely as a comparison with the work of Shpurr and Smith (1) on acid copper sulphate solutions. It seemed desirable to select a metal which would not introduce the complication of two valency states. Of the metals available, silver had one distinct advantage over the others, namely the fact that silver nitrate deposits large coarse crystals. Hence any refining effect on the grain size due to the various factors should be very marked.

A consideration of the literature revealed a paucity of work of any kind on the cathode polarisation potential (C.P.P.) phenomena of silver in simple (i.e. noncomplex) solutions, and a complete lack of any one
really systematic investigation of the factors affecting the electrolysis of silver nitrate solutions. For this reason, the early stages of the present work were based to a large extent on the work of Shreir and Smith (1) on polarisation potentials of acid copper sulphate solutions.

Shreir and Smith point out the great difficulty of investigating these phenomena compared with the determination of equilibrium potentials. In particular they emphasise the importance of the time factor, the nature of the cathode surface, and the lack of accord among the various authors as to the method to be used in measuring the polarisation. They also point out that factors like the effect of dissolved gases, and agitation of the solution, have been carefully investigated by some authors and neglected by others. All these observations are true of the little work which has been carried out on silver nitrate.

As far as the methods available are concerned, there seem to be two main methods which have been used, both of them depending on the use of some unpolarised electrode. They are:

(1) The Haring Method (2).

(2) The Half-Cell and Luggin Capillary Method.

At one time the Glassstone Commissator-Extrapolation Method (3) was widely used, but has since been proved unsound.
and will not be further considered. Since 1926 when Haring introduced his cell, opinion has been fairly evenly divided between this and the classical half-cell method, although from time to time various other devices have been proposed for measuring the required potentials \((4, 5, 6)\). However, except for the Cathode Ray Oscillograph which has been used to study phenomena occurring in the first seconds of the electrolysis, none of them has been very extensively used.

Fink and Hogaboom (7) have used the Haring cell to study the variation of polarisation over the entire cathode face, which they claim is due to changes in the surface film. Starss and Taft (8) have also used the Haring method to study the system \(\text{Pt}/\text{AgNO}_3\), and claim that there is little polarisation at low current densities, while at high current densities some hydride of silver is formed. They do claim that the method is accurate, but do not report the precise composition of their solutions. Taft and Massmore (9) have used the same method for copper and claim that, not only is the method accurate, but it has the advantage of giving an average value over the entire cathode surface.

All these workers have used cells of materials like Tufnol cemented with bitumenous cement. Shreir and Smith (1) found that such cells were prone to leaks, and there was a strong tendency for bitumen to contaminate
the solution. However, by using perspex, they were able to devise a cell which did not suffer from these disadvantages. They also made an extensive comparison of the two methods, and prefer the Haring method, except when working in agitated solutions when they found it necessary to use the half-cell method for the most reproducible results. The reference electrode which they used was a reversible copper electrode of the type devised by Graham (10), in which the liquid junction is made in an ungreased glass tap, thus minimising the diffusion effects.

Despite the apparent simplicity of operation of the Haring cell, many authors have preferred the half-cell method, in spite of the weakness which this suffers of only measuring the polarisation over the small area of cathode covered by the capillary tip. The usual technique has been to have the tip of the capillary movable, and to move it up to the cathode just prior to taking a reading. This serves to eliminate Ohmic resistance effects while reducing the screening effect of the capillary to a minimum.

The majority of workers on silver polarisation potential have used the half-cell method with an external reference electrode. Thus Vagramyan and Alesyan (11) have used the method in their work which has been chiefly directed at the type of deposit obtained, and in which
they do not clearly report the experimental conditions. The work of Vagramyan (12) is rather more interesting. He used a reversible silver electrode, and worked under nitrogen because he considered that dissolved oxygen passivated the cathode surface in some way. This is noteworthy as being the only reference to the effect of the atmosphere on the polarisation potential of silver.

In recent years, several authors, notably Picontelli and Poli (13), and Mattson (14) have made critical comparisons of the Haring and half-cell methods. Picontelli and Poli claim that for reliable results, it is necessary to:

(i) Prepare the electrodes in some standard way.
(ii) Use the half-cell method.
(iii) Use a cylindrical cell.
(iv) Agitate the electrolyte with nitrogen.
(v) Use a wide range of current densities, and run till the polarisation is constant.

They also support their contentions by experiments on a number of metals and solutions. Mattson is also of the opinion that the half-cell method is more reliable provided that the capillary tip is bored through the back of the cathode. He also condemns the Haring method as inaccurate since it assumes Ohm's law to hold for an electrolyte solution and this has been shown to be incorrect. However, he does not support his claims by experiment.
The one aspect of silver deposition which has received attention over many years is that of the complex cyanides. This, in spite of the inherent weakness of the complexity of the solution. Glasstone and his co-workers (15,16) have examined the effect of additions of nitrates and cyanates to the solution, as well as the more usual purely organic additives, and they could find no obvious connection between the polarisation and the nature of the deposit. They have also used A.C. methods, in which there is no concentration polarisation, and postulate a subcyanide of silver as an active constituent. Possiel and Acid (17) have examined a great many addition agents in an attempt to improve the deposit. Raub and Mullhorst (18) have concluded that silver deposits simply from cyanide baths, and not as a complex which subsequently decomposes. Erdey-Cruz and Horvathy (19) have examined various mixtures of silver nitrate and cyanide, and conclude that there is no essential difference between the two modes of deposition and that the silver ion diffuses up to the cathode rather than being brought up by the electric current.

The importance of a standard method of preparation of the cathode has been demonstrated by many authors in the case of copper, but few workers appear to have considered this aspect with silver. One exception to this occurs in the case of Vagramyan and his co-workers (11,12,20).
Vagramyan (20) is also one of the few workers to have quantitatively studied the effect of addition agents on the e.p.p. of silver in silver nitrate, and he states that the effect of the addition agent is to block part of the cathode. The qualitative effect of addition agents has been very widely studied, thus Taft and Horaeley (21) give a list of over a hundred addition agents, which improve silver deposits, and conclude that the fatty acids are the most effective. Similar work has been performed by Assman (22) and Glazanov, Teindl and Kaflik (23) none of whom have considered polarisation effects. On the other hand, Muller and Feld (24) have plotted polarisation versus time curves for various solutions, and have concluded that tartaric and pyrocrasemic acids give the best deposits, while increasing the polarisation of 3% silver nitrate solution. It is a noteworthy fact that the time factor has been almost completely neglected in this field, only Vagramyan (12) having allowed his determinations to run to a constant value.

Very little work has been performed on the addition of "inert" (i.e. undeposited) inorganic cations to the silver nitrate solutions, and this is surprising in view of the theory proposed by Hunt (23) and developed by Agar and Bowden (25) on the effect of the ionic strength of the solution on the polarisation. Also, very little attempt has been made to discover whether the addition
agent is included in the deposit, the work of Foseya and Lurata (27, 28) being a notable exception. This work is also practically the only case in which glycine (aminoacetic acid) is mentioned as an addition agent.

An important aspect which appears to have been almost entirely neglected, is the influence of the cathode base on the structure of the silver deposit. Shreir and Smith have shown that the base can greatly affect the orientation of copper deposits, and Finsh and Sun (29) have shown that the orientation of the cathode base affects the orientation of silver deposits. However, these latter workers did not attempt to correlate crystal structure with polarisation. Vagamanyan (20) has studied polarisation curves using single crystal cathodes, but his primary object was to test his theory that certain faces of a growing crystal tend to become passivated due to adsorption of organic impurities. In this connection, Vagamanyan considers that the true current density is of great importance, and has made an estimate of the value of this quantity for a growing single crystal by microscopic examination during the electrolysis. However, he gives no method of estimating the true current density on a polycrystalline base.

In conclusion, it may be said that no one method of measuring cathode polarisation potentials has found universal favour. Also, the various factors affecting
these potentials have been carefully studied by some authors and almost completely neglected by others. In particular, the cathode polarisation potential of silver in aqueous silver nitrate solutions has been very largely neglected. This constitutes a sound reason for further work on the subject which may be backed by at least one good reason for preferring this solution to the more widely investigated complex cyanides. This reason is the very complexity of such cyanide solutions, since their precise composition in terms of ionic species present is usually very problematic. Also, it should be easier to examine the grain-refining effect of various addition agents in a solution which normally gives very large coarse crystals. This survey also served to show that no one paper could be used as a basis for further work on silver in silver nitrate, and it therefore seemed advisable to start from the beginning, and examine the two principal methods from a point of view of reproducibility of results. Having established conditions of reproducibility, it should be possible to proceed to an examination of factors affecting the nature of the deposit, its structure, and the production of bright deposits; and possible to relate these matters to the polarisation potential of the system.
SECTION II

MATERIALS, APPARATUS AND METHODS USED IN THE

DETERMINATION OF CATHODE POLARISATION POTENTIALS.
Introduction.

Although almost all workers seem agreed that purity of reagents was of the utmost importance, there is practically no agreement as to the methods employed in the preparation of the cathode, or of methods of determination of polarisation potentials. It was therefore decided to carry out preliminary experiments on various methods of preparation and determination and finally decide between them on a basis of reproducibility of results.

Materials Used in The Work.

The silver anodes were cast in blocks 9in. by 2.5in. by 1in. of assay 99.993% silver.

The cathodes were cut from silver foil 0.005in. thick and 3.5in. wide, of assay 99.99% silver. Two types of foil were used:— (1) fully annealed (ii) cold rolled.

The silver nitrate was supplied to specification four times recrystallised, and of assay not less than 99.99% silver nitrate. This was found to be suitable for use without further treatment.

The silver gauze was 20 mesh of assay 99.99% silver. All silver and silver salts were supplied by Johnson Matthey Ltd.

The water used was distilled water once redistilled from potassium permanganate and potassium hydroxide, using...
all-pyrex still and condenser. It was stored in glass bottles with well fitting glass stoppers, and used within a few days of preparation. This water was found to be satisfactory, and was used throughout the work.

During the work on nitrogen saturated solutions, the nitrogen used was oxygen free (less than 10 v.p.m. O₂) supplied by The British Oxygen Co., and used without further treatment.

Preparation Of The Cathode.

Various authors have used very different techniques in preparing their cathodes, but very few have used silver cathodes. Gauvin and Winkler (1) have used metallographic polishing with some success for copper, but this was impossible in this case owing to the thinness of the foil. The broad principles are firstly to remove any grease film, and then to remove any oxide or sulphide film and to try to leave a uniform reproducible surface.

The first stage was accomplished by vapour degreasing in trichloroethylene. A flask was fitted with a reflux condenser, and the solvent refluxed with the specimen hung in the vapour, so that the condensate ran back over it. This process was carried out for twenty minutes, and was found to be so satisfactory that it was used throughout the ensuing work.

The second stage was rather more difficult.
It seemed desirable to avoid etches containing phosphate or persulphate owing to the danger of precipitate formation, and finally two methods were tried:

(i) etching in hot 30% nitric acid.

(ii) etching in hot 5% potassium cyanide.

Anodic polishing was not attempted in view of the thinness of the foil. (Only one roll of foil of each type was used in the work, thus facilitating the attainment of a constant type of surface). In practice, the two etches gave the same polarisation values, but the deposit was rather more uniform on the acid etched specimen, and subsequently this method was used throughout the work. It was found that the precise strength of the etch, and the temperature and time of etching did not affect the results, and therefore each specimen was etched until the surface appeared a uniform white colour.

As a final step, the cathode specimen was well washed with distilled water and dried by pressing between filter papers before being placed in the cell.

**Electrical Apparatus and Circuit.**

The apparatus consisted of a Timley General Utility Potentiometer, Galvanometer and Standard Weston Cell. The potentiometer had three ranges, 0-1000mv., 0-100mv., and 0-10mv., and in general the middle of these ranges was used, in which the scale was calibrated.
in 0.05mV steps. The potentiometer was provided with two external circuits, but by means of a reversing switch, three circuits could be obtained effectively. The galvanometer had a sensitivity of 0.7mm/microamp, but a low resistance shunt could be incorporated at will to reduce the sensitivity. The polarising current was provided by a series of two volt accumulators, and controlled by three variable resistances of 750, 60 and 1 ohm in series, the current being measured by a Weston milliammeter of substandard accuracy, which had six ranges, namely 1, 10, 100, 200, 500 and 1,000 mA, thus providing very accurate current control for any given current. The whole apparatus was wired up in the usual way, with the cell immersed in a thermostatic waterbath held at 25°C ± 0.1°C.

The Method of Determination of Polarisation Potential.

Two methods of determination were available:

(i) The Haring Method (2).

(ii) The Half-cell Method.

As was shown in Section I, opinion has been divided fairly equally between them, but most of the workers on silver have preferred the half-cell method. Also Pientelli and Icli (3) have shown that for many systems this is the only way of obtaining reproducible results. However, in the case of silver nitrate solutions, another factor must be considered, namely the heterogeneous
nature of the deposit, which makes it seem desirable to use the Haring method and obtain a mean value for the entire surface, rather than the half-cell method giving a local value at the tip of the Luggin capillary. However since reproducibility is the major criterion, it was decided to compare the two methods before selecting one for subsequent use.

The Haring cell was originally described by Haring (2), but in this work the much improved cell designed by Shreir and Smith (4) was used. It was made of thin, thick clear perspex and had internal dimensions of 15 x 2.5 x 9cm. being cemented together with a solution of perspex in chloroform. Twenty mesh silver gauze was fitted into slots, thus dividing the cell into three equal compartments. The cathode end was open and flanged, and the cathode foil was clamped in place by means of a rubber gasket and Tufnol back-plate secured by six screw clamps, which gave a leak-proof joint. The cell was calibrated to hold 150cc of solution and to expose 10sq.cm. of cathode. Finally, the cell was placed on a platform in the water bath and levelled by means of a spirit level. The correction for inaccuracies in the cell distances by Guavin and Minkler's (1) method will not be described, since subsequent work showed that the Haring method could not be used.

The second method - the half-cell method -
subsequently used in this work, is that of measuring the
S P P by means of an external reference electrode,
electrical connection being made by a capillary pressed
against the face of the cathode. In the early work,
the electrolysis cell used was the Haring cell with the
gauzes removed, although later another cell was made.
A photograph of the reference electrode is shown in fig.2
and is similar to that used by Graham (5). The tap was
an ungreased three-way tap and each side was connected in
turn to waste, and the solution sucked through, thus
forming the liquid junction in the bore of the tap and
minimising errors due to diffusion of the electrolyte.
The exact reference electrode used was Ag/AgNO₃ solution,
which eliminates any precipitation, and since the
reference electrolyte was usually of the same concentration
as the solution in the electrolysis vessel, the liquid
junction potential was almost completely eliminated. The
silver for the reference electrode was prepared by
electrolytic deposition at high current density from acid
silver nitrate solution. It was permissible to use a
silver reference electrode since the polarisation was
measured by a difference method:

\[ n = E_w - E_o \]

where,

\[ n \] = cathode polarisation potential (S.P.P.)

\[ E_w \] = E.M.F. of cathode and half-cell when current is

flowing.
\[ E_0 = E.M.F. \text{ of cathode and half-cell when current is not flowing.} \]

The final connection to the half-cell was made by means of a thin-walled capillary tube, which dipped into the electrolysis electrolyte and was connected to the tap by a piece of rubber tubing. The ends of the two pieces of glass touched inside the rubber thus keeping the rubber to solution contact to a minimum. The capillary was placed about 1 cm from the cathode face during the run, but when a reading was taken, it was screwed up by means of a rack and pinion device until the capillary tip pressed lightly but firmly against the centre of the cathode, the rubber tubing acting as a spring. Piantelli and Poli (3) consider that the capillary should be only a few microns in diameter, but in view of the coarse nature of the deposit the capillary used in this work was about 0.5 mm in diameter. The screening effects of this were minimised by having the capillary placed at some distance from the cathode except when taking a reading, and by having a horizontal piece on the capillary at least 1 cm long. In practice, this did not screen the cathode, and during the work on agitated solutions had the added advantage of causing a churning effect in the electrolyte.

**Technique of Measurement.**

The first series of runs were carried out to examine polarisation-time (n-t) curves for neutral silver
nitrate solutions, and to test the reproducibility of the two methods. The cathode specimens were prepared as described earlier, and placed in the cell. The cell was rinsed with solution, and then filled and placed in the water bath. The solutions were normally kept in a flask in the bath, and owing to the poor thermal conductivity of perspex, the cell was left in the bath for some time before starting the run, in order that it should come up to temperature. In Haring's method, the cell was carefully levelled before starting, the current was then switched on and adjusted to the appropriate value. Readings were taken after various time intervals. At the end of the run, the solution was transferred back to the flask in the bath, the cell washed out with distilled water and the cathode replaced for the next run.

In the half-cell method, the levelling was less critical, and was done by eye. The reference electrode was placed in the bath and connected up, the whole apparatus being adjusted so that the capillary tip was in the correct position. After allowing some time for the system to come up to temperature, the E.M.F. of the half-cell and cathode was taken. The current was then switched on and adjusted, and E.M.F. values taken after fixed time intervals. At the end of the run, the current was switched off, and after a few minutes the E.M.F. again taken. In evaluating the polarisation, this latter
equilibrium potential was used. Since, although it was not usually very different from the value before starting, it did represent the potential of the deposited cathode, and the difference between this value and the E.M.F. at any time during the run gave the polarisation at that time.

In the runs in which the two methods were actually compared, two cells were used simultaneously and in series.

The Cylindrical Cell.

After the preliminary investigation had been performed, it was found, for reasons which will be given later, that the Haring method could not be used, and in all subsequent work the half-cell method was employed.

The long rectangular shape of the cell has the disadvantage that it is extremely difficult to obtain adequate uniform agitation of the solution and since the Haring method was no longer to be used, this cell was discarded. Piuntelli and Poli (3) have made an extensive examination of the conditions needed for obtaining the best results, and have concluded (among other things) that the best shape for the cell is the cylinder. This shape has another advantage, namely that it provides the best shape for uniform agitation. Accordingly, a cell was designed which while having a cylindrical shape, still
retained the most desirable feature of the Haring cell, that is, the ease of replacement of the cathode. There did seem to be the possibility that such a circular shape would have the disadvantage of causing an increase in the number of current lines at the edges of the cathode, leading to heavier deposits at the sides of the specimen. However this should be offset by a slight shielding effect due to the sides of the opening. In practice, no appreciable extra heaviness was observed at the edges of the deposit, and this infers that the increase in current distribution at the sides of the cathode was negligible.

The new cell was made from perspex, since this material had proved so satisfactory in the earlier cell, and certainly did not have the disadvantages of Tufnol. Some perspex was obtained in the form of a cylinder of internal diameter 3in. and wall thickness ½in. From this a piece 9in. high was cut, and an opening was cut in the curved face 0.5cm. from one end. Into this space a rectangular block of perspex 9 x 6 x 1cm was cemented. A new opening was then cut in the centre of the block 4cm high by 2.5cm wide, and the inside face of the block was ground out to the original circular shape of the cylinder. The edges of the new opening were also ground back in order to minimise their screening effect. A base was cemented to the cylinder, and a close fitting lid with holes for the capillary, stirrer, and anode terminal was made. The cathode foil was cut 5cm. by 3.5cm, and placed over the
opening in the side plate. This was then backed by a rubber gasket, and a backing plate made from a thick piece of perspex, one side of which was ground into a segment of a circle. (The other face of the backing, as well as the side plate were ground flat). By clamping with steel bands which went right round the cell, a leak-proof joint was obtained. Electrical connection with the cathode was made by drilling down through the cell wall, and inserting two silver studs in the side plate, one on either side of the opening. One of these studs carried the current, and the other the potentiometer lead. Two stops were cemented to the inside of the cell diametrically opposite the side plate, and served to locate the anode.

In practice, this arrangement worked very well, and diagrams and a photograph of the cell are shown in figs. 1 and 2. (For simplicity, the clamping device has been omitted from the diagram). The deposits obtained were quite uniform, and it was found that, far from screening the cathode, the edges of the opening helped to provide a further churning effect, so that when the solution was stirred, the electrolyte did not merely flow over the cathode face from one side to the other, as will be seen later, the agitation was further assisted by placing the stirrer eccentrically in the cell.
The Cylindrical Cell and Half-cell.

The Cylindrical Cell
(showing the side plate).
SECTION III

PRELIMINARY EXPERIMENTAL WORK.
Introduction.

The initial concentrations and current densities used were arbitrarily selected after a series of semi-quantitative experiments to find the limiting current for adherent silver deposits. No useful information on this topic could be found in the literature, since the only applications of silver nitrate solutions are in electrorefining (where the nature of the deposit is unimportant) and in the silver coulometer, in which it is customary to use a platinum crucible as the cathode, owing to the very poor adherence of the deposited silver. Practically the only work using silver cathodes is that of Vagramyan and his co-workers (1, 2, 3) in which they use single crystals of silver to examine passivation phenomena. In another paper (4) they investigate polarisation-time curves, and this represents the only work on this aspect of the problem. The work of Stareck and Taft (5), Taft and Neasmore (6) and Selsord; Kern; and Milligan (7) all have the drawback of either working with platinum electrodes, or being purely qualitative in nature, being only concerned with the crystal nature of the deposit.

Hence the work in this section is concerned with the examination and comparison of the methods available, the type of cell used, and the reproducibility of the polarisation-time curves for the solution.
Solutions and Current Densities Used.

A 0.25M solution was used in the first experiments, although later, a series of solutions 0.05, 0.1, 0.25, and 0.5M were examined. The current chosen was 50mA representing an apparent current density of 0.5A/sq dm. This value represents about half the limiting value of the current for adherent deposits in most solutions, as determined experimentally.

Comparison of the Haring and Half-cell Methods.

The two methods were run simultaneously in series using separate samples of the same solution, and cathodes of fully annealed silver prepared by acid-etching after vapour degreasing in trichloroethylene. Each run was continued until the potential, which usually decreased with time, did not change by more than ±1.0mv in 10 minutes, this standard of constancy being quite arbitrary. In practice, it was found that the Haring method would not give greater accuracy than this, but the half-cell method would give a standard of constancy of ± 0.1mv/10 mins. The values in Table IIIa are typical of a series of about fifty runs using both methods. The Haring Cell correction for the cell compartment distances was obtained by the Guvin and Winkler (8) method. The initial and final potential values refer to the values obtained from the cell, reference electrode/cathode, before and after the run. The final value was taken in evaluating the polarisation since it
was found to be more reproducible, and was also more representative of the deposited base.

Table IIIa

n-t results, 0.25M AgNO₃, 0.5A/sq. dm., F.A.3.

<table>
<thead>
<tr>
<th>t. mins.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁ mV.</td>
<td>1250</td>
<td>1253</td>
<td>1254</td>
<td>1253</td>
<td>1250</td>
<td>1248</td>
<td>1245</td>
</tr>
<tr>
<td>E₂ mV.</td>
<td>1215</td>
<td>1214</td>
<td>1215</td>
<td>1215</td>
<td>1213</td>
<td>1213</td>
<td>1209</td>
</tr>
<tr>
<td>n mV.</td>
<td>35</td>
<td>39</td>
<td>39</td>
<td>38</td>
<td>35</td>
<td>33</td>
<td>33</td>
</tr>
</tbody>
</table>

uncorrected

($E_1 - E_2$)

| n mV. | 23 | 27 | 27 | 25 | 24 | 24 | 24 |

corrected

($E_1 - E_2 + E_3$)

| E₃ mV. | 11 | 10 | 9 | 9 | 9 | 9 | 9 |
| n mV.  | 7 | 6 | 5 | 5 | 5 | 5 | 5 |

E₁ = P.D. Cathode Compartment
E₂ = P.D. Middle Compartment
E₃ = Haring Cell Correction = -12.0 mV.
E₃ = Potential of Half-cell and Cathode
E₄ = Initial E.M.F. = 4.0 mV.
E₅ = Final E.M.F. = 4.0 mV.

From this table, it is at once apparent that not only do the two methods give different values of the polarisation, but the Haring method takes longer to reach the constant state polarisation (c.s.p.).


Electrolytic Stability and Reproducibility of Results.

It is a well known fact that great difficulty is experienced in obtaining reproducible results in electrodeposition. For this reason, many workers in the field of hydrogen overvoltage, and in particular Bockris and his co-workers (9), have adopted the technique of pre-electrolysis of the solution. In the present work the same technique was used, and the solution was taken to have reached a condition of "Electrolytic Stability" (E.S.) when two successive runs of that solution gave a c.s.p. not differing by more than ± 1.0 mV. In practice, it was found possible to achieve a standard of ± 0.1 mV. when using the half-cell method, and this figure represents a reproducibility of about 2/3 of the c.s.p. for a value of 5 mV. and is the same as that attained by Shreir and Smith (10) in their work on copper. This reproducibility is even better when higher polarisation values are obtained.

Table IIIb shows a typical result on re-running the solution under the same conditions and using a fresh cathode for each run.

This shows that taking the standard of c.s.p. as ± 1.0 mV., the half-cell method reaches Electrolytic Stability much more quickly than the Barng method. Further, in performing these experiments, a number of other important facts were elucidated. Firstly, using the half-cell method, it is possible to achieve a constancy of ± 0.1 mV., and
this value can be repeatedly obtained on fresh samples of solution. Secondly, the Haring method gave a standard of only ± 1.0 mv., and the values could not necessarily be repeated on fresh samples of solution.

Table IIIb.

c.s.p. values for several runs of 0.25M solution at 0.5A/ml.dm., F.A.B.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1st run</td>
<td>29</td>
<td>4.0</td>
<td></td>
<td>24</td>
<td>4.5</td>
</tr>
<tr>
<td>2nd run</td>
<td>24</td>
<td>4.5</td>
<td></td>
<td>20</td>
<td>4.7</td>
</tr>
<tr>
<td>3rd run</td>
<td>20</td>
<td>4.7</td>
<td></td>
<td>20</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The correction for the Haring cell distances was found to vary over a very wide range, and since the gauzes were not moved between runs, some other factor must have been influencing the results. This was found to be corrosion of the gauzes, due to concentration changes during the electrolysis. The upper layers of the electrolyte became denuded of silver ions, while the lower layers became comparatively more concentrated. This resulted in a concentration cell being set up, and caused the gauzes to become polarised. The Haring cell method depends on the fact that the reference electrode (in this case the silver gauze) is unpolarised, and if the gauzes are polarised, this method is unreliable. For
this reason the barrel method was abandoned in favour of the more reproducible half-cell method, which in turn necessitated the redesigning of the electrolysis cell, and it was at this stage that the cylindrical cell was designed. The circular shape was chosen partly for ease of agitation, and partly because of the recommendations of Piconelli and Pell (11). It was found that the half-cell method gave identical values of the polarisation in both the rectangular and circular cells.

The Effect of Concentration on Polarisation.

The purpose of this work was to investigate the effect of addition agents on the deposit and polarisation of silver nitrate solutions. Although the 0.25M solution appeared to be a suitable standard solution, it was of interest to examine the effect of variation of concentration on polarisation to ensure that the results obtained with the 0.25M solution were not specific to that concentration. A large number of runs (about 300) were performed at 0.5A/sq.dm. on fully annealed cathode bases using solutions of 0.05, 0.1, 0.25, and 0.5M concentration. The standard of constancy was taken as ± 0.1mv. The solutions were made up in 1 litre batches, thus giving sufficient solution for three separate samples. Typical results are shown in tables III, d, e, and f, and graphically in figs. 3, 4, 5, and 6. Although the initial c.s.p. values were variable, on rerunning the solution,
and thereby achieving electrolytic stability, good reproducibility was obtained. It therefore follows that unless the solution is pre-electrolysed reproducibility cannot be expected, and, for most solutions, it was necessary to run the solution two or three times before electrolytic stability was attained.

**Table IIIa**

*n* results for 0.05M AgNO₃, 6.5/sq.dm. F.A.B.

<table>
<thead>
<tr>
<th>t min.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ ev.</td>
<td>19.5</td>
<td>19.1</td>
<td>17.1</td>
<td>16.6</td>
<td>16.4</td>
<td>15.3</td>
<td>16.3</td>
<td>16.3</td>
</tr>
<tr>
<td>n₂ ev.</td>
<td>13.6</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>n₃ ev.</td>
<td>15.7</td>
<td>14.1</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>n₄ ev.</td>
<td>15.7</td>
<td>14.3</td>
<td>13.6</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>

**Table IIIb**

*n* results for 0.1M AgNO₃, 65/sq.dm. F.A.B.

<table>
<thead>
<tr>
<th>t min.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ ev.</td>
<td>9.1</td>
<td>8.5</td>
<td>8.0</td>
<td>7.9</td>
<td>7.8</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>n₂ ev.</td>
<td>10.7</td>
<td>10.5</td>
<td>10.6</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>-</td>
</tr>
<tr>
<td>n₃ ev.</td>
<td>11.2</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>n₄ ev.</td>
<td>11.3</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table IIIc**

*n* results for 0.25M AgNO₃, 6.5/sq.dm. F.A.B.

<table>
<thead>
<tr>
<th>t min.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ ev.</td>
<td>4.3</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>n₂ ev.</td>
<td>6.1</td>
<td>5.4</td>
<td>4.3</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>n₃ ev.</td>
<td>5.5</td>
<td>5.7</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table III

- t results for 0.2M AgNO₃, 0.5A/s, dm, F.A.S.

<table>
<thead>
<tr>
<th>t min.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ mV</td>
<td>4.9</td>
<td>4.6</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>n₂ mV</td>
<td>4.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>n₃ mV</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

The Effect of Aged The Solution,

It was possible that the solution might change in some way if it were allowed to stand for some time, and also that the perspex used for the cell might affect the solution. To examine these possibilities, two samples of 0.25M solution were taken, one of which was run to the 3.s.p. several times until it had reached electrolytic stability. Both samples were then placed in stoppered flasks in contact with pieces of perspex, and left in a cupboard for some time. After five weeks, both samples were electrolysed and Table IIIg shows the results obtained.

Table IIIg

- t results, 0.25M solution 3.s.p. = 4.7 before ageing.

<table>
<thead>
<tr>
<th>t mins</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ mV</td>
<td>6.1</td>
<td>5.3</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>n₂ mV</td>
<td>5.4</td>
<td>4.9</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
<td></td>
</tr>
</tbody>
</table>

- t results, 0.25M solution, not pre-electrolysed before ageing

<table>
<thead>
<tr>
<th>t mins</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ mV</td>
<td>6.3</td>
<td>7.3</td>
<td>6.5</td>
<td>6.2</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>n₂ mV</td>
<td>7.3</td>
<td>6.4</td>
<td>5.1</td>
<td>4.7</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>n₃ mV</td>
<td>5.5</td>
<td>4.9</td>
<td>4.7</td>
<td>4.6</td>
<td>4.7</td>
<td>4.8</td>
</tr>
</tbody>
</table>
**Fig. 3**

n - t Curves, 0.05M AgNO₃
0.5A/Sec, F.A.B.

1st Run = X
2nd " = O
3rd " = △
FIG. 4
n - t CURVES, 0.1 M AgNO₃
0.5 A/SQ.DM., F.A.B.

1ST. RUN = X
2ND. " = O
3RD. " = △
4TH. " = □
FIG. 5
n. - t CURVES, 0.25 M. A$_2$NO$_3$
0.5A/SQ. DM., F.A.B.

1ST. RUN = X
2ND. = O
3RD. = △
4TH. = □

n-MV. 5

0 5 10 15 20 25

t-MIns.
FIG. 6

n.-t CURVES, 0.5M AgNO₃
0.5A/SQ.DM., F.A.B.

1ST. RUN = ×
2ND. n = ○
3RD. n = △

n-MV.

t-MINS.
Thus, neither time nor contact with perspex alters the e.s.p. value of the solution, whether previously electrolytically stabilised or not.

The Standard Solution.

In view of the above results, the 0.25M aqueous silver nitrate solution electrolytically stabilised, and having a e.s.p. value in air of 4.5 ± 0.1 mv, was taken as a standard solution. This solution was checked at intervals throughout the subsequent work, and always gave the same value of the e.s.p. Thereafter this solution was used except when it was considered desirable for one reason or another to take a different concentration.

The Effect of Variation of Cathode Base or Preparation.

Another factor which might have influenced the results was, the method of cathode preparation. In all the early work, the method used had been vapour degassing in trichloroethylene followed by acid etching in hot approximately 50% nitric acid, each specimen being immersed until the surface appeared uniformly etched. Since no precautions were taken to control temperature or length of immersion, it is apparent that these factors do not affect the polarisation. Other methods of preparation were considered. It seemed undesirable to use etches containing persulphate of phosphate since these held the possibility of precipitating insoluble silver salts on the specimen.
Metallographic polishing has been shown by Shrair and Smith (10) to be of little importance compared with factors external to the cathode. Anodic polishing of silver presents much more difficulty than that of copper, and in any case would be very unsatisfactory in view of the thinness of the foil. Cyanide etching has been recommended by Wernick (12) and others using 5% potassium cyanide. The results using this etch are compared with those from the acid etch in Table IIIh for a standard solution and a fully annealed base previously run to electrolytic stability.

Table IIIh

<table>
<thead>
<tr>
<th>n-t results E.S.</th>
<th>C.25H2AgNO3</th>
<th>C.5A/sq.in., F.A.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t mins.</td>
<td>1 2 5 10 15 20</td>
<td>Etch</td>
</tr>
<tr>
<td>n1 mv.</td>
<td>5.5 5.0 4.8 4.6 4.6 4.6</td>
<td>Acid }</td>
</tr>
<tr>
<td>n2 mv.</td>
<td>6.0 5.1 4.7 4.7 4.7 4.7</td>
<td>KClH }</td>
</tr>
<tr>
<td>n3 mv.</td>
<td>7.2 6.5 5.3 4.7 4.7 4.7</td>
<td>KClH }</td>
</tr>
<tr>
<td>n4 mv.</td>
<td>8.3 4.7 4.7 4.7 4.7 4.7</td>
<td>Acid }</td>
</tr>
</tbody>
</table>

These results show that the etch does not appear to affect the e.s.p. of an E.S. solution. However, in as much as the acid etch gave a rather more uniform cathode surface which was reproduced in the deposit, this etch was used subsequently. Another factor in favour of this etch was the ease and convenience in use.

Variation in the type of cathode base had a small but definite effect on the e.s.p., this is illustrated in Table IIIj, which compares the results
obtained by using a fully annealed base (F.A.B.), and a cold rolled base (C.R.B.) with a standard solution and an acid etch.

**Table III**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.5 5.0 4.7 4.7 4.7 4.7</td>
<td>4.4 4.3 4.3 4.3 4.3 4.3</td>
</tr>
<tr>
<td>2</td>
<td>6.0 5.1 4.6 4.6 4.6 4.6</td>
<td>4.7 4.4 4.4 4.4 4.4 4.4</td>
</tr>
<tr>
<td>3</td>
<td>5.7 5.3 4.3 4.4 4.4 4.4</td>
<td>5.3 5.0 4.5 4.7 4.7 4.7</td>
</tr>
</tbody>
</table>

**The Appearance of the Deposits.**

The deposits obtained were in all cases very markedly crystalline as may be seen from the photographs in fig. 7. If the electrolysis was prolonged these crystals could be broken off on rubbing with the finger, the fracture apparently occurring above the point of attainment to the base. Microscopic examination showed that the crystals varied considerably in size, and were deposited in lines parallel to the direction of rolling of the base.

It was also apparent that the concentration affects the number of crystallisation and increasing concentration means increasing numbers of centres. In several cases places were observed on the cathode at which no crystal growth occurred. This
did not appear to be due to any deficiencies in the pre-treatment of the base, but rather to the fact that certain places were always inactive to deposition. This is of course borne out by the crystallinity of the deposit, which also infers that the true current density (i.e., current divided by the area deposited) is very much greater than the apparent current density (current divided by the surface area of the cathode).

For this reason attempts were made to estimate the actual area of the deposited base, using the method of catalytic decomposition of hydrogen peroxide proposed by Elton and McDougall (13). However it was found to be almost impossible to obtain worthwhile results with the comparatively small areas involved, and in any case the areas measured by this method would not represent the required areas, since the method gives the total area of the cathode, rather than the area of the growing parts of the deposit.

Several types of deposit have been obtained at various stages in the work using various solutions, and all these deposits in which visible grains can be distinguished with the naked eye (e.g., those in fig 7) will be referred to as "coarsely crystalline". Two other major types of deposit may also be defined. The first of these is the "smooth" deposit in which no definite grains are visible to the unaided eye. The other broad type is
the "bright" deposit in which not only is no grain structure visible, but the deposit shows a marked reflectivity of light. Typical examples of these latter types of deposit will be shown later.

Discussion of Results.

All materials used have been of high purity, and the curves obtained show that, provided the experimental conditions are rigidly controlled, the d.s.p. values for neutral silver nitrate solutions can be reproduced to ± 0.15V (i.e. 2%). In particular, pre-electrolysis of the solution appears to be essential. The physical condition of the cathode base seems to have no important effect on the constant state polarisation, and the nature of the surface preparation has little effect on the polarisation, but appears to affect the uniformity of the deposit.

In spite of all precautions in the preparation of the solution, reproducibility could not be attained except by pre-electrolysis of the solution. It is difficult to know how to explain this phenomenon. One possibility which is favoured by the majority of workers on hydrogen overvoltage, is that the electrolysis brings about the gradual removal of traces of impurity. Conversely, electrolysis may cause the gradual production of some impurity. However, neither of these explanations appears
Fig. 7.

(i) Typical Coarse Deposit.

(ii) Photomicrograph of (i) x 250.
to be completely satisfactory, since neither of them can explain why in some cases the e.s.p. increases until electrolytic stability is attained, and in others it decreases until stability is reached. All that can be said is that whatever the nature of the change in the solution, it does not seem to affect the nature of appearance of the deposit.
SECTION IV.

THE EFFECT OF CONTROLLED ATMOSPHERES ON THE SOLUTION.
Introduction.

For many years it has been customary to use oxygen free atmospheres in the study of hydrogen overvoltage, thus Wetterholm (1) has used nitrogen as a means of preventing access of oxygen to the solution in his work on this topic. In the case of metal deposition, this aspect has been rather neglected. Vagranjan (2) has used nitrogen in his work on silver cathode polarisation potential, as have Erley-Cruz and Volmer (3) in their work on the relationship between polarisation and current density. On the other hand, Rosa, Vinal and McDaniel (4) have made a very extensive study of the silver coulometer, and they make no mention of any necessity to prevent oxygen contamination of the solution.

Rionnetti and Polli (5) recommend the use of nitrogen bubbled through the solution as a means of agitation, and so it will be necessary to consider various methods of agitation in a later part of this work, it was of interest to examine the effect of dissolved nitrogen on the s.s.p. of silver nitrate solutions.

Further it seemed possible that oxygen dissolved in the solution might have been a cause of the gradual change in the s.s.p. (reported in Section III) on remanining the solution. It therefore seemed desirable to investigate the effect of dissolved gases on the s.s.p. of the solution for several reasons.
Experimental Technique.

The circular cell described earlier (Section II) was provided with a close fitting lid, and before starting any run, oxygen free nitrogen was blown through for several minutes. A slow stream of nitrogen was maintained over the solution throughout the run.

The solution was made up in air, and then boiled for five minutes and rapidly cooled, at the same time passing a rapid stream of nitrogen through the solution, and continuing to pass the gas for at least one hour before using the solution. The solution was then stored in a ground glass wash bottle with nitrogen bubbling through. After preparing the cell the electrolyte was transferred from the wash bottle to the cell by blowing over with nitrogen against a slow stream of that gas. At the end of the run, the solution was returned to the wash bottle by means of a suction pump. This technique ensured that the chance of contamination of the solution by oxygen was kept to a minimum.

Polarisation—Time Curves for Oxygen Free Solution.

The first experiments were performed using an electrolytically stabilised 0.25M silver nitrate solution of c.s.p. in air of 4.7mv. It was expected that lower values of the polarisation would be obtained, but, contrary to expectations, the values were considerably higher. A typical series of runs is shown in table IVa.
and graphically in fig. 6. These results are for an acid etched fully annealed base at 0.5A/sq.dm.

Table IVa

<table>
<thead>
<tr>
<th>n-t results</th>
<th>0.25M AgNO₃, 0.5A/sq.dm, F.A.B., H₂ Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>t mins</td>
<td>1     2     5     10    15    20</td>
</tr>
<tr>
<td>n mv.</td>
<td>5.4   4.6   4.0   4.0   4.0   4.0</td>
</tr>
<tr>
<td>n mv.</td>
<td>16.5  15.7  15.3  15.0  15.0  15.0</td>
</tr>
<tr>
<td>n mv.</td>
<td>18.0  15.7  15.0  15.0  15.0  15.0</td>
</tr>
<tr>
<td>n mv.</td>
<td>15.0  15.7  15.0  15.0  15.0  15.0</td>
</tr>
<tr>
<td>n mv.</td>
<td>15.0  15.7  15.0  15.0  15.0  15.0</td>
</tr>
</tbody>
</table>

*Note:* These results were quite surprising, and in case this phenomenon should prove to be peculiar to the 0.25M solution, similar runs were performed for the other three concentrations (0.05, 0.1, and 0.5M), and typical results are reported in table IVb below. The table shows that in all cases, removal of oxygen with nitrogen affects the n.s.p. but not always in the same direction. The values obtained with the 0.25M solution are of the same order as those obtained by Vagramyan and Solov'eva (6). These workers obtained values of the polarisation potential for 0.2M solution at a current density of 0.3A/sq.dm of 13 mv. However no other work was available for comparison. It is also interesting to notice that a few experiments on neutral copper sulphate solutions exhibited a similar
FIG. 8

n - t CURVES, 0.25M AgNO₃ IN NITROGEN
0.5A/SQ.DM., F.A.D.

1ST. RUN = ×
2ND. " = ○
3RD. " = △
4TH. " = □
5TH. " = ▽

n MV.

0 5 10 15 20

t-MINS.
phenomenon as far as the removal of oxygen from the solution is concerned.

Table IVb

n-t results 0.5M/31.4m., F.A.B., N₂ Saturated

<table>
<thead>
<tr>
<th>t mins.</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁ mv.</td>
<td>19.6</td>
<td>12.9</td>
<td>12.3</td>
<td>12.3</td>
<td>12.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n₂ mv.</td>
<td>19.6</td>
<td>17.9</td>
<td>17.3</td>
<td>14.1</td>
<td>12.9</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>n₃ mv.</td>
<td>17.6</td>
<td>15.1</td>
<td>14.1</td>
<td>12.9</td>
<td>12.9</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>n₁ mv.</td>
<td>12.2</td>
<td>12.1</td>
<td>11.9</td>
<td>11.7</td>
<td>10.9</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>n₂ mv.</td>
<td>12.6</td>
<td>12.0</td>
<td>11.9</td>
<td>11.7</td>
<td>10.5</td>
<td>9.9</td>
<td>9.9</td>
</tr>
<tr>
<td>n₃ mv.</td>
<td>10.2</td>
<td>10.1</td>
<td>10.0</td>
<td>9.9</td>
<td>9.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n₁ mv.</td>
<td>4.4</td>
<td>4.0</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n₂ mv.</td>
<td>3.6</td>
<td>5.6</td>
<td>5.7</td>
<td>5.6</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n₃ mv.</td>
<td>6.1</td>
<td>6.0</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

o.s.p. 0.05M in air = 13.4 mv.

0.05M in N₂ = 12.9 mv.

o.s.p. 0.1M in air = 10.4 mv.

0.1M in N₂ = 10.0 mv.

o.s.p. 0.25M in air = 4.7 mv.

0.25M in N₂ = 15.0 mv.

o.s.p. 0.5M in air = 3.1 mv.

0.5M in N₂ = 5.8 mv.

Interconversion of Air and Nitrogen Saturated Solutions.

In an attempt to find whether the change produced by saturation with nitrogen (and hence removal of oxygen)
was permanent, a series of runs were performed in which
the solution was run to E.S. in air, saturated with
nitrogen, and rerun under that gas. Finally, oxygen was
passed for 1½ hours, and the solution was then
re-electrolysed. Table IVa shows the effect of this
treatment on a 0.25M silver nitrate solution.

Table IVa:

<table>
<thead>
<tr>
<th>n-t results 0.25M AgNO₃ : 0.5A/s dm⁻², F.A.B., E.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t mins</td>
</tr>
<tr>
<td>n mv. 2</td>
</tr>
<tr>
<td>n mv. 3</td>
</tr>
<tr>
<td>n mv. 4</td>
</tr>
<tr>
<td>n mv. 5</td>
</tr>
<tr>
<td>n mv. 6</td>
</tr>
<tr>
<td>n mv. 7</td>
</tr>
<tr>
<td>n mv. 8</td>
</tr>
</tbody>
</table>

Air

Thus, boiling the solution, or saturation with
nitrogen, in no way permanently affects the solution.

It was also possible to demonstrate that the
presence of oxygen, however it is added, gave the most
stable solution from a point of view of electrolysis and
reproducibility of c.s.p. results. Running the solution
in air or oxygen, or even addition of 3% un-stabilised
hydrogen peroxide and then boiling the solution, all gave
c.s.p. values of 4.7 mv. ± 0.1mv. However, on removing
the oxygen by resaturation with nitrogen, the solution
returned to the high c.s.p. of 15.6 mv + 0.1mv. Thus, this phenomenon appears to be reversible.

At this point in the work, another difficulty arose. A new batch of silver nitrate was started, the original being used up, and in order to check this, runs were performed in air and nitrogen saturated solution. The runs in air gave the c.s.p. of 4.7 mv. for 0.2M solution, but the nitrogen saturated solution gave a value of 4.1mv even after rerunning several times. This was clearly a factor requiring investigation.

The Instability of Nitrogen Saturated Solutions.

There seemed to be three possible factors involved:

(i) The distilled water.
(ii) The laboratory atmosphere.
(iii) The silver nitrate.

The first of these factors seemed extremely unlikely as a possible source of inconstancy, since the method of preparation of the distilled water was standard. The second factor seemed fairly likely since the first part of this work was performed in a laboratory where there were many fumes, and the change in the solution coincided with the cessation of work in this laboratory and the transfer to a room with a much purer atmosphere.

It seemed possible that the solution was in some
way picking up one or more of the gases (e.g. 50 etc.) normally present in an analytical laboratory atmosphere, and this, while affecting the solution when run under nitrogen, had no effect on the air saturated solution. To test the possibility of this, the various probable gases were added to a 0.25M solution until either the concentration of the gas was 0.001M, or until the first indications of a visible precipitate were seen. The solution was then run after removing oxygen, in the way described earlier. The gases used were hydrogen sulphide; ammonia; hydrochloric acid; sulphur dioxide; oxides of nitrogen (as nitric acid), and sulphur trioxide (as sulphuric acid). All these failed to give the original c.s.p. of 15.0mv in nitrogen. In several cases there was an increase in the c.s.p., but on resaturating the solution the polarization returned to 4.1mv. In other cases, the c.s.p. value was increased (without attaining the 15.0mv. value), but on resaturating the solution with oxygen a c.s.p. value different to that of the standard solution was obtained. A typical series of results are given in table IVa, for a 0.25M silver nitrate solution with sufficient ammonia added to make the solution 0.001M with respect to that gas. The solution was then run under nitrogen at 0.5A/s1.dm. The first run shows the c.s.p. in nitrogen before adding the ammonia, the next four runs show that the ammonia causes an increase in the c.s.p. in nitrogen, while the last run shows that on resaturating the solution with
oxygen the i.e.p. does not return to the original i.e.p. value in air. Further runs in air show no change in the polarisation.

<table>
<thead>
<tr>
<th>Table IVa</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-t results 0.25M AgNO₃, 0.5A/01.3m, F.A.H., air and H₂</td>
</tr>
<tr>
<td>t mins 1 2 3 10 15 20</td>
</tr>
<tr>
<td>n mv. 6.2 5.2 4.6 4.1 4.1 4.1 H₂ no H₂</td>
</tr>
<tr>
<td>n mv. 5.3 5.4 5.3 5.3 5.3 -</td>
</tr>
<tr>
<td>n mv. 10.7 9.1 8.0 7.7 7.7 7.7</td>
</tr>
<tr>
<td>n mv. 10.6 9.3 8.0 7.0 7.0 -</td>
</tr>
<tr>
<td>n mv. 10.6 9.4 8.3 7.1 7.0 7.0 reset, O₂</td>
</tr>
</tbody>
</table>

All the other added gases gave similar polarisation curves. Thus, the laboratory atmosphere is clearly not the variable factor.

The only other possible variable is the silver nitrate. Unfortunately, none of the original bottle of nitrate had been retained, and it was therefore impossible to reinvestigate this aspect. However, it seemed possible that the new bottle might contain some impurity not present in the original. Therefore a sample of the salt was recrystallised from hot redistilled water, filtered on sintered glass, and dried in the oven. Even after carrying out this treatment twice and then running, a solution failed to give a polarisation of 15.0 mv. in nitrogen. Another method tried was that suggested by
Vagramyan (7) of using oxygen bubbled over platinised platinum to remove traces of organic impurity. This also failed to give any appreciable change in the c.s.p. of a nitrogen saturated solution.

There was only one other alternative, namely that the original bottle of silver nitrate contained some polarising impurity which was only active in nitrogen saturated (i.e. air free) solution. It was apparent that the elucidation of the active material would require very prolonged experiments, and would take a long time.

These results show that the polarisation potential of silver in silver nitrate is extremely sensitive to traces of dissolved gases, and also there is difficulty in obtaining reproducible results. It is interesting to notice that examination of the deposits obtained, either microscopically or with the unaided eye, show no evidence of any change in the nature of the deposit from the different solutions. Although previous workers have in some cases recommended the use of air free solutions, no reasons or results have been submitted to justify this procedure.

Since, the air saturated solutions appear to satisfy the criteria of reproducibility of the polarisation potential much more certainly than those run under nitrogen, it was decided to discontinue the use of nitrogen and concentrate entirely on solutions in equilibrium with the atmosphere.
SECTION V.

THE EFFECT OF VARIATION OF CURRENT AND STIRRING ON CATHODE POLARIZATION POTENTIAL.

Influence of variation of current and stirring on the cathode polarization potential was studied. A series of experiments was conducted to determine the effect of current and stirring on the polarization potential. The results showed that increasing the current and stirring significantly affects the polarization potential. The effect was more pronounced in solutions with lower conductivity. 

In another series of experiments, the effect of stirring on the polarization potential was investigated. It was found that stirring reduces the polarization potential significantly. The reduction was more pronounced at higher stirring rates. 

These findings have important implications for the design and operation of cathodic protection systems. It is recommended that careful consideration be given to the choice of current and stirring rates to ensure effective cathodic protection.
Introduction.

A great many authors have investigated the effect of variation of current density on the polarisation potentials of various systems. Hoekstra (1) has plotted log I-n and obtained linear curves for silver in silver nitrate solutions. Samartsay (2) considers that although the apparent current density varies with the applied current, the true current density is constant for silver in silver nitrate, owing to variations in the cross-sectional area of the growing crystals. He is supported in this view by Vagramyan (3). Conversely, Taft and Hibbert (4) consider that increases in current density cause a decrease in the crystal size. This latter conception was first proposed by Blum and Rawdon (5). Erdey-Gruz and Volmer (6) have obtained various types of curves for different systems by plotting $f(1)-n$ (where $f(1)$ is some function of current density).

In the case of agitated solutions, there is remarkably little to be found in the literature and Levin (7) appears to be the only worker in this field.

Experimental Technique.

In all cases the solution was first run several times to c.s.p. at 0.3A/sq dm in order to produce an electrolytically stabilised solution. Runs were then carried out varying either the current, or agitating the
solution. Finally, a series of runs were performed in which the current was varied and the solution agitated.

In the experiments to obtain n-I curves, runs were performed using both increasing and decreasing currents, the changes being by 0.3A/s steps every 10 minutes. Readings were taken before every change in current. The most consistent and reproducible results were obtained with decreasing current, and it was found that under these conditions, the deposit was less likely to be dendritic, and was therefore more adherent.

The effect of stirring was examined by agitating the solution with a high-speed stirrer. A number of authors e.g. Pontelli and Poli (89) have proposed the use of nitrogen as a means of agitating the electrolyte, but in view of the erratic results reported in Section IV, this was considered unwise. We have the expression:

\[ n = n_a + n_a \]

If the electrolyte is strongly agitated, the concentration gradient adjacent to the cathode, and due to the diffusion layer, is largely destroyed, and hence the concentration polarisation \( (n_a) \) is practically eliminated. Thus the polarisation measured in agitated solutions is the activation overpotential \( (n_a) \).

With the apparatus used in this work, it was found that the best results were obtained when the stirrer was placed eccentrically in the cell with the paddle near
the bottom. The precise speed of rotation of the stirrer was not accurately computed, but the rate was such that further increases in the speed caused no appreciable change in the polarization.

The Effect of Variation of Current Density.

Runs were performed using 0.5, 0.25, and 0.1M silver nitrate solution. It was impossible to use the 0.05M solution, since at any apparent current density greater than 0.5A/sq.dm., the deposit was dendritic and gave erratic results.

The standard solution (0.25M) was run to electrolytic stability at an apparent current density of 0.5A/sq.dm. The solution was then rerun using a fresh cathode specimen from 0.1A/sq.dm to 1.5A/sq.dm the current being changed in steps as described earlier. Several runs were performed on each sample of the solution in some of them the current was increased, and in others decreased. The highest current density used was 1.5A/sq.dm. This does not represent the limiting current density, but above this value, the deposit was so coarse and non-adherent as to make further increases valueless. A typical series of runs on two separate samples of solution is shown in table Va and graphically in fig 9. These results show clearly that the values obtained with decreasing current are more reproducible, although it seems likely that the values at the extreme ends of the
range are not the true values. This is especially
true for the values at the beginning of the run since
the time may not be sufficient to attain the constant
value, while at the end, the deposit is so crystalline as
to have a very different area from the true area. It is
also apparent that there is some hysteresis effect
depending on the direction of change of the current, and
this observation agrees with the similar effects obtained
by Irrey-Graz and Volmer (6).

Table Va
n-I results, 0.25M AgNO₃, I charged by 0.2A/sq.dm./10 min.
F.A.S., c.s.p. at 0.3A/sq.dm. = 4.7mv.

<table>
<thead>
<tr>
<th>I mA</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
<th>n,</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.6</td>
<td>1.6</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>3.8</td>
<td>3.8</td>
<td>1.6</td>
<td>1.6</td>
<td>3.8</td>
</tr>
<tr>
<td>30</td>
<td>3.4</td>
<td>3.4</td>
<td>3.2</td>
<td>3.2</td>
<td>3.1</td>
<td>4.0</td>
<td>4.1</td>
<td>3.2</td>
<td>3.2</td>
<td>4.0</td>
</tr>
<tr>
<td>50</td>
<td>4.8</td>
<td>4.9</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
<td>4.3</td>
<td>4.3</td>
<td>4.7</td>
<td>4.7</td>
<td>4.6</td>
</tr>
<tr>
<td>70</td>
<td>6.6</td>
<td>6.3</td>
<td>5.9</td>
<td>5.9</td>
<td>5.8</td>
<td>5.6</td>
<td>5.6</td>
<td>5.9</td>
<td>5.9</td>
<td>5.8</td>
</tr>
<tr>
<td>90</td>
<td>8.6</td>
<td>8.3</td>
<td>7.7</td>
<td>7.7</td>
<td>7.6</td>
<td>7.3</td>
<td>7.3</td>
<td>7.7</td>
<td>7.7</td>
<td>7.6</td>
</tr>
<tr>
<td>110</td>
<td>9.9</td>
<td>10.6</td>
<td>8.5</td>
<td>8.5</td>
<td>8.4</td>
<td>7.6</td>
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<td>7.6</td>
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<tr>
<td>130</td>
<td>11.4</td>
<td>12.3</td>
<td>9.7</td>
<td>9.7</td>
<td>9.6</td>
<td>9.7</td>
<td>9.7</td>
<td>10.4</td>
<td>10.4</td>
<td>9.7</td>
</tr>
<tr>
<td>150</td>
<td>11.8</td>
<td>13.6</td>
<td>13.6</td>
<td>12.8</td>
<td>12.8</td>
<td>10.7</td>
<td>10.7</td>
<td>12.8</td>
<td>12.8</td>
<td>10.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample I</td>
<td></td>
<td></td>
<td>Sample II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The deposit was the same in appearance as in the
earlier runs, though naturally much heavier. In the cases
where the current was increased, there was a marked
tendency for long needle-like crystals to grow at high
FIG. 9
n. - I CURVES, 0.25M. AgNO₃
F. A. B.
current densities, particularly round the edges of the deposit. This was always accompanied by erratic polarisation values.

The curves obtained for the 0.5M and 0.1M solutions were similar to those reported above, except that the more dilute solution was not run above 1.0A/sq.dm owing to the tendency to dendritic growth. A typical series of results is shown in Table Vb:

<table>
<thead>
<tr>
<th>Table Vb</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-I Results, Current decreased by 0.2A/sq.dm./10 min. F.A.B.</td>
</tr>
<tr>
<td>I mA.</td>
</tr>
<tr>
<td>n_1 mv</td>
</tr>
<tr>
<td>n_2 mv</td>
</tr>
<tr>
<td>n_3 mv</td>
</tr>
<tr>
<td>n_4 mv</td>
</tr>
</tbody>
</table>

| n_1 mv | 2.5 | 6.7 | 10.4 | 16.5 | 22.5 | - | - | - |
| n_2 mv | 2.4 | 5.4 | 10.5 | 16.7 | 24.3 | - | - | - |
| n_3 mv | 2.5 | 6.4 | 10.4 | 16.6 | 23.1 | - | - | - |
| n_4 mv | 2.5 | 6.4 | 10.4 | 16.6 | 23.5 | - | - | - |

c.s.p. 0.5M = 3.1mv at 0.5A/sq.dm

c.s.p. 0.1M = 10.2mv at 0.5A/sq.dm

The discrepancies in the initial readings (at high c.d.) is almost certainly due to the same effect as that observed in n-t runs, in which high values are obtained owing to the solution not having reached its equilibrium state. The first readings in such runs are
nearly always higher than the e.s.p., but the e.s.p. is usually attained after 10 mins. (See Table III p 29). However, in some cases the solution took rather longer to reach the e.s.p. value, and this explains the variations in the quoted values of the polarisation at the highest r.d. in table Vb, which were always taken ten minutes after starting the run. This was confirmed by taking several readings in the first ten minutes when the polarisation values decreased in the same way as for a n-t run.

**The Effect of Agitation of the Solution.**

The electrolyte was agitated by means of a high speed stirrer, as has been described earlier. The purpose of the experiments was to examine the variation of the activation overpotential \( (n_a) \) with time and current density. Since all the previous work had shown the standard (0.25M) solution to be typical of all solutions, only this solution was examined. The results obtained for this solution in agitated conditions are reported in table Vc and in fig.10. The solution was rerun several times using a fresh cathode specimen in each run, and the results show that this rerunning is necessary to establish electrolytic stability in the solution.

The deposits obtained from the agitated solutions were in all cases similar to those from unstirred solutions. They usually appeared to be slightly finer crystals to the
FIG. 10

\( \eta_{\text{aq}} - t \) CURVES. O.25M \( \text{AgNO}_3 \) F.A.D.

0.5A/SQ.DM.

\( \times \) = 1ST. RUN

\( \bigcirc \) = 2ND. "

\( \triangle \) = 3RD. "

\( \square \) = 4TH. "

\( \eta_{\text{aq}} \) MV,
naked eye, but microscopic examination showed this difference to be insignificant, since both the stirred and unstirred solutions gave crystals of widely varying size on each specimen. In fact, the deposits from agitated solutions were typically coarsely crystalline.

<table>
<thead>
<tr>
<th>Table Vc</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-t results 0.25M AgNO₃ 0.5A/s1.dm., F.A.B.</td>
</tr>
<tr>
<td>t mins</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>25</td>
</tr>
</tbody>
</table>

The precise rate of stirring was not determined, but a speed was taken such that further increases did not affect the polarisation. A typical run with varying speed is shown in Table Vd, the rate of stirring described as "medium" being the minimum rate above which there was no change in the polarisation when the speed was increased.

<table>
<thead>
<tr>
<th>Table Vd</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-t results 0.25M AgNO₃ 0.5A/s1.dm F.A.B., variable speeds.</td>
</tr>
<tr>
<td>t mins</td>
</tr>
<tr>
<td>n mV.</td>
</tr>
<tr>
<td>speed.</td>
</tr>
<tr>
<td>m = medium, s = slow, f = fast.</td>
</tr>
</tbody>
</table>
If the stirring was interrupted, the still conditions were re-established, giving readings similar to the usual n-t run.

**Activation Overpotential—Current Density Results.**

The technique used in determining these curves was the stepwise decrease in current described earlier. The solution was agitated by a high speed stirrer, and it was found that once the constant state conditions were established (usually after 10 mins.), the values of \( n_a \) were practically unaffected by variations in the apparent current density. The solution was electrolytically stabilised before commencing the \( n_a \)-I runs, and it was found that the value for \( n_a \) could be reproduced indefinitely and independently of current density within the range of current densities examined. Results obtained for the standard solution are given in Table Ve and fig.11, and here again, it was better to use decreasing rather than increasing currents.

**Table Ve.**

\( n_a \)-I results, Electrolytically Stabilised 0.35M AgNO₃, F.I.B., I decreased by 0.2A/sq.dm./10 mins.,

c.s.p. agitated solution at 0.5A/sq.dm. = 3.1 mv.

<table>
<thead>
<tr>
<th>I mA</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>130</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_1 ) mv.</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>2.9</td>
<td>3.1</td>
</tr>
<tr>
<td>( n_2 ) mv.</td>
<td>3.0</td>
<td>3.1</td>
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<td>3.1</td>
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<tr>
<td>( n_3 ) mv.</td>
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<td>3.1</td>
<td>3.0</td>
<td>3.0</td>
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<td>3.1</td>
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</tbody>
</table>
Fig. 11

\( n_a - I \) curves, 0.25M \( AgNO_3 \), F.A.B.

\( I \) decreased by 0.2A/sq.dm. /10 min.

- \( X = 1st. \) run
- \( \bigcirc = 2nd. \)
- \( \triangle = 3rd. \)
In this, as in every other case, fresh cathode specimens were taken for every run. It was again found that the polarisation rose to a maximum in the first few minutes of the run, and then gradually fell to the value quoted for 1.5/5 sq. dm. after 10 mins. This shows that the solution must first establish equilibrium conditions, and while doing this high polarisation values are obtained, but the value then decreases to the s.s.p. value at any given current density.

The Variation of Concentration Polarisation with Time & Current Density.

We have the equation:

\[ n = n_a + n_g \]

and measurements in unstirred solution give the total polarisation \( n \), while those in agitated solution give the activation overpotential \( n_a \). Thus curves of concentration polarisation \( n_g \) against any given factor may be constructed by taking the difference between the two values obtained in unstirred and stirred solutions.

In practice, since the technique of intermittent stirring takes a considerable time for the stirred and unstirred conditions to become established, the curves were obtained by taking the difference of two runs one of which was stirred, and the other unstirred. (Although some experiments with intermittent stirring gave similar results). Table VI shows the results
FIG. 12.

\( n_c - t \) CURVES, 0.25 M \( \text{AgNO}_3 \) F.A.B.

0.5 A/SQ. DM.

\( \times = n_{MV} \)

\( \bigcirc = n_a MV \)

\( \triangle = n_c MV \)
obtained for the \( n_t \) curves for the solution at 0.5A/31.
dm and they are also shown graphically in fig 12.

**Table VI**

<table>
<thead>
<tr>
<th>( t ) mins</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
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<td>4.7</td>
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<td>3.5</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>( n = n - n_a )</td>
<td>1.0</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Thus at 0.5A/sq dm apparent current density, the concentration polarisation represents about 30\% of the total polarisation.

Curves of \( n_t \) were constructed in exactly the same way, with the current density decreased from beginning to end of the run in the way described earlier. Results for the standard solution are shown in Table VI and fig.13. The solution was subjected to pre-electrolysis before the runs reported were made.

**Table VII**

| \( n - I \) results, 0.25M \( \text{AgNO}_3 \), I decreased by 0.2A/sq dm/10min. |
| I ma | 10 | 30 | 50 | 70 | 90 | 110 | 130 | 150 |
| nmv. | 3.2| 3.2| 4.6| 5.0| 6.2| 6.4| 9.6| 10.0|
| nmv. | 3.1| 3.1| 3.2| 3.2| 3.2| 3.2| 3.2| 3.9|
| \( n = n - n_a \) | 0.1| 0.1| 1.5| 2.3| 4.0| 5.2| 6.5| 6.9|

The slight curvature of the \( n_a - I \) curve at the highest c.d. is due to the solution not having attained the s.s.p. in the 10 mins which elapsed before taking the
FIG. 13

n_0 - I CURVES, 0.25 M. AgNO_3 F.A.B.

I DECREASED BY 0.2 A/SQ. DM/10 MIN.

X = n. MV.

O = n_0 MV.

Δ = n_0 MV.
reading. Some experiments using the technique of intermittent stirring (i.e., using one solution and cathode base and taking readings in stirred and unstirred conditions) showed that although the values of $n_3$ obtained by taking the difference of two separate runs (one stirred and the other unstirred), may be slightly too low at the lower current densities, the majority of the values quoted in Table 7g are correct. It is worth noting that in all the experiments in which the current density was varied, the values of the polarisation at the lowest current density were always somewhat erratic.

**Discussion of Results.**

The experiments have shown that the activation overpotential of silver in silver nitrate is practically independent of the apparent current density. This would seem to infer that the true current density is constant, that is, the depositing area increases as the current increases. This view was first proposed by Samartsev (2) and has been adopted by practically all the Russian workers. They are of the opinion that the surface of the growing crystal is more or less passivated due to adsorption of traces of organic impurity in the solution. This would infer that the extent of adsorption is governed in some way by the current. Further, if this view is accepted, the concentration polarisation should also be independent of the apparent current density.
and the results reported above show that this is not the case.

The assumption that organic impurities cause passivation of the growing crystal surface, (which in turn causes the true current density to be a constant) may best be examined by investigating the effect of inorganic and organic additions to the solution.

It was now considered that the experimental technique was sufficiently well established to allow work to proceed on this the major aspect of the work with the added reason of the necessity of testing the hypothesis of passivation of the cathode.
SECTION VI.

THE EFFECT OF INORGANIC IONIC ON THE POLARISATION POTENTIAL OF SILVER.
Introduction.

Although the effect of hydrogen ions on the polarisation potential of many metals, has been widely studied, only Solosud, Kern and Halligan (1) have attempted to investigate acid silver nitrate solutions in any detail. These workers claim that nitric acid is reduced to ammonium nitrate during electrolysis, but they do not report any polarisation measurements. No work has been reported on the effect of non-depositing metallic cations, although Muller (2) has discussed the probable effect of inorganic colloids from a theoretical standpoint, while Raub (3) has examined the effect of such substances on the deposit.

This paucity of information is remarkable in view of the theory proposed by Hunt (4), and developed by Agar and Bowden (5), that the ionic strength of the electrolyte is a contributory factor to the polarisation, and that the nature of the deposit is influenced by the ratio of depositing ions to the total number of ions in the solution. Since the deposits obtained from silver nitrate solutions are so markedly crystalline, and should therefore be greatly affected by any additions, this system would seem ideal for an examination of the Agar and Bowden treatment of the effect of inorganic non-depositing cations.

Reagents and Technique.

The purity of the silver nitrate and the method
of preparation of the distilled water have been
described earlier, and the following inorganic reagents
were used:

Nitric acid and the nitrates of sodium,
potassium, copper, barium and thorium were of "AnalaR"
standard, and were used without further treatment.
However, the nitrates of lithium, calcium, and
aluminium could only be obtained of pure chemical
standard, and these reagents were once recrystallised
from redistilled water and dried before use, using methods
described by Meller (6).

The silver nitrate was made up in 1 litre batches
of 0.5M solution, and the other salts in 500ml batches
of 0.5M concentration. Appropriate amounts of these
solutions were taken and diluted to give a working solution
of 0.25M silver nitrate plus 0.001M or 0.25M added inorganic
salt.

The techniques of measurement and cathode
preparation have been described earlier. The cathodes used
were in all cases fully annealed foil. Six runs were
performed on each solution, the first three of these were
n-t runs, at 0.5A/cm², and in all cases, the c.s.e.
values on the second and third determinations agreed to
± 0.1mV. Following this, determinations of n-I, nₐ-I were
made in the way described earlier, and in all cases where
the current was varied, the changes were decreases of 0.2A/s.
an./10 min. as previously described.

Experimental Results.

The general shape of the n-t curves was similar to that obtained for the standard silver nitrate solution, but in most cases there was a pronounced increase in the c.s.p. value of the electrolytically stabilised solution. The curves for the addition of thorium show an appreciable rise in the early stages, which may be connected with the fact that thorium salts are extensively hydrolysed in solution.

Table VIa shows the results obtained with 0.001M addition, and table VIb and fig 14 those for additions of 0.35M inorganic solution. The third n-t run is quoted in all cases. Tables VIa, VIb, and VIc, show the n-I, na-t and na-I results obtained for the various solutions.

In the case of copper, the values obtained for na were greater than those for n, and this is almost certainly due to the fact that solutions containing copper tended to give a deposit consisting of long dendritic needles which were non-adherent, and this phenomenon is always associated with erratic polarisation values.
# Table VIa

n-t results of 0.25M AgNO₃ + 0.01M inorganic ion.

<table>
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<th>t mins.</th>
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<th>3</th>
<th>5</th>
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<td>4.6</td>
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<td>4.6</td>
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# Table VIb.

n-t results, 0.25M AgNO₃ + 0.25M A.A., 0.5A/51. dm, F.A.D.

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<th>t mins.</th>
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</table>
FIG. 14.

$n-t$ CURVES, 0.25M AGNO$_3$ + 0.25M AA.

0-5A/SQ. DM.

- $Ba(NO_3)_2$
- $LiNO_3$
- $KNO_3$
- $HNO_3$
- $Th(NO_3)_4$
- $Ca(NO_3)_2$
- $Al(NO_3)_3$
- $NaNO_3$
- $Cu(NO_3)_2$

No Addition
Table VII

n-L results 0.2MH AgNO₃ + A.A., F.A.B.

I decreased by 0.2A/si.dm./10 min.

<table>
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<th>I mA</th>
<th>10</th>
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<th>40</th>
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Table VII.

n-t results, 0.02M AgNO₃ + A.A., F.A.E., 0.5 A/sl. dm.
<table>
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<th>I ma</th>
<th>10</th>
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<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>130</th>
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<td>3.2</td>
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<td>HNO₃</td>
<td>(0.25)</td>
<td>3.7</td>
<td>3.8</td>
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<td>3.8</td>
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<tr>
<td>LiNO₃</td>
<td>(0.01)</td>
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<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>(0.25)</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
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<tr>
<td>KNO₃</td>
<td>(0.01)</td>
<td>3.1</td>
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<td>3.0</td>
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<tr>
<td>Cu(NO₃)₂</td>
<td>(0.25)</td>
<td>9.4</td>
<td>9.5</td>
<td>9.4</td>
<td>9.4</td>
<td>9.3</td>
<td>9.2</td>
<td>9.5</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>(0.01)</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>(0.25)</td>
<td>3.7</td>
<td>3.7</td>
<td>3.6</td>
<td>3.6</td>
<td>3.7</td>
<td>3.7</td>
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<tr>
<td>Al(NO₃)₃</td>
<td>(0.01)</td>
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<td>4.0</td>
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<td>4.0</td>
<td>4.0</td>
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<tr>
<td>Th(NO₃)₄</td>
<td>(0.01)</td>
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<td>5.5</td>
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<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
The reason for including copper was that the presence of copper in silver electro-refining baths is considered to give short stocky crystals. Also, it seemed possible that those elements whose electrode potentials were near that of silver, might, by analogy with hydrogen in nickel plating, have very large effects on the deposit of silver.

It is wrong to place too much emphasis on the disparity of values in tables VIa and VIb for the polarisation at 0.5A/sq.dm., since these values were obtained under different experimental conditions. In general, no difficulty was experienced in obtaining the quoted values under given conditions, so that although no attempt was made to repeat the runs on fresh samples of solution, there seems no reason to suppose that they would reproduce with less certainty than the values for the standard solution. This view was confirmed when, after an interval of more than six months, selected typical solutions were checked, and gave identical results within the limits of experimental error.

Appearance of the Deposits.

In no case was any very marked change in the grain-size of the deposit observed. It seemed that the thorium salt might give a very slight diminution on the crystal size, and also give rather better covering of the cathode. However, this was extremely difficult to judge
even under the microscope, because the size of the crystals varied a great deal. Barium and potassium also appeared to have a slight grain-refining effect, but again the same difficulty was encountered. It was in fact impossible to say that any ion had a specific effect on the grain size in the deposit. On this basis, the Hunt theory of polarisation potentials would appear to be lacking in some respects, since, if we accept the concept that ionic-strength of the solution is an important factor, then there should be some obvious difference between the deposits from a simple silver nitrate solution and one containing large amounts of added cation.
THE INFLUENCE OF ORGANIC REAGENTS ON THE CATHODE
POLARISATION POTENTIAL OF SILVER.

SECTION VII.

The investigation of the influence of organic reagents on the cathode polarisation potential of silver was carried out as part of the project of small battery development. In this context, cathodic potential measurements were made to establish the relationship of chemical stability in the presence of organic compounds. The results of this study indicated that certain organic substances can significantly affect the stability of the cathode potential, altering the equilibrium of the reaction involved. The investigation showed that the presence of organic reagents can reduce the cathode polarisation potential, thereby improving the performance of the battery. This finding is significant for the development of more efficient and stable battery systems.
Introduction.

The literature on the effects of organic addition agents in electroplating baths is very extensive. In connection with silver deposition, Kern (1) as early as 1909 studied the effect of gums and gelatine on the adherancy of silver deposited from silver nitrate solutions. This investigation and most of the early work, was naturally directed more at improving the deposit than at investigating polarisation phenomena. This desire to produce a useful electroplate from non-cyanide solutions is understandable in view of the toxic effects of the latter type of solution. The work of Fussya and Murata (2) showed that complex ion formation is likely to play a part in the production of smooth deposits, but these workers did not attempt to correlate their work to polarisation potentials. The work of Assman (3) which showed that thiourea improved the silver deposit from nitrate solutions is of interest in view of Shreir and Smith's (4) investigation of the anomalous effects produced by that substance in acid copper sulphate solutions. They showed that this was one of the few examples of an addition agent which not only improved the brightness of the deposit, but also decreased the polarisation. A number of authors have shown sulphur containing compounds to be effective brightening agents in silver cyanide baths (5), and Fischer (6) considers that in such cases, some submicroscopic form of silver
sulphide is the active agent.

On the other hand, Taft and Horseley (?), who tried over a hundred additives, consider the fatty acids to be particularly active, while Muller (3) and his coworkers favour hydroxyacids. On the theoretical side, Muller (3) and Vagramyan and Solov'eva (10) seem to favour colloid formation as the important factor.

It therefore seemed desirable to re-examine the effects of sulphur compounds, hydroxyacids, and aminoacids on the polarisation potential, and the nature of the deposit of silver from silver nitrate solutions.

Reagents and Technique.

The techniques employed were precisely the same as those used in Section VI, namely, each solution was run six times, the first three determinations were of m-t, and were also used to attain conditions of electrolytic stability. The last three determinations were of \( n_{d}-t \), \( n_{d}-l \), and \( n_{d}-l \) respectively. The following reagents were employed:

- Aminoacetic acid; citric acid; tartaric acid;
- and glucose all of AnalR standard. Gelatine; thiourea;
- and thioglycollic acid all of B.D.H. pure chemical standard. The AnalR salts were dried before use. The pure chemicals were used as obtained, except the thiourea whose purity was doubtful, and this reagent was once recrystallised from hot redistilled water and dried before
The use of the selected reagents was prompted by several considerations. The two hydroxyacids show a marked tendency to form complexes, they have been widely used as addition agents, and it has even been proposed that they should be used with silver nitrate as a commercial plating bath. Gelatine is a well-known addition agent to commercial plating solutions, and aminocetic acid was chosen as typical of the probable hydrolysis products of gelatine. Glucose was selected as typical of the non-complexing additives to plating baths. Thiourea has been widely used in copper electro-refining solutions, and is a likely hydrolysis product of carbon disulphide (which has been used as a brightener in commercial silver cyanide plating solutions). Finally, thioglycollic acid was selected as a sulphur compound with a very different C-S link from thiourea.

As far as possible, all the reagents were used at two concentrations, namely, 0.01M, and 0.2M. In the case of the hydroxyacids, other concentrations were also used. In several cases, particularly that of the sulphur compounds, it was found that even the 0.01M solution tended to give a slight precipitate either of the addition agent, or of some insoluble reaction product. Thus, the solution was below the concentration indicated, and was saturated with respect to the insoluble substance. The sulphur compounds all gave white precipitates which finally
became dark brown, presumably due to some complex
decomposing to silver sulphide.

Except where otherwise stated, the standard
solution (0.25M Ag₂O₃) was used throughout the work. In
general, the results reported were not repeated at the
time, but selected solutions were checked after an interval
of several months, and agreed with the original
determinations within the limits of experimental error.

Experimental Results and Appearance of the Deposit.

In no case did an addition agent lower the
polarisation. It was however apparent that the reagents
could be divided into two distinct groups on a basis of
their effect on the deposit:

(a) The active group which increased the c.p.p.
and reduced the grain size of the deposit considerably.

(b) The inactive group which, while increasing
the c.p.p., did not appreciably change the deposit.
The first group comprised of citric acid, tartaric acid,
aminoacetic acid and gelatine, while the second group
consisted of thioars; thiglycollia acid and glucose.
As will be seen later, a number of wetting agents were
also used in this part of the work, and when they alone
were present in the solution, they behaved as members of
the inactive group.

The experimental results will dealt with on a
basis of this grouping.
The Inactive Group.

The thioacetone solution was limited to 0.00001M, as any greater concentration than this gave a white precipitate which rapidly turned brown. (Presumably an insoluble silver-thioacetone complex was decomposing to give silver sulphide.) Even at the concentration used, a precipitate eventually formed. The results obtained with this solution are given in Tables VIIa and VIIb below, and also graphically in figs. 13 and 15.

Table VIIa.

n-1 and n_d-1 results, 0.25M AgNO_3 + 0.00001M thioacetone.

<table>
<thead>
<tr>
<th>t mins</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
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<tbody>
<tr>
<td>n mv.</td>
<td>21.9</td>
<td>22.4</td>
<td>22.3</td>
<td>22.3</td>
<td>22.3</td>
<td>22.3</td>
</tr>
<tr>
<td>n_d mv.</td>
<td>35.1</td>
<td>25.4</td>
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<td>21.4</td>
<td>21.4</td>
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</table>

Table VIIb.

n-1 and n_d-1 results, 0.35M AgNO_3 + 0.00001M thioacetone.

<table>
<thead>
<tr>
<th>I min</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>130</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>n mv.</td>
<td>21.5</td>
<td>21.7</td>
<td>21.8</td>
<td>21.9</td>
<td>22.0</td>
<td>22.0</td>
<td>22.3</td>
<td>22.5</td>
</tr>
<tr>
<td>n_d mv.</td>
<td>20.4</td>
<td>20.4</td>
<td>20.4</td>
<td>20.3</td>
<td>20.3</td>
<td>20.5</td>
<td>20.5</td>
<td>20.5</td>
</tr>
</tbody>
</table>

In all cases, the deposit was similar to that obtained from a simple silver nitrate solution, and no visible brightening occurred. This is at variance with the results reported by Assman (3) and also shows that in the case of silver, thioacetone increases the polarisation,
whereas a similar concentration in acid copper sulphate solution decreases the polarisation.

In the case of the thioglycollie acid solution, the addition agent was added to 0.01M concentration, and the heavy precipitate formed was filtered off. Thus, the solution was saturated with respect to the complex formed. The results for this solution are shown in Tables VIIIa and VIIIb and in figs. 15 and 16.

Table VIIIa.

n-t and n_a-t results, 0.25M AgNO₃ + 0.01M thioglycollie acid, 0.5A/sq.dm., F.A.B.

t mins. 1 2 3 10 15 20 25
n mv. 21.4 21.3 20.7 29.1 29.1 29.1 29.1
n_a mv. 19.9 21.4 16.6 16.2 16.5 16.3

Table VIIIb.

n-I and n_a-I results, 0.25M AgNO₃ + 0.01M thioglycollie acid, I decreased by 0.2A/sq.dm./10min., F.A.B.

I ma. 10 30 50 70 90 110 130 150
n mv. 22.7 24.6 27.1 27.9 29.2 30.1 31.1 32.1
n_a mv. 12.5 15.1 15.2 15.3 15.3 15.1 15.2 15.3

Again, the deposit was coarsely crystalline, and differed very little from the deposit obtained from the standard solution.

The addition of glucose was not attended by precipitation difficulties, and therefore both 0.01M and 0.25M concentrations were used.
FIG. 15
n-t vs n.e.t CURVES, 0.25M AgNO₃ INACTIVE
0.5A/SQ.DM.

X = 0.0001M THIOUREA
O = 0.001M THIOGLYCOLLIC
□ = 0.001M GLUCOSE

n-t
n.e-t
n.e-t

n.t

n.t No Addition
n.e-t No Addition.
Fig. 16

n-I, n_a-I curves, 0.25 M AgNO₃

+ inactive organic additions,

- 0.00001

X = Thigurrea.

[] = 0.001 M glucose.

○ = 0.001 M thioctanoic acid.

n - I, n_a - I curves with no addition.

n_a - I curves with no addition.
In both cases there appeared to be no reduction in grain size of the deposit, although there was a pronounced increase in the c.s.p. The results for the more dilute solution are shown graphically in figs. 15 and 16. The curves for the stronger solution are not shown, but they resemble the former curves in shape, and the c.s.p. value for the unstirred solution was 26.6 mv. at 0.5A/s. dm.

Results for the Active Group of Addition Agents.

This group, which consisted of citric; tartaric; and eminocetic acids; and gelatine, all gave smooth deposits. These deposits were of very small grain size, and showed no obvious crystals either to the naked eye, or under the microscope. Citric and tartaric acids were used at 0.0001M; 0.001M; 0.05M; and 0.75M and at all concentrations, the deposit was very markedly different from that of a simple silver nitrate solution. However, as the concentration of added reagent increased, the smoothing effect increased up to a maximum, after which further additions had no effect. Also, the differences between the polarisation values decreased as the current increased during the determination of n-I curves.

The results obtained for citric acid are shown in Tables VIIe and VIIf, and those for tartaric acid in Tables VIIg and VIIh, while all the results are shown graphically in figs. 17, 18, 19, and 20. Photographs of typical deposits are shown in fig. 21. In all cases, the deposits were grey in colour, and while under the
microscope the deposits from the lower concentrations of citric acid tended to be nodular, those from solutions containing tartaric acid were much smoother. In a few cases, the higher concentration solutions exhibited slight brightening. All the deposits were very highly strained, as is shown by the fact that on removal from the cell, the foil cathode curled up, and on flattening out, the deposit showed a large number of hair cracks.

Table VIIa.

n-t and n_a-t results, 0.95M AgNO₃ + citric acid,
C.5A/sq.dm., F.A.B.

<table>
<thead>
<tr>
<th>t mins.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>conc.</th>
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</thead>
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<td>43.1</td>
<td>38.1</td>
<td>37.0</td>
<td>34.9</td>
<td>34.3</td>
<td>34.3</td>
<td>0.00001M</td>
</tr>
<tr>
<td>n_a mv.</td>
<td>35.9</td>
<td>34.7</td>
<td>33.9</td>
<td>33.9</td>
<td>33.9</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>n mv.</td>
<td>35.9</td>
<td>34.3</td>
<td>34.3</td>
<td>34.3</td>
<td>34.3</td>
<td>34.3</td>
<td>0.001M</td>
</tr>
<tr>
<td>n_a mv.</td>
<td>30.7</td>
<td>29.7</td>
<td>31.0</td>
<td>31.1</td>
<td>31.1</td>
<td>31.1</td>
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</tr>
<tr>
<td>n mv.</td>
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<td>39.6</td>
<td>40.0</td>
<td>42.4</td>
<td>42.4</td>
<td>42.4</td>
<td>0.25M</td>
</tr>
<tr>
<td>n_a mv.</td>
<td>37.3</td>
<td>38.1</td>
<td>38.0</td>
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<td>38.0</td>
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<tr>
<td>n mv.</td>
<td>41.8</td>
<td>45.6</td>
<td>45.6</td>
<td>47.1</td>
<td>47.0</td>
<td>47.0</td>
<td>0.75M</td>
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<tr>
<td>n_a mv.</td>
<td>38.9</td>
<td>39.4</td>
<td>40.0</td>
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Table VII. 

n-I and n$_{a}$-I results, 0.25M AgNO$_3$ + Citric acid.

<table>
<thead>
<tr>
<th>I Min.</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
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<td>n mv.</td>
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<td>28.5</td>
<td>28.5</td>
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<tr>
<td>n$_{a}$ mv.</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Table VIIx. 

n-t and n$_{a}$-t results, 0.25M AgNO$_3$ + Tartaric acid.

<table>
<thead>
<tr>
<th>C.5A/sq. dm., F.A.B.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t mins.</td>
</tr>
<tr>
<td>n mv.</td>
</tr>
<tr>
<td>n$_{a}$ mv.</td>
</tr>
<tr>
<td>n mv.</td>
</tr>
<tr>
<td>n$_{a}$ mv.</td>
</tr>
<tr>
<td>n mv.</td>
</tr>
<tr>
<td>n$_{a}$ mv.</td>
</tr>
<tr>
<td>n mv.</td>
</tr>
<tr>
<td>n$_{a}$ mv.</td>
</tr>
</tbody>
</table>
n-t, n_o-t CURVES,

0.25 M AgNO_3 + CITRIC
ACID, 0.5A/SQ. DM.
FIG. 18

\( n^-I = n_a^-I \) CURVES, 0.25 M \( \text{AgNO}_3 \) + CITRIC ACID, \( I \) DECREASED BY 0.2 A/SQ. DM./10 MIN.
FIG 19

\( n-t, \eta_c-t \) CURVES, 0.25 M \( \text{AgNO}_3 + \text{Tartaric Acid} \)

0.5 A/SQ. DM.
\( n-I, n_\alpha-I, \text{Curves, 0.25 M AgNO}_3 + \text{Tartaric Acid, } I \text{ Decreased by 0.2 A/Sq.DM./10 Min} \)
(i) Deposit from non-complex solution.

(ii) Deposit from citric acid solution.

(iii) Deposit from tartaric acid solution.

(iv) Deposit from aminocetic acid solution.

The results were complete when glutine was used, the results were complete and the galvino value in this case was 7.157, at both times. The fall results are not reported, since the solution...
Table VIII

n-I and \( n_a \)-I results, 0.25M \( \text{AgNO}_3 \) + tartaric acid.

I decreased by 0.2A/sq.dm./10min., F.A.E.

<table>
<thead>
<tr>
<th>I (min)</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>28.1</td>
<td>28.3</td>
<td>28.5</td>
<td>28.7</td>
<td>28.9</td>
<td>29.3</td>
<td>29.7</td>
<td>31.7</td>
</tr>
<tr>
<td>( n_a )</td>
<td>25.3</td>
<td>25.4</td>
<td>25.4</td>
<td>25.3</td>
<td>25.6</td>
<td>25.4</td>
<td>27.1</td>
<td></td>
</tr>
<tr>
<td>( n )</td>
<td>23.5</td>
<td>24.0</td>
<td>25.9</td>
<td>31.0</td>
<td>33.0</td>
<td>34.8</td>
<td>35.4</td>
<td>42.6</td>
</tr>
<tr>
<td>( n_a )</td>
<td>21.5</td>
<td>21.3</td>
<td>21.4</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>20.9</td>
</tr>
<tr>
<td>( n )</td>
<td>24.5</td>
<td>27.5</td>
<td>22.0</td>
<td>35.2</td>
<td>38.2</td>
<td>39.5</td>
<td>41.4</td>
<td>44.5</td>
</tr>
<tr>
<td>( n_a )</td>
<td>19.4</td>
<td>24.0</td>
<td>25.9</td>
<td>27.2</td>
<td>29.4</td>
<td>29.3</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>( n )</td>
<td>24.4</td>
<td>30.6</td>
<td>34.9</td>
<td>39.1</td>
<td>42.7</td>
<td>44.3</td>
<td>45.6</td>
<td>50.3</td>
</tr>
<tr>
<td>( n_a )</td>
<td>23.7</td>
<td>29.4</td>
<td>31.8</td>
<td>33.8</td>
<td>35.7</td>
<td>38.3</td>
<td>38.3</td>
<td>33.8</td>
</tr>
</tbody>
</table>

In the experiments using gelatine as the added reagent, the solution was initially made about 1% with respect to gelatine. When the solution was run at this high concentration, a very marked smoothing of the deposit occurred, but the polarisation measurements were very erratic. The values obtained were only very approximate, since the potentiometer setting varied as fast as the reading was obtained. However, the e.e.p. value was as high as 42.0 mv. at 0.5A/sq.dm., and in general the curves were similar to those for citric acid. The erratic results were almost certainly due to the fact that the solution gradually set, since, when a solution 0.001% gelatine was used, the results were completely normal. The e.e.p. value in this case was 9.6 mv. at 0.5A/sq.dm. The full results are not reported, since the solution
behaved very similarly to one 0.001M to citric acid.

The experiments with amincacetic acid were of very great interest. At first, this reagent was studied in the same way as the other addition agents had been. That is to say, solutions were used 0.001M and 0.25M to amincacetic acid, and these were run on fully annealed foil cathodes. The results of these runs are shown in Tables VIIJ and VIIK and in figs. 22 and 23. It was found that the polarisation values were increased compared with the standard solution, being of the same order as those for the hydroxysalts. However, the difference between the polarisation potentials and the deposits was much less marked than in the case of the solutions containing hydroxysalts at the same concentration. Thus, there is more comparison with the solutions 0.25M and 0.75M to citric acid, although the actual values of the c.e.p. for these solutions is greater. The deposits from the solutions with amincacetic acid were all of a yellow-brown colour, and even the deposits from the dilute solution were markedly smoother than those from the standard solution, or from solutions containing hydroxysalts at comparable concentrations. In some cases the deposit showed appreciable brightening.

The deposit obtained from the concentrated solution was of particular interest. In general, these deposits were similar to those from citric acid, but, when the solution was electrolysed with decreasing current
n-t, n-\(n_0-t\) CURVES, 0.25 M AgNO\(_3\) + AMINOACETIC ACID, 0.5 A/SQ. DM.

![Graph showing n-t and n-\(n_0-t\) curves for 0.25 M AgNO\(_3\) + AMINOACETIC ACID with 0.5 A/SQ. DM.](image)
FIG. 23.

n-I, n$_{a}$-I, 0.25 M AgNO$_3$ + AMINOACETIC ACID

I DECREASED BY 0.2A/SQ. DM./10 MIN.

\[ \eta - n, \eta_{a} - n, 0.25 M AgNO_{3} + AMINOACETIC ACID \]

\[ I \text{ DECREASED BY 0.2A/SQ. DM./10 MIN.} \]
under agitated conditions \( (n_a-I) \), the deposit had almost a mirror finish. This deposit was of a brightness comparable to that of a polished deposit from a bright silver cyanide bath.

Table VIIIa.

\( n-t \) and \( n_a-t \) results, \( 0.25 \text{M} \text{AgNO}_3 + \text{Aminoacetic acid} \),

\( 0.5\text{A/s}_1\text{dm.}, \text{F.A.B.} \)

<table>
<thead>
<tr>
<th>t mins.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>concn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n ) mv.</td>
<td>30.4</td>
<td>30.0</td>
<td>50.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>0.001M</td>
</tr>
<tr>
<td>( n_a ) mv.</td>
<td>25.7</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>0.001M</td>
</tr>
<tr>
<td>( n ) mv.</td>
<td>32.3</td>
<td>27.3</td>
<td>25.6</td>
<td>23.4</td>
<td>23.4</td>
<td>23.4</td>
<td>0.25M</td>
</tr>
<tr>
<td>( n_a ) mv.</td>
<td>25.0</td>
<td>22.6</td>
<td>21.7</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>0.25M</td>
</tr>
</tbody>
</table>

Table VIIIb.

\( n-I \) and \( n_a-I \) results, \( 0.3 \text{M} \text{AgNO}_3 + \text{Aminoacetic acid} \),

I decreased by \( 0.2\text{A/s}_1\text{dm.}/10\text{min.}, \text{F.A.B.} \)

<table>
<thead>
<tr>
<th>I mi.</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>110</th>
<th>130</th>
<th>150</th>
<th>concn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n ) mv.</td>
<td>25.9</td>
<td>25.1</td>
<td>30.1</td>
<td>31.1</td>
<td>32.1</td>
<td>33.4</td>
<td>33.5</td>
<td>33.4</td>
<td>0.001M</td>
</tr>
<tr>
<td>( n_a ) mv.</td>
<td>20.1</td>
<td>20.1</td>
<td>22.6</td>
<td>22.7</td>
<td>22.7</td>
<td>22.7</td>
<td>22.7</td>
<td>22.7</td>
<td>0.001M</td>
</tr>
<tr>
<td>( n ) mv.</td>
<td>16.5</td>
<td>20.5</td>
<td>23.2</td>
<td>25.3</td>
<td>28.4</td>
<td>30.4</td>
<td>34.1</td>
<td>35.8</td>
<td>0.25M</td>
</tr>
<tr>
<td>( n_a ) mv.</td>
<td>14.4</td>
<td>19.6</td>
<td>20.5</td>
<td>21.2</td>
<td>22.5</td>
<td>23.3</td>
<td>23.9</td>
<td>24.1</td>
<td>0.25M</td>
</tr>
</tbody>
</table>

An immediate attempt was made to repeat the very bright deposit using a fresh sample of solution, but although the deposit was noticeably bright, it had far less reflectivity than the original deposit. This was clearly an aspect which might yield a considerable amount of interesting information, and further more detailed work on
the subject is reported in Section VIII.

The Effect of Wetting Agents on the Polarisation.

With the exception of glucose, all the additional agents used so far, have been of a type likely to complex with the silver ions to a greater or lesser extent.

It was of interest, in view of the fact that adsorption is considered to play a part in the processes of bright electrodeposition, to examine the effect of wetting agents on the deposit and polarisation. Such reagents, are highly surface active, and are therefore likely to be very strongly adsorbed on the cathode. However, they are unlikely to form complexes with silver ions to any marked extent.

Three such reagents were obtained, namely, cetyl pyridinium bromide (a cationic); sodium dodecane-1-sulphate (an anionic); and pentaerytritol (a neutral) wetting agent. The cetyl pyridinium bromide was converted to the corresponding nitrate (C.P.N.) by passing a very dilute solution through a column of the anion exchange resin I.R.A. 400. A solution was then made of 0.25M AgNO₃ + 0.0001M cetyl pyridinium nitrate (this represented the limit of solubility of the reagent). This solution was then electrolysed using fully annealed silver foil as the cathode in the usual way. The results obtained with this solution are reported in Tables VIII and VIIIm.
results.  

Table VIII.  

<table>
<thead>
<tr>
<th>t mins.</th>
<th>n mv.</th>
<th>n_a mv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.0</td>
<td>14.4</td>
</tr>
<tr>
<td>2</td>
<td>14.1</td>
<td>14.4</td>
</tr>
<tr>
<td>5</td>
<td>14.7</td>
<td>13.4</td>
</tr>
<tr>
<td>10</td>
<td>14.7</td>
<td>13.4</td>
</tr>
<tr>
<td>15</td>
<td>14.0</td>
<td>13.4</td>
</tr>
<tr>
<td>20</td>
<td>14.0</td>
<td>13.4</td>
</tr>
<tr>
<td>25</td>
<td>14.0</td>
<td></td>
</tr>
</tbody>
</table>

Table VIIIa.  

<table>
<thead>
<tr>
<th>I ma.</th>
<th>n mv.</th>
<th>n_a mv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>12.7</td>
<td>11.5</td>
</tr>
<tr>
<td>30</td>
<td>12.9</td>
<td>11.7</td>
</tr>
<tr>
<td>50</td>
<td>13.3</td>
<td>12.0</td>
</tr>
<tr>
<td>70</td>
<td>13.9</td>
<td>11.9</td>
</tr>
<tr>
<td>90</td>
<td>14.5</td>
<td>11.9</td>
</tr>
<tr>
<td>110</td>
<td>15.4</td>
<td>12.0</td>
</tr>
<tr>
<td>130</td>
<td>16.9</td>
<td>12.0</td>
</tr>
<tr>
<td>150</td>
<td>16.2</td>
<td></td>
</tr>
</tbody>
</table>

There appeared to be a slight diminution in grain size of the deposit compared with the standard solution, but this was not very marked. From the tables, it is apparent that the general shape of the curves is quite normal, although the maximum values do not appear to be attained quite so quickly.

Similar solutions were made of 0.25M AgNO_3 + 0.0001M sodium dodecane-1-sulphate, and 0.25M AgNO_3 + 0.0001M pentaerythritol and run in the usual way. In these cases, there was practically no diminution in grain size. However, there was an increase in polarisation, the c.s.p. values being 7.1 mv. for the sodium dodecane-1-sulphate, and 8.3 mv. for the solution containing pentaerythritol, both values being for an apparent current density of 0.5A/sq.dm.. The curves obtained were similar.
Thus the effect of the surface active non-complexing reagents is analogous to that of the inactive group of complex forming organic addition agents.
SECTION VIII.

BRIGHT DEPOSITS FROM SOLUTIONS CONTAINING AMINOACETIC ACID.
Introduction.

The bright deposit obtained from an agitated solution of 0.25M AgNO₃ + 0.25M Aminoacetic acid, and the fact that this effect could not be reproduced readily on a fresh sample of the solution, was of particular interest. It was therefore decided to make a more systematic investigation of this solution.

It was at first considered that a critical ratio between the concentrations of the silver nitrate and the aminoacetic acid was necessary in order to obtain the brightening effect, and therefore, several solutions were examined with different ratios of the two constituents. However, the other factors involved in the deposition process such as pH, rate of agitation, and the method of determining nₐ-I curves were not precluded.

The Effect of Variation of Concentration.

A number of solutions were made up, all of which had a silver nitrate concentration of 0.25M, but in which the concentration of aminoacetic acid varied from 0.2M to 0.5M. Thus, the ratio of the components was varied from greater to less than one. These solutions were then electrolytically stabilised by electrolysis at 0.5A/sq.dm. in un stirred conditions. Attempts were then made to obtain a bright deposit from these solutions, using as far as possible the same technique as was originally used to determine nₐ-I curves, that is by
running under agitated conditions with decreasing current.

Although all the solutions gave some brightening, the deposit was in no case as good as that originally obtained. The c.a.p. values for all these solutions were of the same order as that for the original solution, i.e. 23.6mv. for the unstirred, and 28.0mv. for the stirred solution at 0.5A/sq.dm. Thus relative concentration did not appear to account for the brightening effect.

The next series of experiments were directed towards finding whether the apparent current density was the controlling factor. An E.S. solution containing 0.25M AgNO₃ + 0.25M aminoacetic acid was run at different constant current densities in the range 0.1A/sq.dm. to 5.0A/sq.dm. under agitated conditions. The brightest deposits were obtained from the solution between 1.0 and 2.0A/sq.dm. apparent current density, but again the extent of brightening was not comparable to that in the original deposit reported in section VII. Thus, variations in the apparent current density are not the controlling factor in the production of bright deposits.

The Production of Bright Deposits.

The next step consisted of the addition of small quantities of acid and alkali to the solution. It is wellknown that the aminoacetic acid molecule exists in aqueous solution as a "zwitterion" of the form:

\[ +\text{CH}_3\text{CH}_2\text{COO}^- \]
This structure is attained by the transfer of a proton from the carboxylic acid group to the amino group. Thus this is an acid-base reaction, and as such, the extent to which the molecule will now ionise is governed by the pH of the solution. Therefore, in acid solutions the ionisation of the amino group (which in this case acts as a proton donor) will be repressed, and the carboxyl group will take up a proton, leaving the molecule cationic. In more alkaline solutions, the reverse conditions will occur. Thus the pH of the solution will control the tendency of the aminoacetic acid to migrate to the cathode. However, the aminoacid will tend to resist small changes in pH by adjusting its' extent of ionisation. That is, it will tend to buffer the solution to its' own equilibrium pH.

Hence, trace additions of acid or alkali will not materially alter the pH.

On the other hand, any slight increase in the hydrogen ion concentration may cause more extensive adsorption of the protons on the cathode, or if, as is quite likely, ammonia is hydrolised out of the aminoacid molecule, the ammonium ion might be adsorbed. Either of these processes might be the active cause of brightening. It was therefore decided to examine the effect of additions of nitric acid and ammonia to the solution.

The first addition used was nitric acid. A quantity of concentrated nitric acid was added to a previously electrolytically stabilised solution until the
solution was 0.004M to nitric acid. The solution was then run under agitated conditions with varying current (n_a-I curve). This failed to give a bright deposit, and in fact the deposit was noticeably less smooth, although the n_a-I results were identical with those for a similar solution without added nitric acid. Thus, addition of nitric acid will not brighten the deposit.

The next attempt was made with ammonia. A solution was made 0.03M AgNO_3 + 0.25M aminoacetic acid, and run to E.S. Ammonia was then added to a concentration of 0.002M, and the solution electrolysed under agitated conditions with varying c.d. A very marked increase in brightness of the deposit was observed which persisted even after several re-runs using a fresh cathode for each run.

It was now decided to examine the effect of various quantities of ammonia, both on the polarization, and on the appearance of the deposit. This was accomplished in the following way. An E.S. solution 0.05M to both silver and aminoacid was used. This solution was run several times under agitated conditions at 1.5A/sq. dm., using a fresh cathode for each run. The c.d. used represented the middle of the most effective c.d. range as previously determined. Before starting each run, ammonia solution was added. The ammonia was 0.1M, and by adding 0.06mL the concentration of ammonia could be increased by 0.00001M steps in the electrolysis solution without materially altering the concentration of other reagents.
A typical series of runs are shown in Table VIIIa in which the appearance of the deposit is also reported. The table shows that the addition of traces of ammonia make the deposit very bright, but above a certain concentration (0.0002M approximately), further additions not only do not improve the deposit, but actually make it less bright. In the later runs ($n_4$ onwards), there was a visible precipitate formed, possibly of silver-ammonia complex, so that it is improbable that the concentration of the ammonium ions ever attains a very high value.

Table VIIIa.

$n_3$-t results, 0.25M AgNO$_3$ + 0.25M NH$_2$CH$_2$COCH + Ammonia,

1.5A/sq.dm., F.A.B.

<table>
<thead>
<tr>
<th>Conc. NH$_3$ deposit</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$ mv.</td>
<td>32.6</td>
<td>25.1</td>
<td>23.6</td>
<td>24.2</td>
<td>24.1</td>
<td>24.1</td>
</tr>
<tr>
<td>$n_2$ mv.</td>
<td>33.0</td>
<td>30.1</td>
<td>29.9</td>
<td>29.6</td>
<td>29.6</td>
<td>29.5</td>
</tr>
<tr>
<td>$n_3$ mv.</td>
<td>33.2</td>
<td>33.4</td>
<td>31.5</td>
<td>31.5</td>
<td>31.5</td>
<td>31.5</td>
</tr>
<tr>
<td>$n_4$ mv.</td>
<td>33.6</td>
<td>31.6</td>
<td>31.5</td>
<td>31.5</td>
<td>31.5</td>
<td>31.5</td>
</tr>
<tr>
<td>$n_5$ mv.</td>
<td>32.4</td>
<td>31.5</td>
<td>31.0</td>
<td>31.1</td>
<td>31.1</td>
<td>31.1</td>
</tr>
</tbody>
</table>

s.b. = slightly bright.  b. = bright  v.b. = very bright.

The table also shows that when the conditions are such as to give the brightest deposits, the polarisation is at a maximum.

The problem now arose as to whether the active
constituent of the ammonia was the ammonium or the hydroxyl ion. This was resolved by using sodium hydroxide in place of the ammonia, when it was found that comparable amounts of NaOH would also brighten the deposit. However, it seemed probable that the ammonium ion played some part in the process, since the sodium hydroxide did not brighten as well as the ammonia.

In order to show that the effect was not specific to solutions complexed with aminoacetic acid, a series of experiments were performed using α-alanine (α-aminopropionic acid) in place of the aminoacetic acid. This work was complicated by the fact that the silver/alanine complex is not so soluble as that between silver and aminoacetic acid. A solution was made 0.25M to both reagents, and the resulting precipitate filtered off. The solution was then run, with additions of ammonia, at 1.0A/sq.dm. in agitated conditions. Again, some brightening was observed when the concentration of ammonia was 0.00005M, although the effect was not as marked as in the case of aminoacetic acid. The c.s.p. in agitated solution at 1.0A/sq.dm. was 36.4mv.

It was also possible to obtain brightening with solutions 0.05M to silver and aminoacetic acid, but in this case there was a tendency for the deposit to be very finely crystalline, and the effect was only observed at low current densities of the order 0.2A/sq.dm. It is also interesting to notice that in all the above cases,
that if the stirring was interrupted, the solution immediately reverted to the non-bright type, and in order to obtain a bright deposit, further additions of ammonia were necessary.

**Bright Deposits From Solutions Containing Citrate.**

Although attempts were made to determine the pH of the solutions complexed with aminoacetic acid, these were unsuccessful owing to precipitation of insoluble silver salts. However, in view of the extremely small quantities of ammonia needed to brighten the deposit, it seems unlikely that the primary cause of brightening is pH changes in the solution. However, it does seem probable that the ammonia acts by forming small quantities of colloidal silver oxide, which may then be adsorbed on the cathode. If this is the case, pH may have the secondary effect of affecting the stability or even the formation of the colloid. There is some evidence to support colloid formation, namely, the fact that the conditions of adding the ammonia (rapid addition at high concentration) favour colloid formation.

By means of indicator papers, it can be shown that the pH of the silver nitrate/aminoacetic acid solution is about 5.6. The pH of an equimolecular solution of silver nitrate and citric acid is very much less than 5.0. However, if a solution could be made using sodium citrate as a complexing agent, it might be possible to attain a pH which would allow the brightening
action of the ammonia to occur. Secondary sodium citrate has a pH in aqueous solution of about 4.9, and is used with sodium hydroxide in Sorensen's Buffer (1). A solution 0.25M AgNO₃ + 0.25M Secondary sodium citrate was pre-electrolysed (after filtering off the precipitate) and then run in agitated conditions at 0.5A/sq.dm. Additions of ammonia gave no brightening effect in the deposit. However, on making up a fresh solution of Sorensen's Buffer of pH 6.0, and using this to complex the silver, it was possible to obtain a marked brightening effect, under the same conditions of current and agitation, upon addition of ammonia up to approximately 0.001M.

The Brightening Action of Wetting Agents.

The previous work had shown conclusively that the addition of small amounts of a reagent, likely to form a colloidal precipitate with the silver ions, would cause brightening of the deposit from a complexed silver nitrate solution. This brightening effect would only occur if the solution was not too acid. The most probable explanation of the effect is that a silver containing colloid is formed which may then be adsorbed on the cathode. It was of interest to attempt to determine whether the active brightening action was the formation of some silver containing colloid, or the process of adsorption.

In an attempt to clarify the position, it was decided to use an addition agent which, while being unlikely to form any colloidal substance by reaction with the silver
ions in solution, would nevertheless, be strongly adsorbed. Such a reagent is cetyl pyridinium bromide ($C_{16}H_{33}N(C_6H_5)Br$). This substance is in fact colloidal, but it does not contain any silver. In order to avoid any possibility of formation of colloidal silver bromide, the reagent was first converted to cetyl pyridinium nitrate (C.P.N.) by passing a saturated solution through an anionic exchange column. A solution was then made of

$$0.25M \text{AgNO}_3 + 0.25M \text{NH}_2\text{CH}_2\text{COOH} + 0.001M \text{C.P.N}.$$  

This solution was pre-electrolysed to electrolytic stability, and then run in agitated conditions at various constant current densities, using fully annealed cathode foils. The results obtained are shown in Table VIIIb, together with a note of the appearance of the deposit and the c.d. used in each run. These results are of great interest. They show that it is not necessary to use a brightening agent which reacts with the depositing ion. It is however, necessary to use a reagent which is adsorbed at the cathode. The brightest deposits obtained with this addition agent were much brighter than any deposits previously obtained. It must however be pointed out that in many cases the deposits from this solution were not uniformly bright, due apparently to some deficiencies in the agitation, and presumably connected with the fact that the wetting agent is very strongly adsorbed.

The result quoted in the last column of the table is of interest in that it represents the only case in which
appreciable brightening was observed in un-stirred solution.

Table VIIIb.

<table>
<thead>
<tr>
<th>t mins.</th>
<th>( n_1 ) mV</th>
<th>( n_2 )</th>
<th>( n_3 )</th>
<th>( n_4 )</th>
<th>( n_5 )</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>23.3</td>
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<td>44.8</td>
<td>31.9</td>
</tr>
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<td>38.3</td>
<td>42.0</td>
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<tr>
<td>5</td>
<td>31.6</td>
<td>49.6</td>
<td>36.6</td>
<td>42.0</td>
<td>29.5</td>
</tr>
<tr>
<td>10</td>
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<td>44.5</td>
<td>35.7</td>
<td>39.8</td>
<td>26.8</td>
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<tr>
<td>15</td>
<td>31.6</td>
<td>35.8</td>
<td>35.6</td>
<td>39.9</td>
<td>26.7</td>
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<tr>
<td>20</td>
<td>31.6</td>
<td>35.9</td>
<td>36.6</td>
<td>39.9</td>
<td>26.7</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>35.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a.d.</td>
<td>1.0</td>
<td>1.5</td>
<td>2.5</td>
<td>4.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

\( \text{A/sq.dm.} \)

<table>
<thead>
<tr>
<th>deposit</th>
<th><strong>b</strong></th>
<th><strong>v.b.</strong></th>
<th><strong>v.b.</strong></th>
<th><strong>b.</strong></th>
<th><strong>a.b.</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>stirred</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>unstirred</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

s.b. = slightly bright, b. = bright, v.b. = very bright.

Similar experiments with an anionic wetting agent (sodium dodecane-1-sulphate) and a neutral wetting agent (pentaerythritol) gave little or no brightening.

Thus it seems that bright deposits are obtained by the use of two separate addition agents, at least one of which is strongly adsorbed on the cathode. However, neither of the added reagents will cause brightening if it is used alone. The precise significance of all these
results will be discussed later.

The Effect of Additions of Gelatine to the Solution.

A solution was made 0.25M AgNO₃ + 0.35M aminoacetic acid + 10mg/l. gelatine. This solution was run in the usual way, using fresh cathodes for every run, in both stirred and unstirred conditions. It was found that in agitated solution with current densities in the range 1.0 to 2.0 A/sq. dm, a very bright deposit was obtained. Outside that range, the deposit was still bright, but not to the same extent. In the case of the unstirred solution, there was no appreciable brightening even at current densities as low as 0.5A/sq. dm.

Photographs of typical deposits obtained in this part of the work are shown in fig. 24.

Structure of the Deposits.

In an attempt to find whether there was any major structural difference between the smooth and bright deposits, a series of microscopic examinations were undertaken.

Very thick deposits of both types were built up on fully annealed cathode foils by prolonged electrolysis. Transverse and longitudinal sections of these deposits were cut from various parts of the specimens. All these samples were mounted for metallographic examination. It would have been impossible to have polished each specimen
separately, and therefore the specimens were placed

in solution consisting of Tartaric Acid Solution

and Ammonia Solution. After Polishing.

(1) Smooth Deposit From Tartaric Acid Solution. Ammoniac Acid Solution.

(iii) Bright Deposit From Aminoacetic Acid
And Ammonia Solution

(iv) Bright Deposit From Aminoacetic Acid
And C.P.M. Solution

(v) Bright Deposit From Aminoacetic Acid
After Polishing.

electrodeposits are not necessarily layered.
separately, and therefore all the specimens were placed together in such a way that the edges to be examined were in the same plane, and so that they formed a "sandwich" of alternate layers of cathode base and deposit. The "sandwich" was then mounted in a bakelite resin. The cut edges could now be polished without the danger of breaking the highly strained deposit. Polishing was carried out through the usual grades of emery paper (1, 01, 001, 000) using paraffin as a lubricant. The final polish was on Selvyn cloth with "Bluebell" and "Silvo". Finally, the specimen was etched for two minutes in a mixture of 5% potassium cyanide and 5% ammonium persulphate.

Microscopic examination showed the deposits to consist of closely packed small columnar crystals of silver. There was no evidence of a banded structure consisting of alternate layers of silver and complexing agents. Neither was it possible to detect any difference in structure between the smooth and bright deposits. Thus an examination of the microstructure of these deposits confirms the work of Raub (2) which states that bright electrodeposits are not necessarily layered.
SECTION IX.

POLARISATION DURING DEPOSITION ON SILVER SINGLE CRYSTALS AND X-RAY EXAMINATION OF THE DEPOSITS.
Introduction.

The nature of the cathode base, both with regard to the surface condition of working and also the orientation, has a marked influence on both the structure of the deposit and on the polarisation potential. For this reason, many workers have attempted to examine the structure of the deposit produced on cathodes of definite orientation and with different degrees of working. It is very difficult to obtain cathodes all of which have been worked to precisely the same extent, but it is fairly easy to obtain specimens of definite orientation. However, very few workers have examined the polarisation potentials of different planes of a single crystal in the course of electrodeposition.

Vagramyan (1) has determined the polarisation on one crystal growing in a polycrystalline cathode, and at the same time has observed the growing crystal under a microscope. This work led him to conclude that passivation phenomena played an important part in silver deposition. However, he has made no attempt to examine the structure of the deposit. Kaishev and his co-workers (2) have reported that only certain faces of a silver single crystal deposit under given conditions of current density, and as the applied current increases, more planes start to deposit.

In recent years, Swathmey and Leidheiser (3) have reported very great differences in the structure of
the copper deposit on different planes of a single copper crystal. Even more recently, the same workers (4) have reported a pronounced brightening effect during the deposition of nickel on certain planes of single crystals of that metal.

Thus, it seemed that an examination of the polarisation and the deposit obtained during the deposition of silver on single crystals of silver might yield interesting information.

Method of Preparation of Single Crystals.

The most practicable method of preparation of single crystals appears to be that of re-crystallisation from the melt. The principle of this method is that if a melted specimen of the metal is allowed to cool slowly from one end, then re-crystallisation will start at that end and extend along the specimen. Under these conditions, the first crystal formed will continue to grow throughout the length of the specimen. Gwathney, Leidheiser and Smith (5) have used this method for the preparation of large crystals of various metals.

The single crystals used in the present work were grown from cylindrical bars 1 in. in diameter, and of 99.99% purity, supplied by Johnson Matthey Ltd.

The Single Crystal Furnace.

The essential process in the method of preparing
single crystals is to establish a temperature gradient through which the molten specimen is passed. This causes recrystallisation to start at one end and gradually extend right up the bar. In the present work, the temperature gradient was established by slowly lifting the furnace off the specimen.

The furnace consisted of a fused alumina cylinder 16in. long and of 2.75in. internal diameter, which would withstand a temperature of 1200°C. The windings were of 20 s.w.g. "Brightray" wire, and two windings in parallel were used. The first winding was made directly on to the tube, while the second was made over a thin layer of alumina furnace cement which served to separate the two coils. Both windings were made heavier at the ends of the tube in order that a uniform temperature might be maintained throughout the length of the tube. The electrical resistances of the windings were approximately 54 ohms for the inner, and 50 ohms, for the outer coil. To heat the furnace, both windings were run at 3-3.5 amps., but once the required temperature had been attained, one winding sufficed to maintain the temperature. The double winding was a safety precaution, since, if one winding broke down (as not infrequently happened when the furnace was used to grow copper crystals), the other could be brought into use. Each winding was provided with a variable resistance and an ammeter in series, and the heating was controlled by a Sunvic Energy Regulator through a Hotwire Vacuum Switch. The temperature was measured by a platinum/platinum-rhodium
thermocouple and a millivoltmeter calibrated in degrees Centigrade. The thermocouple was carried through a cement "stopper" which closed the top of the furnace.

The tube and windings were mounted in a rectangular box and packed with powdered magnesium oxide to provide thermal insulation. The whole furnace was mounted vertically in a carriage which ran in a vertical "railway", and was lifted vertically by means of a series of pulleys and a counterweight. The bottom of the counterweight was connected to a wire passing round an axle which was driven through a reduction gear by an electric motor. The gearing was such that the furnace was lifted vertically at a rate of 0.5 in./hr. This speed of lifting could, however, be varied as desired. A photograph and diagram of the furnace are shown in figs. 23 and 26.

The Preparation of Single Crystals.

The silver specimen was cut 4.5 in. long, and turned down to 0.75 in. in diameter with a point at one end. The point had an angle of about 50°. The precise angle was unimportant so long as it was considerably less than a right angle. The specimen was polished to remove the worst of the turning marks, and lightly etched with hot 50% nitric acid.

The specimen was then mounted point down in a graphite crucible, the internal diameter of which was 1.25 in. Some powdered graphite was placed in the bottom of the
Fig. 26.

Prior to switching on the furnace large vitreous were continued dropped into the crucible, and the specimen placed into it. Here powdered graphite was then added, and carefully packed down with a hammer for a short time. A little more powder was added until the crucible was full.

The Single Crystal Furnace.

The heating was started with an initial current of 80 amperes of the large elements of 3100 ohms; and the temperature allowed to rise to about 50°C. above the melting point of silver (1230°C.).

The energy regulator was then adjusted to maintain a temperature of 1090°C. After allowing some time for the
crucible, and the specimen pressed into it. More powdered graphite was then poured in, and carefully packed down with a brass cylinder which fitted fairly tightly round the specimen and into the crucible. The graphite was added a little at a time, and packed tightly round the specimen until the packing was level with the top of the silver. In this way, the shape of the specimen was maintained when molten. Finally, a loose fitting lid covered the crucible.

The specimen and crucible were now placed top first into a Vitreosil tube 24in. long and closed at one end which fitted into the furnace. The crucible was propped up near the top end of the Vitreosil tube by means of a long thin inlet tube of Vitreosil. This thin tube, with another similar but shorter tube, was carried in a large rubber hung which served to close the mouth of the larger Vitreosil tube. Thus, the lowest part of the silver specimen was the pointed end, and the position of the furnace was now adjusted so that the point on the specimen was about 6in. from the bottom of the furnace.

Prior to switching on the heater current, a slow stream of oxygen free nitrogen was passed through the large Vitreosil tube, and continued throughout the run. The heating was started with an initial current on both elements of 2.5amps., and the temperature allowed to rise to about 50°C above the melting point of silver (963°C). The energy regulator was now adjusted to maintain a temperature of 1010°C. After allowing some time for the
temperature to become constant, the lifting mechanism was started, and the furnace lifted vertically from the Vitreosil tube containing the specimen at a rate of 0.6in./hr for a distance of 13-14ins. At the end of the run, the specimen was 1-2ins below the bottom of the furnace. At this stage, the heating and lifting motor were switched off, and when the furnace had cooled to about 600°C., the nitrogen was also cut off. After the furnace had cooled to room temperature, the specimen was removed from the crucible and cleaned in hot nitric acid. The complete run occupied about 30hrs, and was carried out overnight.

The Orientation of the Single Crystal.

The crystal was examined for absence of polycrystalline material and its orientation checked by X-ray diffraction. The X-ray unit was a Metropolitan-Vickers Continuously Evacuated Unit, and the method used was the Laue back-reflection method. The target used was of copper, and the X-rays were generated at 45Kv. and 15mA. Each exposure took about 1 hour.

A scratch mark was made on the surface of the specimen, parallel to the axis of the cylinder, and served as a reference axis. The specimen was placed point uppermost in the mounting of the Laue camera. The mounting could be adjusted about three perpendicular axes. The specimen was placed so that the X-rays were incident at an angle of 180° to the scratch mark, which was adjusted by means of a telescope until it was vertical and centrally
in the eyepiece. The specimen to film distance was adjusted until the specimen was parallel to and 3 cm. from the film. Ilford blue-base X-ray film was used.

The X-rays were now switched on, and an exposure made for 1 hour. The film was developed and fixed using Kodak D163 developer and May and Baker "Amfix" fixer. The developer was used slightly stronger than the recommended strength, while the fixer was used in the usual 3:1 dilution.

The diffraction pattern consisted of sharply defined spots lying on definite arcs, and thus confirmed the crystal as being single. (It was fairly certain that the crystal was single, since the process of cleaning with nitric acid after removal from the furnace, failed to show any evidence of grain boundaries.) The precise orientation of the specimen was determined by identifying the various diffraction spots on the film. This identification was carried out by means of a Greninger chart, and the table of interplanar angles quoted by Barrett (6). Since all the planes in a single crystal are at definite fixed angles to each other, it follows that there will be a definite angular relationship between the spots of the diffraction pattern. The Greninger chart provides a method of measuring the angles between the diffraction spots from their stereographic projection on the film. Thus, given the specimen to film distance, it is possible to identify the plane causing a particular spot, and hence to determine its position with respect to the reference scratch mark. The
observed angles agreed very closely with the theoretical values in all cases.

Preparation of the Specimen for Deposition.

From each cylindrical bar, two specimens for deposition experiments were obtained in the following manner:

The bar was mounted in a lathe using a piece of lead foil to prevent excessive marking by the chuck. The specimen was turned into the form of a sphere of diameter 0.6in. with a shank 0.25in. in diameter and 0.75in. long. Turning was accomplished at high speeds with a fine cut to minimise the distortion of the crystal. Before cutting the finished specimen free from the parent bar, the original scratch mark was copied on the shank so that the orientation was known. The advantage of the spherical shape lies in the fact that every possible plane of the crystal is exposed at some point on the surface. However, polarisation determinations on such a surface are by no means easy.

The specimen was next electropolished to remove the work hardened layer. The electropolishing was accomplished by making the specimen anodic in a silver cyanide solution, (of a typical composition used for electroplating) with a cylindrical foil cathode surrounding the anode. The use of a silver cyanide bath for electropolishing is recommended by Wernick (7) and also by
Gilbertson and Forder (8). The operating conditions were about 2 volts P.D. from anode to cathode, with approximately $1.7 \times 10^{-4}$ anodic current density. The precise polishing conditions were obtained separately for each specimen. The applied voltage was varied until a periodic "flashing" was observed on the anode. This flashing was accompanied by "kicks" in the current and voltage. Polishing was carried on under these conditions for about 1 hour, and the specimen again examined by X-rays, being set up in the camera in as nearly as possible the same position as for the original exposure. If necessary, the process of polishing was repeated until there was no evidence of polycrystalline work hardened material on the X-ray film. Usually, only one polish was required to remove the layer completely. It proved impossible to attain a very high polish by this method, but the surface was smooth and free from the etch pits, which always accompany any form of extensive chemical etching. As a final stage, the specimen was lightly etched in hot 50% nitric acid immediately before starting any polarisation determination.

**Preliminary Experimental Work.**

Each specimen was mounted on the end of a piece of glass tubing by means of a piece of rubber tubing. A silver wire wrapped round the shank and passing through the glass tubing served to make electrical contact. A diagram of the specimens and the experimental set-up for
this part of the work is shown in fig. 27. The electrolyte was placed in a 100 ml. beaker, and a piece of silver foil round the inside wall of the beaker served as a cylindrical anode. The specimen was clamped in the centre of the beaker with the glass tube held in a clamp. The reference half-cell was placed with the capillary in the electrolysis vessel.

The usual connections were made to the potentiometer, and polarisation determinations made at 0.5A/sq.dm. apparent current density. The polarisation readings were taken after various time intervals as described earlier. However, in order to study the nature of the deposit and polarisation on different crystal planes, readings were taken with the capillary in several different positions round the sphere. This was accomplished by rotating the glass tube carrying the specimen, and then bringing up the capillary to press against the surface of the sphere. Three readings were taken after every time interval, with the capillary tip in positions roughly corresponding to the normals to the \{100\}, \{110\}, and \{111\} planes as previously determined by X-rays. Under the experimental conditions, it was almost impossible to be certain that the capillary was always pressed against the required spot on the cathode, so that disparities quoted in Table IIA for the polarisation on any given plane do not necessarily mean that there were actual variations in the polarisation on that plane.
FIG. 27

DIAGRAM OF SINGLE CRYSTAL & LAYOUT FOR POLARISATION & DEPOSITION EXPERIMENTS

(1) Specimen as grown.

(2) The spherical specimen.

(3) Experimental arrangement for chemical work.

(4) Arrangement for deposition on crystal planes.

Not to scale.
Since it was desired to examine the deposits by X-ray diffraction methods, each run was carried on for 5 hrs. at 0.5 A/sq.dm. in order that the deposit should be thick enough to completely eliminate the diffraction pattern of the base. This period was found to be completely satisfactory, and was based on the values quoted by Shreir and Smith (9) for the thickness of copper to destroy the silver pattern of the base, and since is a better adsorbent of X-rays than copper, the thickness used was more than adequate.

At the end of each determination, three X-ray exposures were made with each specimen so placed in the camera that the X-ray beam was incident along the previously determined normals to the \{100\}, \{110\}, \{111\} planes respectively. The precise position of the specimen for each exposure was determined by calculation from the original orienting photograph, and also checked by experiment on the undeposited base.

This technique of deposition and subsequent X-ray examination was used to investigate the polarisation and crystal structure of the deposit obtained from five typical electrolytes. The five solutions used were:

(i) 0.25M AgNO₃.
(ii) 0.25M AgNO₃ + 0.25M citric acid.
(iii) 0.25M AgNO₃ + 0.25M tartaric acid.
(iv) 0.25M AgNO₃ + 0.25M aminoaetic acid.
(v) 0.25M AgNO₃ + 0.25M aminoaetic acid + 0.001M ammonia.
For purposes of comparison, a polycrystalline sphere was also made, and the polarisation measured at three arbitrarily selected positions round the sphere during deposition.

The results obtained for all the solutions are shown in Table IIa together with a note as to the structure of the deposit on the different planes as determined by X-ray diffraction. The crystal planes referred to in the table, are the actual planes whose normals were parallel to the incident X-ray beam, and the approximate planes on to which the capillary pressed during the polarisation determinations. The table shows that although the polarisation values obtained under these conditions are not very reproducible, (probably largely owing to inaccuracies in the position of the capillary during measurement), nevertheless, there is a significant variation in polarisation from place to place on the sphere which is not due to any dissymmetry in the position of the various parts of the sphere with respect to the anode. This latter fact is demonstrated by the concurrence of values for the polycrystalline sphere. It therefore appeared to be desirable to examine the variation of polarisation with crystal plane rather more carefully.

In order to perform this more systematic examination, it was necessary to devise a means for bringing the capillary up to the same plane for every reading, and at the same time to prevent deposition on every plane except the selected plane.
### Table Ika.

**Polarisation and X-ray Examination of Deposits on Single Crystals of Silver.**

<table>
<thead>
<tr>
<th>t mins.</th>
<th>1</th>
<th>30</th>
<th>60</th>
<th>180</th>
<th>240</th>
<th>360</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Soln.</td>
<td>P (1)</td>
<td>S (1)</td>
<td>P (1)</td>
<td>S (1)</td>
<td>P (1)</td>
<td>S (1)</td>
</tr>
<tr>
<td>12.9</td>
<td>16.5</td>
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<td>19.7</td>
<td>19.7</td>
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</tr>
<tr>
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<td>11.2</td>
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<td>10.8</td>
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<tr>
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<td>4.8</td>
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<td>8.5</td>
<td>8.5</td>
<td>8.5</td>
<td>8.5</td>
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<tr>
<td>4.7</td>
<td>4.9</td>
<td>11.3</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

**Base:** P = Polycrystalline.  
S = Single.  
Deposit: A. = Polycrystalline.  
B. = Polycrystalline with preferred orientation.  
Solutions: See pl36. Solution (v) was stirred.
The Preparation of Selected Planes for Deposition.

In order to examine more carefully, the phenomena reported above, a method was devised for exposing selected planes of the crystal to deposition, while at the same time preventing deposition on other parts of the crystal. The method consisted of mounting the specimen in a cold setting resin, and then cutting through the mount and crystal in such a way as to expose the required plane.

Since silver crystallises in the face centred cubic system, it is possible by means of two mutually perpendicular rotations to bring any desired plane into any desired position. The position of the normal to the selected plane was determined with respect to the scratch mark, by means of a carefully prepared back reflection picture, and checked by further X-ray diffraction experiments.

The specimen was mounted on a graduated circle, in such a way that the former could be rotated about a horizontal axis through any desired angle. The mould for the plastic mount was placed on another graduated circle so that it could be rotated about a vertical axis. The mould was made from a piece of square brass tubing. Each side of the square was 1 in. long, and the mould was 1 in. high. The tubing was open at both ends, and was placed on a flat piece of plate glass. Thus, the four vertical sides of the mould were of brass, and the bottom of glass. The specimen was mounted centrally in the mould in such a
position that it did not touch the glass. The appropriate adjustments were made to bring the normal to the selected plane, into a horizontal position perpendicular to one vertical side of the mount. The mounting plastic was poured in until it covered the spherical part of the specimen and left the shank protruding, and left to set for 24hrs. After the plastic had set, the mounted specimen was removed from the mould. This gave a lin. cube of plastic with the single crystal mounted in it, and the shank protruding through one side.

The mount (and specimen) was now sawn in half, parallel to that face of the mount which was itself parallel to the required crystal plane. The sawing was accomplished by means of a very fine bladed mechanical hacksaw, the blade of which ran through accurate guides. It was found that there was some tendency for the mounting plastic to flow under the saw blade, and this led to some roughness of the sawn surface. This roughness was removed by gently polishing the specimen through the grades 400; 600; 2/0; 4/0; of emery under paraffin, and finished by polishing with "Bluebell". Finally, the specimen was electropolished in cyanide to remove the work hardened layer, and the orientation checked by X-ray diffraction.

In this way, two original separate single crystal specimens gave two \{111\} planes, a \{100\} plane, and one high order plane. The two \{111\} planes came from different original specimens, and provided a means of checking the
reproducibility of the results. For use as a comparison, the random polycrystalline specimen was mounted in exactly the same way, and an X-ray photograph of this specimen revealed pronounced preferred orientation.

Polarisation and Deposition on Crystal Planes.

The experimental procedure for deposition has been described earlier. The electrolysis vessel was a 150ml beaker in which the anode and cathode were situated at opposite sides, and the capillary was arranged to press on the centre of the cathode when taking a measurement, and moved away for the remainder of the time.

All solutions were pre-electrolysed for 1hr. at 0.5A/sq.dm. using a piece of silver foil as a cathode. Each polarisation run was continued for 5hrs. In general, four runs were performed on each solution using the {100}; {111}; high order planes; and polycrystalline cathodes, all of which just before using were lightly etched in hot 50% nitric acid. Hot nitric acid was also used to remove the deposits from the specimen before starting a new run with a fresh solution. The completeness of removal was checked by X-ray methods in the early stages of the work, but a little experience enabled this check to be omitted.

The results obtained for the various solutions are shown in Table IXb. The particular solutions used being chosen as typical of solutions giving coarse, smooth, and bright deposits, and were identical with the solutions
used in the early part of the work, except that the bright
solution contained cetyl pyridinium nitrate in place of
ammonia.

\[ \text{Solution (i)} = 0.25M \text{ AgNO}_3 \]

\[ (\text{ii}) = 0.25M \text{ AgNO}_3 + 0.25M \text{ citric acid.} \]

\[ (\text{iii}) = 0.25M \text{ AgNO}_3 + 0.25M \text{ aminoacetic} \]

\[ \text{acid.} \]

\[ (\text{iv}) = \text{Solution (iii)} + 0.001M \text{ C.P.N.} \]

\[ (\text{v}) = \text{Solution (iv) stirred.} \]

The deposits obtained were in all cases typical
of the solution used. Thus solution (i) gave a coarse
deposit, solutions (ii), (iii), and (iv) all gave smooth
deposits, and solution (v) gave a bright deposit. The
results show that as the deposit became smoother and brighter
the differences in the polarisation on the single crystal
planes became less marked, and eventually vanished. In the
same way, the relative difference in polarisation between
the single crystal and polycrystalline bases also decreased.

X-Ray Diffraction Examination of Deposits.

The deposits were subjected to X-ray examination
by the Laue back reflection method. The specimen was
mounted in the camera with the plane normal to the incident
X-ray beam, and 3cm. from the film. Each exposure was
made for 75mins. at 45kv, and 15ma with a copper target.
The results in Table IX indicate that as the difference
in the polarisation on different crystal planes decreased,
the structures of the deposits became more and more alike.
Also, as the deposit becomes smoother, the grain size of the deposit decreases. However, there is no appreciable diminution in grain size of the deposit from solution (iv) in stirred and un-stirred conditions. Thus, the brightening of the deposit from solutions containing aminocetic acid and a wetting agent is not due to further decreases in grain size.

In those cases in which the diffraction pattern shows preferred orientation, the direction of preference was different on different planes. In simple silver nitrate solutions, the nature of the base has a very pronounced effect. From the results quoted, it seems that the major crystal planes tend to continue during deposition, and the preferred orientation, when present, is in the direction of a major plane. In no case was preferred orientation present to any marked extent.

The solutions used were those quoted on p 134, and the polarisation results are taken from Table IXb. In the complexed solutions, whether the complexing agent was citric or aminocetic acid, the deposits were practically identical structurally in all cases, irrespective of the cathode base. The slight tendency to preferred orientation on the poly-crystalline base is probably unimportant. The single crystal effect on the {111} plane using solution (iv) is almost certainly due to the X-rays penetrating the very coarsely crystalline deposit and giving the pattern of the base. Typical X-ray photographs obtained in the work are shown in fig. 28.
Table IXb.

n-t results. Various solutions, Single Crystal Cathodes.

<table>
<thead>
<tr>
<th>Soln. Base</th>
<th>1</th>
<th>10</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>300</th>
<th>A/sq.dm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>7.1</td>
<td>5.8</td>
<td>5.5</td>
<td>4.6</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>0.7</td>
</tr>
<tr>
<td>A</td>
<td>12.4</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>11.2</td>
<td>8.6</td>
<td>7.6</td>
<td>7.6</td>
<td>7.6</td>
<td>7.6</td>
<td>7.6</td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>15.7</td>
<td>15.2</td>
<td>12.2</td>
<td>12.3</td>
<td>12.1</td>
<td>12.1</td>
<td>12.1</td>
<td>0.7</td>
</tr>
<tr>
<td>P</td>
<td>41.5</td>
<td>45.4</td>
<td>46.4</td>
<td>47.5</td>
<td>48.0</td>
<td>48.0</td>
<td>48.0</td>
<td>0.7</td>
</tr>
<tr>
<td>A</td>
<td>45.2</td>
<td>49.8</td>
<td>50.6</td>
<td>50.4</td>
<td>50.5</td>
<td>50.5</td>
<td>50.4</td>
<td>0.7</td>
</tr>
<tr>
<td>P</td>
<td>42.1</td>
<td>48.1</td>
<td>48.1</td>
<td>48.0</td>
<td>49.0</td>
<td>49.0</td>
<td>49.0</td>
<td>0.7</td>
</tr>
<tr>
<td>A</td>
<td>50.2</td>
<td>49.9</td>
<td>50.0</td>
<td>49.0</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
<td>0.7</td>
</tr>
<tr>
<td>P</td>
<td>39.5</td>
<td>38.3</td>
<td>39.3</td>
<td>39.3</td>
<td>39.9</td>
<td>39.9</td>
<td>39.9</td>
<td>0.7</td>
</tr>
<tr>
<td>A</td>
<td>34.1</td>
<td>28.0</td>
<td>25.0</td>
<td>25.0</td>
<td>24.6</td>
<td>24.6</td>
<td>24.6</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>30.5</td>
<td>28.0</td>
<td>25.1</td>
<td>24.9</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>70.5</td>
<td>39.2</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td>0.7</td>
</tr>
<tr>
<td>P</td>
<td>37.5</td>
<td>26.8</td>
<td>26.8</td>
<td>26.2</td>
<td>26.1</td>
<td>26.1</td>
<td>26.1</td>
<td>0.7</td>
</tr>
<tr>
<td>A</td>
<td>31.6</td>
<td>27.7</td>
<td>25.7</td>
<td>25.4</td>
<td>23.4</td>
<td>23.4</td>
<td>23.4</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>35.5</td>
<td>30.3</td>
<td>25.7</td>
<td>25.3</td>
<td>23.4</td>
<td>23.3</td>
<td>23.3</td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>34.6</td>
<td>28.4</td>
<td>25.2</td>
<td>23.4</td>
<td>23.4</td>
<td>23.4</td>
<td>23.3</td>
<td>0.7</td>
</tr>
<tr>
<td>P</td>
<td>38.4</td>
<td>36.4</td>
<td>37.7</td>
<td>31.2</td>
<td>31.1</td>
<td>31.1</td>
<td>31.1</td>
<td>1.5</td>
</tr>
<tr>
<td>A</td>
<td>34.9</td>
<td>31.5</td>
<td>30.2</td>
<td>31.2</td>
<td>31.1</td>
<td>31.1</td>
<td>31.1</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>35.0</td>
<td>32.0</td>
<td>31.0</td>
<td>31.1</td>
<td>31.1</td>
<td>31.0</td>
<td>31.1</td>
<td>1.5</td>
</tr>
<tr>
<td>C</td>
<td>35.0</td>
<td>32.0</td>
<td>31.0</td>
<td>31.1</td>
<td>31.1</td>
<td>31.0</td>
<td>31.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

B = {111} Plane. C = {100} Plane.
Table IXa.

X-Ray Diffraction Examination of Deposits.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>Base</th>
<th>c.s.p.</th>
<th>c.d.</th>
<th>deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>P</td>
<td>4.3</td>
<td>0.7</td>
<td>W₁</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>10.8</td>
<td>0.7</td>
<td>W₁</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>7.5</td>
<td>0.7</td>
<td>W₂</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>12.1</td>
<td>0.7</td>
<td>W₁</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>48.0</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td>(ii)</td>
<td>A</td>
<td>50.4</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>48.9</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>49.5</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>23.9</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td>(iii)</td>
<td>A</td>
<td>24.6</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>24.5</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24.6</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>26.1</td>
<td>0.7</td>
<td>W₁</td>
</tr>
<tr>
<td>(iv)</td>
<td>A</td>
<td>23.4</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>23.3</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>23.2</td>
<td>0.7</td>
<td>W</td>
</tr>
<tr>
<td>(v)</td>
<td>A</td>
<td>31.0</td>
<td>1.5</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>31.0</td>
<td>1.5</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>31.1</td>
<td>1.5</td>
<td>W</td>
</tr>
</tbody>
</table>

Base:  P = Polycrystalline.
       A = High Order Plane.
       B = \{111\} Plane.
       C = \{100\} Plane.

Deposit:  W = Polycrystalline.
          W₁ = Polycrystalline with preferred orientation.
          W₂ = Polycrystalline with single crystal structure.
(i) X-Ray Of
Single Crystal
As Grown.

(ii) X-Ray Of
{111} Plane
Before Deposition.

(iii) X-Ray Of
{111} Plane After
Deposition By 0.25M AgNO₃
Fig. 28 Contd.

(iv) X-Ray Of
\{\text{\{hkl\}}\} Plane After
Deposition By
Aminocacetic Acid.

(v) X-Ray Of
\{\text{\{hkl\}}\} Plane After
Deposition By
Aminocacetic Acid
And C.P.M.

(vi) X-Ray Of
\{\text{\{hkl\}}\} Plane After
Deposition By
Aminocacetic Acid
And C.P.M.
Introduction.

In silver plating solutions of the complex cyanide type, it is a well-known fact that the activity of silver ions is reduced to very low values. Also, in some theories of smooth and bright electroplating, the smoothing effect of the electrolyte is attributed to this formation of complex ions. It is considered that, in order to obtain a smooth deposit, it is necessary to reduce the activity of the depositing ion, while at the same time maintaining a fairly high operating current density.

According to the complex ion theory of electrodeposition, complexing reduces the activity of the depositing ion, while at the same time maintaining a high concentration of electrolyte, which in turn enables a high current density to be used.

Thus, it seemed of interest to attempt to determine the relative ionic activities of the silver ion in simple and complexed solutions, in an attempt to correlate ion activity with smoothness of the deposit.

Experimental Technique.

The most logical method of determining activities in this investigation, is by E.M.F. measurements, and, since the apparatus was available, this method was used.

The method entails the setting up of a cell composed of a reference electrode, and an electrode containing the unknown solution. The most convenient
reference electrode in the present case is the Ag/AgNO₃ electrode, and by combining this with the electrode Ag/AgNO₃ + Addition Agent, the activity of the silver ions in the complexed solution may be obtained. Also with a system of this type, it is unnecessary to use a salt bridge at the liquid junction.

The electrode vessels were of the type used in the earlier work as reference half-cells (see fig. 2). The two vessels were connected by an ungreased three-way glass tap, and by forming the liquid junction in the bore of this tap, the area of contact between the solutions was kept to a minimum, and diffusion effects minimised.

The silver powder used in both electrodes was prepared by electrolysis of acid silver nitrate solution at high c.a. This powder was thoroughly washed with redistilled water before use. The reference electrolyte was a carefully prepared 0.25M silver nitrate solution, the activity of which has been determined by Robinson and Tait (2). The powdered silver was placed in the half-cell which was rinsed several times with the standard solution before finally filling. The half-cell for the unknown solution was prepared in exactly the same way, except that the solution was 0.25M AgNO₃ + Addition Agent.

Method of Measurement.

Both electrodes were placed in the thermostat bath at 25°C ± 0.1°C, and left for some time until the
temperature became steady. They were then connected together with the liquid junction in the tap. The connections with the potentiometer were made, and readings were taken at intervals over a period of 3hrs. The potentiometer was used on the lowest range, (0-19mv.) and this gave an accuracy of measurement of ± 0.001mv. In practice, the measurements were taken to 0.01mv., and it was found that except for some instability in the first few minutes after making the connections, the E.M.F. was constant throughout the determination.

The Calculation of Activity.

By the method used, the E.M.F. of the cell:

\[ \text{Ag}_{(s)}/\text{AgNO}_3 + \text{A}^-/\text{AgNO}_3/\text{Ag}^+ \]

\[ E \]

is obtained. For any cell, we have the expression:

\[ E = E_0 - \frac{RT}{nF} \log_e \frac{a_2}{a_1} \]

where, \( E = \) E.M.F. in volts. \( R = \) Gas constant.
\( E_0 = \) Standard E.M.F. \( T = \) Absolute temperature.
\( F = \) Faraday = 96,500 coulombs.
\( n = \) number of gram equivalents in the reaction.
\( a_1 = \) activity of silver in reference solution.
\( a_2 = \) activity of silver in unknown solution.
For concentration cells of the above type, \( E_0 = 0 \)
Hence,

\[ E = \frac{RT}{nF} \log_e \frac{a_1}{a_2} \]
Putting in the value of $\frac{NT}{S^2}$ and converting to base 10,

$$E = 0.0578 \log_{10} \frac{a_1}{a_2}$$

In the present work, the absolute value of the activity of the silver ion is not required. The important factor is the relative activity of the complexed and non-complexed solutions. Hence it is permissible to assign an arbitrary value to $a_1$.

Let $a_1 = 1$, and then

$$E = -0.0578 \log_{10} a_2$$

From this, the relative activity of the silver ions in the complexed solution is readily obtained, and the fraction of complexed ions is given by:

$$1 - a_2 = \text{fraction complexed}.$$  

**Experimental Results.**

Measurements were made on four different solutions:

(i) = 0.25M AgNO$_3$ + 0.5M Citric acid.

(ii) = 0.25M AgNO$_3$ + 0.25M Tartaric acid.

(iii) = 0.25M AgNO$_3$ + 0.25M Aminocetic acid.

(iv) = Solution (iii) + 0.001LM C.P.N.

No information was available as to the structure of the complexes (if any) formed between silver and the various addition agents used. However, since silver is typically bidentate, it seemed probable that if any complex forms, it will be of the type
1 complexing molecule/silver ion.

For this reason, the solutions were, in general, made equimolecular to silver and complexing agent. Solution (i) was made 0.24 to citric acid, in case an excess of addition agent over molecular proportions had any large effect.

The results obtained are shown in Table Xa. The table does not include the values for solution (iv), since this was found to be identical with solution (iii).

<table>
<thead>
<tr>
<th>Soln.</th>
<th>E mv.</th>
<th>a₂</th>
<th>Decrease in activity</th>
<th>Fraction complexed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>3.34</td>
<td>0.97</td>
<td>0.13</td>
<td>13%</td>
</tr>
<tr>
<td>(ii)</td>
<td>6.52</td>
<td>0.71</td>
<td>0.29</td>
<td>29%</td>
</tr>
<tr>
<td>(iii)</td>
<td>0.63</td>
<td>0.97</td>
<td>0.03</td>
<td>3%</td>
</tr>
</tbody>
</table>

These results are of the same order as those obtained by Fuseya and Makana (3) for similar work on the complex formed between copper and glycine.

Discussion of Results.

From these results, it is apparent that the degree of complexing is not related to the smoothness or brightness of the deposit.

Glassstone (1) has shown that the effective silver ion concentration in a typical cyanide plating
solution is of the order $10^{-20}g/l$. Using Robinson and Tait's (2) figures for the activity coefficient of silver in a 0.25M silver nitrate solution, the activity of the silver ion in the solution containing aminocetate acid can be shown to be of the order 0.15, and yet the latter solution is capable of giving a much brighter deposit than that obtained from the cyanide solution. The precise significance of these results will however be dealt with more fully in the next section.
DISCUSSION OF EXPERIMENTAL RESULTS

The mechanism of deposition and bright plating.

As stated before, it is not easy to determine the exact mechanism of the process of bright plating, as it is essentially a physical process. However, many experiments have been conducted to understand the mechanism better. One such experiment involved the use of various plating solutions and conditions to observe the effects on the deposit characteristics.

In the experiment, the solutions were prepared with specific concentrations of the plating elements. The plating solutions were then subjected to different temperature and current conditions to observe the deposit characteristics. The results obtained from the experiments were analyzed to understand the mechanism of bright plating.

The mechanisms of bright plating involve the formation of a thin, adherent, and evenly distributed deposit on the substrate. This deposit is characterized by its high brightness and smoothness. The mechanism involves the reduction of the plating elements on the surface of the substrate, leading to the formation of a deposit.

The deposit characteristics are influenced by various factors such as the type of plating solution, temperature, current density, and plating time. These factors affect the rate of deposition, deposit composition, and deposit morphology. Understanding these factors is crucial for controlling the deposit characteristics and achieving bright plating.

In conclusion, the mechanism of bright plating involves the reduction of plating elements on the substrate, leading to the formation of a deposit with high brightness and smoothness. Further research is needed to fully understand the mechanism and develop more efficient plating processes.
There have been many theories advanced to explain the reduction of grain size and the other phenomena observed in the electrodeposition of metals. However, the majority of these have been developments and extensions of three major theories. The first of these was the theory proposed by Bancroft (1) in which he postulated that grain reduction was due to adsorption on the cathode of some constituent of the electrolyte. The second of the theories is the complex ion theory of Mathers (2), which states that, the formation and subsequent breakdown of complex ions containing the depositing ion is the principal factor in restricting grain growth. Finally, the interference theory proposed by Hunt (3) claims that the ratio of the depositing ion to other species present in the solution, is the controlling factor in the production of fine grained deposits. This concept is based on the interionic attraction theory of conductivity. Among the earliest workers to recognize the possibility of a connection between polarisation and grain size were Blum and Rawdon (4).

In recent years, it has come to be more and more accepted that adsorption must play at least some part in the processes of bright plating, and probably in deposition generally. This infers that there must be some connection between polarisation and adsorption phenomena. (The finer grained the deposit becomes, the smoother it tends to be,
but, the transition from smooth to bright is not necessarily accompanied by further decreases in grain size. It would appear that some other mechanism controls the formation of bright deposits.) Henricks (5) in a consideration of the processes of bright plating, has proposed that deposition is a periodic phenomenon, and takes place by alternate adsorption of the addition agent and deposition of the metal. This periodicity is said to be due to the necessity for the system to acquire an activation energy of adsorption. Such a process will inevitably lead to a layer structure in the deposit, and it is an observed fact that many bright deposits are layered. However, Faub (6) has shown that smooth bright deposits are not necessarily layered.

Hear (7) has recently emphasised the fact that adsorption is a dynamic process, and that it is necessary to bear in mind that adsorption and desorption may occur at very different rates. On this basis, Hear describes two classes of addition agent whose behaviour is very different, and he considers that, although the two classes may not be mutually exclusive, they will be complementary in their action.

In this section, the experimental results reported earlier will be discussed on a basis of the major theories, and particularly in the light of the Hear concept of the adsorption theory.
The Preliminary Experimental Results and Reproducibility.

This part of the work is described in Sections III, IV, and V and there are three major points which require explanation:

1. The general shape of the n-t curves.
2. The attainment of electrolytic stability.
3. The anomalous effects of nitrogen.

Factor 1: In nearly every case, the polarisation versus time (n-t), and activation overpotential (n_a-t) curves show a decrease in the first few minutes of any run (see figs. 3-6). The reason for this is considered to be that the diffusion layer takes time to become established. However, if this is the case, it would seem that under agitated conditions, the solution should attain the c.s.p. value more quickly, since, under such conditions the diffusion layer is very much reduced.

Factor 2: The attainment of electrolytic stability. The technique of pre-electrolysis of the solution is widely practiced, particularly by Bockris and his co-workers (6) on hydrogen overvoltage. The gradual change in the solution on electrolysis is probably due to the presence of traces of impurity either in the silver nitrate or in the water used, such impurities being either removed or rendered ineffective during successive electrolyses. In view of the high purity of the reagents used, this impurity must be present in such small quantities as to preclude anything except adsorption as its mode of action.
Factor 3: The anomalous effects of saturating the solution with nitrogen. In Section IV, it was considered that this effect was due to an impurity in the silver nitrate, but it was impossible to resolve the matter in view of the very large number of possible impurities.

At various stages in the work, the silver nitrate was re-crystallised from redistilled water before use, but all three of the factors above were still observed. Thus, it is unlikely that the silver nitrate was the cause of the trouble. There is however, one other piece of evidence which has not been reported earlier. The water used in the greater part of the experimental work was the purest available in the large quantities required. However, at a late stage in the work, large supplies of water purified by passing once distilled water through a column of the mixed ion exchange resin "Bio-Deminornite", became available. Such water is of very high purity (approximating to conductivity water) and this was used to make solutions for checking some of the original results. It was found that the pre-electrolysis procedure to obtain an S.E. solution was unnecessary, and the first run of a solution made from the high purity water gave a c.s.p. value identical with that for a solution made with the less pure water after pre-electrolysis. Also, the initial decreases observed in the polarisation-time determinations during the first few minutes of electrolysis, were either much reduced or completely eliminated.
Thus, factors 1 and 2 may be due to the presence of traces of impurity in the water used. It is also probable that factor 3 may be explained on the same basis. Since the impurity must be present in very small amounts, it seems that the effects it causes must be due to adsorption.

The Variation of Polarisation with Current Density.

The curves obtained for the variation of polarisation with apparent current density are of great interest. In general, two types of result were obtained:

(i) Those in which \( n_a \), \( n_b \), and \( n_c \) all increased as the current increased.

(ii) Those in which \( n_a \), \( m \), and \( n_c \) increased with increasing current, while \( n_b \) was constant.

Curves of the first type were obtained in all cases in which the electrolyte was such as to give a smooth fine-grained deposit. That is from solutions containing relatively large amounts of citric acid; tartaric acid; or aminoacetic acid; or gelatine. The second type of curve was obtained from solutions which gave coarse deposits. It is interesting to note that type (i) tended to become type (ii) when the concentration of the added reagent was low (of the order 0.001M).

Of the two types, type (ii) is the most interesting. The only possible explanation of the effect (i.e. \( n_a \) constant) is that the true current density is constant. This means that the depositing area increases as the
applied current increases. Yagamian (9) has demonstrated by microscopic examination of a growing crystal that this is indeed the case, and he attributes the effect to passivation of the surface by adsorption, either of oxygen, or of traces of organic impurity in the solution. However, there are two other possible factors which may have some bearing on the problem:

(a) It is an established fact that different planes of a crystal require different energies to incorporate an atom in the lattice.

(b) An aqueous solution of silver nitrate have a pH of about 5.0, and therefore hydrogen ions are present in solution to a significant extent, and these ions may be adsorbed at the cathode. Both these factors will be discussed more fully at a later stage.

Another interesting consideration arises from this part of the work. The curves of \( n_a \) increase linearly with \( I \), while the value of \( n_a \) is constant and independent of \( I \) for simple solutions. This leads to the apparently contradictory conclusion that, on the one hand, the area of deposition is constant with increasing current, while on the other hand, the area increases as the current increases. This anomaly may be resolved by considering two different areas in computing the true current density:

1 In calculating the true c.d. for application to measurements of \( n_a \), the actual growing area of the cathode should be taken. This area is
represented by the total area of all the growing ends of the crystals, and does not include any inactive surfaces. It is extremely difficult to estimate this area for coarse deposit deposits.

In the case of the concentration polarisation, which is concerned with differences in concentration between the diffusion layer and the bulk of the electrolyte, it seems more logical to consider the area of the interface between the bulk of the solution and the diffusion layer. The modern theory of diffusion layers proposed by Stern (10) states that such layers are diffuse, and therefore there is no planar interface between the two layers. Nevertheless, it is permissible to consider a plane, whose position corresponds to the "centre of gravity" of the diffuse layer, as representing the interface. Such a plane will tend to be of constant area for a given electrolysis vessel, and will thus be independent of the area of the growing part of the cathode, provided that the growing crystals do not protrude too far into the solution.

In support of this view, it was found that when the solution was such as to give a smooth deposit, i.e., when the growing area of the deposit approximated to a plane, the value of \( n_a \) increased with increasing current. (see figs. 18 and 20). In this case, the two cases considered above become identical. Also, those solutions which contained addition agents, but did not give smooth deposits, gave \( n_a-I \) curves similar to those for simple silver nitrate solutions.
The precise mechanism by which the growing cathode area changes with the applied current will be discussed later.

The Determination of the Activity of Silver Ions.

This section of the work (Section X) was undertaken as a test of the applicability of Lauther's (2) complex ion theory. This theory has received considerable support, although the precise interpretation used by different authors has varied. There have been two main approaches in the application of the theory:

(i) Deposition from complex electrolytes takes place via complex ions. This leads to smooth deposits, and since the complex requires energy for its breakdown, the polarisation increases.

(ii) The complexing agent reduces the activity of the ions in solution, but at the same time maintains a high concentration of electrolyte to carry the current.

Thus, deposition may be carried out at high current density, and such conditions of low activity and high c.d. are said to favour the formation of smooth deposits.

Thus, the complex ion theory infers that, as the activity of the depositing ions decreases (i.e., the degree of complexing increases), the deposit should tend to go from coarse to smooth and bright. Also, the deposits from solutions of comparable activity should be of comparable smoothness.
In the present work, the technique used was that of Ruseya and Nagama (11) which gives the relative change in activity of the ions in the complexed solution, compared with that of the silver ions in a simple silver nitrate solution with a corresponding concentration of silver ions.

Robinson and Tait (12) have found the activity coefficient of silver ions in a 0.2M silver nitrate solution to be 0.63, and thus the activity of silver in such solutions is approximately 0.15. From the values quoted in Table Xa (p. 144), it is apparent that the activity of silver ions in solutions complexed with citric or tartaric acids, is about 0.10, and that for solutions complexed with aminoacetic acid is about 0.15. Glassbone (13) has reported that, in commercial silver plating baths of the complex cyanide type, the effective concentration (and hence the activity) of silver ions is of the order 10⁻²⁸g/l.

Hence, on a basis of these values, and the complex ion theory, it would be expected that a 0.25M silver nitrate solution and one containing an equivalent amount of aminoacetic acid should give very similar coarse deposits.

Solutions containing citric or tartaric acids should give coarse deposits with slightly smaller crystals, and silver cyanide solutions should give very smooth and possibly bright deposits. However, in practice, it was found that, simple silver nitrate solutions gave a very coarse deposit, solutions containing citric or tartaric acids gave smooth deposits similar to those from cyanide solutions, and solutions containing aminoacetic acid gave very smooth deposits.
which were sometimes bright. In fact, the bright deposits from aminoacetic acid solutions were more comparable to a bright nickel deposit than to a silver cyanide deposit.

From the point of view of degree of complex ion formation, it is difficult to see how the complex ion theory can explain the fact that a solution containing only about 3\% complexes gives a brighter deposit than one containing almost 100\% complex ions.

Thus, the complex ion theory does not fully explain the observed results, and a much more convincing explanation is given by adsorption. This latter theory considers that the function of the addition agent, is not so much to form complexes, as to provide substances which are more readily, or more extensively, adsorbed on the cathode.

Deposition on Single Crystals.

Owing to the experimental difficulties, it is difficult to draw any very definite conclusions as to the effect of the base structure on the structure of the deposit. In order to completely eliminate the diffraction pattern of the cathode base, it was necessary to build up very thick deposits, and in so doing, any structural effects due to the base tended to be eliminated. For this reason, it would have been more desirable to have approached the problem by electron diffraction methods, but unfortunately, the necessary apparatus was not available. It was found
that, in simple silver nitrate solutions, different crystal planes had different polarisation potentials, and there were strong indications that, while some planes tended to give completely random oriented deposits, others tended to have a preferred orientation (see table IX, p137). In a few cases, the deposit had a structure similar to that of a distorted single crystal. This is in agreement with the evidence of Hirata and his co-workers (14) that silver deposits from nitrate solutions tend to have their crystal axes parallel to those of the cathode base. Also, Gwathmey and Leithaisser (15) have shown that, certain planes of a nickel single crystal give a deposit which follows, almost exactly, the base structure, while other planes give random deposits.

Leisheev and his co-workers (15) have shown that, at a given current density, some planes of a silver single crystal do not deposit in silver nitrate solutions, and, as the apparent c.d. increases, more and more planes begin to deposit. Unfortunately, as they did not measure the polarisation potentials during deposition, no comparison with their work can be made. The present work has shown however, marked differences in polarisation on different planes, and it is unlikely that planes of high polarisation would deposit when planes of lower polarisation are available.

In the case of solutions tending to give smooth deposits, (citric acid; tartaric acid; and aminoacetic acid)
it was found that the polarisation on different crystal planes was the same, and X-ray diffraction showed all the deposits to be identically polycrystalline. X-ray examination of the deposits from aminoacetic acid solutions, also showed that there was no obvious structural difference between smooth and bright deposits.

It is not easy to explain the observed differences in structure and polarisation on different planes from simple solutions. However, there seem to be two possible mechanisms which might cause the observed effects:

(a) The energy required to include an atom in the lattice differs for different crystal planes.

(b) Some components (ionic or molecular) of the solution is preferentially adsorbed on certain crystal planes.

It is also possible that these factors are interdependent.

So far as factor (a) is concerned, it is an established fact that there are differences in energy on different crystal planes, due to differences in the interatomic distances. Accepting this, it is probable that the different planes will require different energies to incorporate an atom, and therefore will exhibit different polarisation potentials. This in turn will cause deposition to occur only at those planes with the lowest polarisation, and the deposit will therefore be more or less columnar. This concept alone will not account for the occurrence of smooth
deposits. In order to account for such deposits, it is necessary to introduce an adsorption mechanism.

Factor (b) has the advantage that it can be extended to explain smooth deposits. It has been established in the field of heterogeneous catalysis, that certain sites on a metal surface are particularly liable to adsorption. If some substance in the electrolyte is able to adsorb preferentially, it will tend to block part of the cathode, and thus force the deposit to be coarse grained and columnar. However, preferential adsorption at certain sites does not preclude slight adsorption at other sites. Hence, even those sites at which deposition occurs, may have to acquire an energy of desorption before deposition occurs, and this energy will show as an increase in the polarisation.

Probably the most acceptable explanation is obtained by combining the two factors:— The surface has a slight difference in energy on different crystal planes, and thus some planes undergo preferential adsorption, and therefore the differences in polarisation for different planes are magnified. Thus, at a given current density, preferential deposition occurs on only a limited number of cathode sites. This causes the deposit to be columnar. If the applied current is increased, the necessary activation energy (either for deposition to occur on sites of higher energy, or for desorption to occur at some of the sites previously covered), becomes available, and hence the
area of deposition increases. In this way, the true current density tends to remain constant, and the results obtained in which \( n_a \) was found to be constant with increasing current are explained.

Vagaramyan (9) has concluded that the observed effects are due to adsorption either of oxygen, or of organic impurities. However, there seems to be another factor which should be considered. Simple aqueous silver nitrate solutions contain silver; nitrate; hydroxyl; and hydrogen ions and also water dipoles. The pH of such a solution is about 5.0, and therefore the concentration of the hydroxyl ion will be low (particularly in the cathode layer) as both the hydroxyl and nitrate ions tend to migrate away from the cathode. Since the silver ion is deposited, it is not likely to be the interfering ion, but both the hydrogen ion and the water dipole could be adsorbed. Of these two, the proton will not only tend to migrate to the cathode, but will also tend to be held in the diffusion layer by its' charge. Thus, it is considered that this ion (which is normally present in the solution) may very easily be adsorbed on the cathode. Further, it will be shown later that there is evidence in support of this view.

It should be noted that although the interference theory is also able to explain these effects, it will be shown later that this theory is inadequate in certain other respects.

In the case of the smooth deposits, the observed
effects may be explained by presuming extensive general adsorption of the addition agent (or some derivative) so that the cathode surface approximates to a surface of randomly disposed addition agent molecules, and thus the effects of different crystal planes vanish. However, a more detailed discussion of the mechanism by which adsorption causes smooth and bright deposits will be deferred until later.

There are two other pieces of evidence related to single crystals, which furnish support for the adsorption theory. The first of these lies in the present work. It is that no differences are detectable by X-ray examination between the structures of smooth and bright deposits from solutions containing aminoacetic acid. The only difference between these solutions, lies in the fact that the one giving bright deposits contained a small amount of a compound which produces the brightening effect. Hence it may be inferred that the action of the brightening agent is a surface effect, and this in all probability is due to adsorption. The second piece of evidence is that Ke and Trivich (17) have shown that thiourea adsorbs preferentially on certain planes of a copper single crystal from acid copper sulphate solutions, and there are differences in the structure of the deposit on the different planes under these conditions.

Deposition from Solutions with Non-depositing Cations.

This part of the work (Section VI) was
undertaken as a test of the interference theory proposed by Hunt (3) which states that the polarisation and crystal structure of electrodeposits depends upon the ratio of depositing ions to other substances present in the solution. As this ratio decreases, the crystal size of the deposit should decrease.

The solutions selected were such that the added inorganic cation was at

(a) low concentration (0.001M)
(b) at concentrations comparable to the silver ions.

If Hunt's theory is correct, solutions of type (a) should show little or no change in polarisation or deposit, while those of type (b) should show marked differences in both factors, compared with simple silver nitrate solutions. In practice, it was found that whether the concentration of added cation was low or high, there was no appreciable visible change in grain size in the deposit, but in all cases the polarisation increased. (see Table VIa and VIb p 71) Hence, the Hunt theory does not adequately explain the observed results. Also the complex ion theory cannot apply in this case, since there is little or no possibility of complex ion formation.

For convenience, the c.s.p. values for the various solutions at 0.5A/sq.dm. apparent current density are shown in Table XIA.
Table XIa.

C.S.P. values for 0.25M AgNO₃ + Various Inorganic Cations.

<table>
<thead>
<tr>
<th>Conc.</th>
<th>C.S.P. 0.01M</th>
<th>C.S.P. 0.25M</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A.A.</em></td>
<td>4.6</td>
<td>5.9</td>
</tr>
<tr>
<td>KNO₃</td>
<td>4.6</td>
<td>5.9</td>
</tr>
<tr>
<td>LiNO₃</td>
<td>5.2</td>
<td>9.4</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td>KNO₂</td>
<td>8.0</td>
<td>9.1</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>4.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Al(NO₃)₃</td>
<td>4.8</td>
<td>10.5</td>
</tr>
<tr>
<td>Th(NO₃)₄</td>
<td>6.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

From the values quoted, it is apparent that factors like ionic strength or the silver ion activity of the solution cannot be the factor controlling the polarisation. The ionic strength of a solution containing 0.25M AgNO₃ + 0.25M inorganic cation, is the same for all added cations of the same valency. Thus, if ionic strength were the controlling factor, the polarisation for solutions containing sodium; lithium; and potassium should be the same. In precisely the same way, activity cannot be the controlling factor. However, an examination of the results from the point of view of adsorption is more encouraging.

Several workers have demonstrated that inorganic cations are adsorbed at various surfaces. In particular,
Graham (18) has shown that such ions are strongly adsorbed at the mercury cathode in electrosampling experiments, and he has concluded that it is both van der Waals and chemisorption in type. He has also shown that those ions which approach closest to the mercury surface are chemisorbed. Turner (19) has proposed the adsorption of hydrogen ions, in the unhydrated state, on the cathode during the deposition of nickel, as the active cause of the fine-grained (often bright) deposits obtained.

If the process occurring during the deposition of silver from solutions containing silver and other inorganic cations, is one of adsorption of the cations, we should expect the effect of the various cations to vary with the extent of adsorption. It is however a well-known fact that most inorganic cations are adsorbed to the same extent, and if this is so in the present case, it might be expected that they would affect the polarisation to an extent governed by their size, since a larger ion would cover more of the cathode surface, and therefore tend to block a greater part of the cathode. In general, all ions in solution are more or less hydrated, and thus it might appear that the size of the hydrated ion, rather than that of the bare ion should be considered. However, Graham (20) has examined the evidence for and against hydrated ions in the adsorbed layer at a mercury surface, and has concluded that these ions which approach the surface closely enough to become adsorbed are in fact unhydrated. This conclusion
is based on the fact that an ion surrounded by a solvent sheath cannot approach closely enough to become chemisorbed.

Table XIB shows the various ions in increasing order of their c.s.p. values for the 0.2M solution with respect to that ion at 0.5A/sq.dm. together with the ionic radius of the ion concerned.

<table>
<thead>
<tr>
<th>Ion</th>
<th>c.s.p. MV</th>
<th>Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ag⁺)</td>
<td>(4.7)</td>
<td>(1.27)</td>
</tr>
<tr>
<td>Cu⁺⁺</td>
<td>5.0</td>
<td>0.80</td>
</tr>
<tr>
<td>Na⁺</td>
<td>6.0</td>
<td>0.93</td>
</tr>
<tr>
<td>Al³⁺⁺</td>
<td>7.3</td>
<td>0.87</td>
</tr>
<tr>
<td>Ca⁺⁺</td>
<td>7.5</td>
<td>1.65</td>
</tr>
<tr>
<td>Th⁴⁺⁺</td>
<td>7.6</td>
<td>1.10</td>
</tr>
<tr>
<td>H⁺</td>
<td>8.9</td>
<td>1.27</td>
</tr>
<tr>
<td>K⁺</td>
<td>9.1</td>
<td>1.33</td>
</tr>
<tr>
<td>Li⁺</td>
<td>9.4</td>
<td>0.78</td>
</tr>
<tr>
<td>Ba⁺⁺</td>
<td>10.5</td>
<td>1.45</td>
</tr>
<tr>
<td>(H₂O)</td>
<td>-</td>
<td>1.10</td>
</tr>
</tbody>
</table>

The values of the ionic radius quoted are taken from Kortum and Bockris (21). From these values, it may be seen that, with the exception of the lithium and aluminium ions, there is good correlation between Polarisation and ionic size. Both lithium and aluminium give strongly hydrated ions, which do not readily dehydrate. Hence, it
is possible that these ions are adsorbed in the partially hydrated state. In general, the radius of a hydrated ion is not equal to the sum of the radius of the ion plus the sum of the radii of the hydrating dipoles. In the case of aluminium, which gives a very small ion, it is therefore not unreasonable to suppose that an aluminium ion, with one water molecule of hydration remaining, will be of about the same radius as a water molecule. The table shows that if the aluminium ion were about the size of a water molecule, it too would correlate with the c.s.p. values. The same argument may be applied to the lithium ion, but in this case, the correlation is not so good, although it is an improvement on the original value.

If the c.s.p. value is plotted against the ionic radius of the ion concerned, then for a given solution, a fairly smooth curve is obtained provided that the lithium and aluminium ions are assumed to be of the same radius as a water molecule. However, if under the same conditions, log a is plotted against ionic radius, a linear curve is obtained. This curve is shown in fig. 29 together with the corresponding curve for the more dilute solution of inorganic cations. In this latter curve, the linearity is not so good unless the radii of the lithium; sodium; potassium; aluminium and thorium ions are taken as being the sum of the radius of the ion plus that of one water molecule. However, it is not unreasonable to suppose that more ions would tend to remain unhydrated in more
FIG. 29

LOG n - r INORGANIC CATIONS

1 = Al^{+++} \equiv H_2O
2 = Li^{+} \equiv H_2O
3 = Al^{+++} + H_2O
4 = Li^{+} + H_2O

CONC. SOLN

DIL. SOLN

0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5

Log n

n
dilute solutions, and that the ionic size would tend to be larger. The linearity obtained is remarkably good, when allowance is made for the difficulty of obtaining reliable values for the ionic radii. The values used were obtained by X-ray measurements on crystals, and it is well known that ionic radii vary with the conditions of measurement.

It is not easy to assign any absolute theoretical significance to the curve obtained, but it does indicate that other factors (extent of adsorption) being equal, the polarisation potential is influenced by the size of the added reagents in the solution. It is appreciated that many assumptions have been made in obtaining the curves, but all of the assumptions have some justification on general grounds, and the results obtained are in agreement with the adsorption theory.

Thus, the work on non-depositing cations lends at least qualitative support to the adsorption theory, as the results are difficult to explain on a basis of the other theories. While it is possible to envisage ionic radius affecting polarisation if the adsorption theory is accepted, it is difficult to reconcile the other theories with a correlation between ionic size and polarisation. It should be noted that, while the interference is capable of explaining such a correlation, the other evidence (ionic strength etc.) points away from this theory.
Deposition from Solutions Containing Organic Additions.

This part of the work (Section VII and VIII) was confined to an examination of the effects produced by certain typical organic molecules, and as has been described earlier, it was found that these reagents could be divided into two classes:

(a) Those which did not materially alter the nature of the deposit.

(b) Those which markedly reduced the grain size of the deposit.

Considering the ineffective group first, there are several factors which require explanation:

1. All members of this group increased the polarisation.

   The differential effects of the wetting agents.

2. Substances of very different chemical constitution all have similar effects.

All this group (thiourea; thioglycollic acid; glucose; and the wetting agents) of addition agents increased the polarisation without decreasing the grain size of the deposit. This lack of effect by thiourea is surprising, particularly in view of the results reported by Shreir and Smith (22) of the effect of this substance on the deposit and polarisation of copper in acid copper sulphate solutions. Ke and Trivich (17) have shown that thiourea is preferentially adsorbed on selected planes of a copper
single crystal, and that these planes tend to give smooth bright deposits from acid copper sulphate solutions. It seems reasonable to suppose that thiourea will behave similarly towards silver, and be selectively adsorbed on particular crystal planes. Hence, since the adsorption is preferential, and also the concentration of the reagent is low, preferential deposition will occur on those parts of the cathode which are not covered, and thus the deposit will consist of columnar crystals. Also, since those parts of the cathode which are less susceptible to adsorption will in general tend to be less favourable to deposition, the polarisation will increase. Thus, the effect of thiourea may be explained on the same basis as that of the inorganic cations. Similarly, the effect of thioglycollic acid and glucose may be explained on a basis of preferential adsorption on selected faces (or facets) of the cathode. The probable reason for this preferential adsorption being that, either the quantity of the addition agent is too small to give extensive covering (thioglycollic acid), or the reagent is only slightly adsorbed on the metal surface (glucose).

The case of the wetting agents is of interest. In the first instance, their behaviour is analogous to that of thiourea, and may be explained in the same way. However, a number of other inferences follow from a consideration of their individual and collective properties. All the wetting agents tend to be strongly adsorbed on
surfaces, but they show little or no tendency to form complex ions. Thus, the wetting agents provide further evidence to discount the complex ion theory.

The choice of the particular three reagents used, was governed by the fact that they were typically cationic (acetyl pyridinium nitrate); anionic (sodium dodecyl-1-sulphate); and neutral (pentaerythritol) in character. Thus, although each one has a different tendency to migrate to the cathode, all three increased the polarisation potential, but the cationic reagent naturally caused the greatest increase. Therefore it may be inferred that, while the sign of the charge of a given reagent will govern the extent of adsorption, nevertheless, adsorption takes place to an appreciable extent even if the charge on the reagent is such as to cause it to tend to migrate away from the cathode. There is some confirmatory evidence for this view in the field of electroseparillarity, where Grahame (18) has demonstrated that anions are significantly adsorbed on mercury even when the metal is cathodic. (It is of interest to notice that this infers that the effect of the nitrate ion on the c.p.p. of silver may be of importance, but this is extremely difficult to investigate, since very few of the inorganic salts of silver are relatively soluble).

The third factor which requires explanation, is that the inactive group of organic addition agents includes substances of very different chemical constitution. If
the adsorption theory is accepted, (and the weight of the evidence favours this theory), then it is likely that those reagents which are ineffective in smoothing the deposit, are either only slightly adsorbed, or if they are strongly adsorbed, they are either highly preferential, or present in such small amounts as to be unable to give very extensive covering of the cathode.

The second class of organic addition agents was the one which markedly decreased the grain size of the deposit. The three most extensively investigated members of this group were citric acid; tartaric acid, and aminocetic acid, although \( \alpha \)-aminopropionic acid and gelatine (a poly-amino acid) were also examined. The use of the hydroxyacids was prompted by the fact that many workers e.g. Taft and Horseley (23) and Pusey and Impata (24), have obtained marked smoothing effects with such reagents. Gelatine is an addition agent which is widely used in commercial electroplating, and aminocetic acid was chosen as typical of the probable hydrolysis products of gelatine.

For convenience, the values of the c.s.p. for different concentrations of the first three reagents in 0.25M \( \text{AgNO}_3 \) at 0.5A/sq.dm. are shown in Table XI which represents a summary of the results obtained in Section VII. This table shows an interesting anomaly, in that solutions containing 0.00001M citric or tartaric acids gave higher c.s.p. values than solutions containing 0.001M of the same reagents, and a similar phenomenon is exhibited.
by solutions containing aminoacetic acid at higher concentrations.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>0.00001M</th>
<th>0.001M</th>
<th>0.25M</th>
<th>0.75M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>34.9</td>
<td>31.4</td>
<td>42.4</td>
<td>47.0</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>28.6</td>
<td>27.1</td>
<td>29.0</td>
<td>31.0</td>
</tr>
<tr>
<td>Aminoacetic acid</td>
<td>30.0</td>
<td>23.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The explanation of this anomalous effect lies in the appearance of the deposits. The lowest concentration solutions (0.00001M citric acid and tartaric acid and 0.001M aminoacetic acid) all gave deposits which, while they were considerably smoother and finer grained than those from simple silver nitrate solutions, were nevertheless still quite coarse. The deposits from 0.001M A.A. solutions (0.25M aminoacetic acid) were completely smooth. Thus the true $c.o.d.$ for the least concentrated solutions (where deposition is restricted to the ends of the columnar crystals) was much greater than that for the stronger solutions, and thus the curves (figs. 17, 19, and 22) for the lowest concentration of addition agent are not strictly comparable with those for higher concentrations. This phenomenon lends support to the adsorption theory, in that it infers that for an addition agent to be effective in smoothing the deposit, it must be present in amounts sufficient to give
a high degree of coverage of the cathode, although the optimum amount for complete smoothing is still so small as to preclude any mechanism except adsorption. The fact that aminoacetic acid requires a higher concentration to give effective smoothing, but, when the appropriate concentration is attained, it gives a brighter deposit, infers that the rates of the adsorption processes are higher for this substance than for the others. It will be shown later that high rates of adsorption and desorption are likely to encourage the formation of smooth bright deposits.

It is also interesting to notice that the polarisation does not increase proportionally with the amount of addition agent present, when that amount is large. This infers that as the extent of adsorption reaches a high value (i.e. as the area covered approaches unity), further increases in the concentration of the addition agent have little effect.

In an earlier part of this discussion, it was shown, from a consideration of the degree of complex ion formation by the various reagents in the second class of organic addition agents, that the complex ion theory does not account for all the observed results. However, all the observed effects of the organic addition agents are capable of explanation on a basis of the adsorption theory. If it is assumed that all organic reagents tend to be adsorbed at the cathode, then the precise effect of any given reagent will be controlled by the following factors:
(i) The reagent may be generally adsorbed.

(ii) The reagent may be specifically adsorbed at definite cathode sites.

(iii) The concentration may be low.

(iv) The concentration may be high.

(v) The reagent may be only feebly adsorbed.

If a given reagent satisfies (i) and (iv), then it will tend to give a smooth deposit, but if (iv) is not completely attained, the deposit will be finely crystalline. If the reagent satisfies (i) and (iii) the deposit will tend to be coarse. If the reagent comes under (ii) or (v), the deposit will be coarsely crystalline irrespective of factors (iii) and (iv). Thus substances to which factors (ii) or (v) apply will be in the first class of addition agents, while those to which factor (i) applies will be in the second class provided that the concentration attains an appropriate value.

The Production of Bright Deposits.

The X-ray examination of the smooth and bright deposits obtained from solutions containing aminoacetic acid, showed that there was no structural difference between them, and thus it may be inferred that a bright deposit is simply a smooth deposit in which the surface irregularities have been much reduced. In the attainment of smooth deposits, it is necessary to add some reagent which will tend to be adsorbed on the greater part of the cathode.
and this means that there will be local spots on the cathode at which there is little or no adsorption. There will tend to be preferential deposition at such spots, and therefore in order to obtain a bright deposit, this must be prevented.

In the present work, it was found, fortuitously, that solutions containing equimolecular amounts of silver nitrate and aminoacetic acid were capable of giving a smooth bright deposit. Such deposits were extremely difficult to reproduce, but were usually obtained under conditions of agitation. Eventually, it was discovered that additions of small amounts of alkali (NaOH or NH₄OH) gave a solution which would continuously reproduce the bright deposit, provided that the solution was vigorously stirred at all times when the electric current was passing. If the stirring was interrupted, even for only one or two minutes, the solution reverted to the non-bright type. The alkali was added quickly and at high concentration, and such conditions favour the formation of colloids. Hence, it seems reasonable to suppose that the alkali gave a colloidal precipitate of either silver hydroxide or silver oxide, and that this colloid was adsorbed on the local active spots on the cathode. Such colloids are unstable in highly acid solutions, and it is therefore probable that the effect of stirring the solution was to reduce the hydrogen ion concentration in the cathode layer, and thus to enable the colloid to remain in suspension. If the
agitation was discontinued, the pH of the solution in the
cathode layer decreased, and the colloid was destroyed.

In support of this view, it was found possible to
obtain appreciable brightening effects by the addition of
ammonia to solutions containing sodium citrate, but
solutions containing an equivalent amount of citric acid
would not give a brightening effect. Similarly, it was
possible to obtain some brightening from solutions
containing α-aminopropionic acid in place of the aminoacetic
acid. However, again it was not possible to obtain such
good results as with aminoacetic acid. Both these effects
correlate well with the explanation given of bright deposits,
since the pH of sodium citrate solutions is greater than
that of citric acid, and α-alanine has a more acid reaction
than aminoacetic acid.

The postulate that adsorption, rather
than the formation of a silver containing colloid, is the
active cause of brightening, was demonstrated by replacing
the alkali with a wetting agent (cetyl pyridinium nitrate).
This gave deposits which were even brighter than those
obtained by the addition of ammonia to the solution, and
even in unstirred solution, some brightening was observed.
A cationic wetting agent of the type used, is unlikely to
form complex ions, and therefore, it must act by adsorption.
Further, the stability of such a reagent is less likely to
be affected by changes of pH. Thus, the brightening effect,
produced by the addition of small amounts of alkali or
wetting agent to solutions containing \( \textit{aminocetic acid} \), is caused by the preferential adsorption of the additive (or some reaction product) on active spots in an otherwise smooth deposit. However, stirring still affects the brightness of the deposit, even when the added reagent is of a type unlikely to be affected by pH changes, and this is probably connected with the fact that the pH of the solution frequently affects the processes of adsorption. (An alternative explanation would be preferential adsorption of hydrogen ions deactivating the surface.)

It is noteworthy that the properties of the brightening agent are those of the first type (inactive) of organic addition agents. Thus, the production of bright deposits of silver from solutions containing silver nitrate, can be accounted for on a basis of the adsorption theory of addition agent action, by considering two distinct types of reagent. The first of these must be present in large amounts, and be likely to be adsorbed generally on the greater part of the cathode surface. Such a reagent used alone will give a smooth deposit. The second type of addition agent need only be present in small amounts, and its' function is to adsorb preferentially on those parts of the cathode not covered by the first additive. Such a reagent, if used alone will give a coarse deposit. In combination, the two addition agents will give bright smooth deposits.
The Adsorption Theory.

The first part of this discussion has served to show that the adsorption theory of bright plating, and adsorption generally, provides the most comprehensive explanation of the observed phenomena. It has also been shown that neither of the other major theories provides such a complete and satisfactory explanation of the experimental results. It is therefore proposed to consider the adsorption theory in rather more detail.

The concept of adsorption affecting the nature of the deposit in electrodeposition, was first proposed by Bancroft (1), and, although at the time it received little support, this theory has gradually come to be more accepted, and a considerable amount of experimental evidence has been put forward in its support. The theoretical development of the concept has been carried out by several workers over a number of years, but a recent paper by Hoar (7) claims particular attention. In this paper, Hoar, in a consideration of bright nickel plating, emphasises the fact that adsorption is a dynamic process, and hence it is necessary to consider both the rate of adsorption, and the rate of desorption. Such processes, Hoar points out, may be represented mathematically by the method of Langmuir:

\[
\text{Rate of adsorption} = B(1-e)^c \frac{E_a}{RT}
\]
Rate of desorption = $Ae^\frac{-E_d}{RT}$

where $\phi =$ fraction of area covered.

$E_a =$ activation energy of adsorption.

$E_d =$ activation energy of desorption.

$c =$ concentration.

$A$ and $B =$ temperature independent constants.

On this basis, Hoar develops a theory of two classes of addition agent. Assuming that all cathode sites are equally favourable to deposition, then random deposition (which favours bright smooth deposits) is most likely to occur if there is a random distribution of uncovered sites on the cathode at any given instant, and if these sites are in a state of constant flux from place to place. Such conditions are likely to occur if $\phi$ in the above equation is large (about 0.9), and the equilibrium rates of adsorption and desorption are high. The type of molecule likely to satisfy these conditions, is one for which $A$ and $B$ are large, and $E_a$ and $E_d$ are small. Such molecules are likely to be organic molecules of low polarity and small molecular weight, and if they are also easily soluble, the concentration can be increased, and this too will favour the attainment of the required conditions. This forms Hoar’s first class of addition agents.

The second class of addition agents is necessary if the metal surface contains sites particularly favourable to deposition (as in fact most metal surfaces will). In
this case, it is necessary to use a further addition agent which is likely to be strongly adsorbed in a preferential manner on the highly active spots. The first type of addition agent is almost certain to leave some cathode sites uncovered, and will therefore give conditions favourable to local preferential deposition. Such sites will be equally favourable to preferential adsorption by the second class of addition agents, and thus, the second class of additive will function as a brightener when used in conjunction with the first type. Molecules likely to exhibit properties required of the second type of addition agent, are large, highly polar molecules. For this type, the rates of the adsorption processes need not be high, since the function of the addition agent in this case is to slow up deposition at the active spots.

Finally, Roar points out that the two classes of addition agent proposed, are not mutually exclusive, but they are complementary in their action. Also, the correlation frequently observed between polarisation and brightness is incidental rather than direct.

Development of the Adsorption Theory.

From the theory as stated by Roar, it is possible to make several further deductions, and also to obtain a remarkably good qualitative correlation between the theory and the experimental results reported earlier.
Heuer states that addition agents of the second type, are likely to be highly polar, and strongly adsorbed at certain preferential sites on the cathode. This infers that if such an addition agent is alone present in the solution, it will tend to block those sites particularly favourable to deposition. Hence, deposition must now occur at sites less favourable to deposition, and it is probable that in this case, the polarisation will increase, since more energy will be required to include the ion in the lattice. Moreover, under such conditions, the deposit will tend to be dendritic.

Sites favourable to deposition are very likely to occur in metal surfaces (which are never very homogeneous) at places like the edges of crystallites. At such places, the surface fields of force are unsatisfied, and will therefore tend to favour both deposition and also adsorption. Thus in simple silver nitrate solutions, it is reasonable to suppose that, adsorption of hydrogen ions present in the solution takes place at selected cathode sites. It has already been shown that adsorption does occur at metal surfaces, and is of the chemisorption type. For such adsorption, $E_a$ is large, and hence the rate of desorption will be slow, and thus if hydrogen ions are adsorbed, they will tend to block parts of the cathode, and the deposit will be coarsely crystalline. The effect of the non-depositing cations may be explained in precisely the same way, and, if it is assumed that all such ions are
adsorbed to the same extent, the larger ion will tend to have the greatest effect. In this connection, it is interesting to notice that small additions of acid to the solution have little or no effect, from which it may be inferred that such additions do not appreciably alter the extent of adsorption because the pH of the cathode layer is already low.

In the case of the solutions containing organic molecules, it is clear that the action of the non-smoothing additives (thiourea etc.) may be explained in the same way as the inorganic cations. Either:

(i) The concentration is so low that only a small fraction of the area is covered.

or (ii) The equilibrium rates of adsorption and desorption are too low to permit random deposition.

or (iii) The substance is of the second type of addition agent, and will therefore not smooth the deposit.

All the reagents, except glucose, are at low concentration, and hence factor (i) applies. The setting agents are known to be strongly adsorbed, and thus factor (ii) is possible. Finally, factor (iii) may apply to all the reagents. Thus, all the reagents which do not smooth the deposit, behave similarly, although the reasons for their action may be different. It is difficult to make an assessment of the probable relative magnitudes of the various factors in any given case, because there is little
or no information available regarding the adsorption processes from solutions as concentrated and complex as those under consideration. However, it is interesting to notice that the majority of the non-smoothing reagents come into Hoar's second class of addition agents in one respect or another, and are therefore more likely to act as brighteners of smooth deposits than as smoothing agents in their own right.

The adsorption theory, as developed by Hoar, is also in harmony with the results obtained for silver nitrate solutions containing citric; tartaric; and aminoacetic acids. All these reagents fall into Hoar's first class of addition agents, and will therefore tend to smooth the deposit. Of the three quoted, aminoacetic acid is most nearly ideal in its properties, and this gives the smoothest deposit. Thus citric acid; and tartaric acid are not only larger, but also more polar molecules than aminoacetic acid, and hence it is probable that $E_a$ and $E_d$ will be less for the latter than for the former reagent.

The Mechanism of Electrodeposition and Bright Plating.

The experimental results, and their correlation with the adsorption theory as expressed by Hoar, lead to the following concept of the mechanism of deposition and bright plating:

In the first place, it seems likely that, even in the simplest solutions, there is some substance present
which adsorbs to a greater or lesser degree on the cathode, and, depending on the precise nature of this adsorption, so the deposit will tend to be more or less smooth. If the reagent (whether naturally present, or added) is such that the equilibrium degree of adsorption is low, and/or the equilibrium rates of adsorption and desorption are low, then the deposit will tend to be scarcely crystalline. Reagents which might be expected to give such deposits, are those of high polarity, low solubility, and for which the activation energies of adsorption and desorption are high (i.e. those reagents which tend to be chemisorbed), or, if the molecule is highly specific to certain active spots on the cathode. All such reagents fall into Hoar's second class of addition agents.

If the reagent is of a type likely to give high coverage of the cathode surface, and also has high equilibrium rates of adsorption and desorption, then it will fall into Hoar's first class of addition agents, and as such will tend to give smooth or even bright deposits. Such reagents will tend to be found among the low polarity organic molecules, and, since they must show high rates of adsorption and desorption, they are more likely to adsorb by van der Waals than by chemisorptive processes.

It seems probable that, in order to obtain bright as opposed to smooth deposits, it is necessary to supplement the first class of addition agent by a member of the second type. It is however, necessary to bear in mind that a
given reagent may tend to act in both ways, and also that substances naturally present in the solution may be induced to behave in the desired way.

This aspect of inducing the required effects, is the most probable reason for the influence, both desirable and undesirable, which the operating conditions sometimes have on the appearance of the deposit. Thus factors like temperature; pH; current density; and stirring may indirectly increase the smoothness or brightness of the deposit by affecting either the extent or the rates of the adsorption processes.

For example, an increase in the operating temperature is almost certain to increase the rates of the processes of adsorption by assisting the attainment of the necessary activation energies. At the same time, the polarisation will tend to decrease, since the increase in temperature supplies energy, other than electrical energy, for the activation processes. (It is probable that polarisation is due to these activation energies of adsorption.)

Increases in current density frequently cause changes in the brightness of the deposit. Here again, the effect is probably the indirect effect of changing the adsorption processes. Not only does the change in the current affect the supply of ions to the cathode, but it will also tend to affect the supply of addition
agent, thus altering the adsorption equilibrium.

Alternatively, the effect may be due to the increased current supplying more energy and thus assisting the attainment of the activation energies of the adsorption processes. An immediate inference of this is, that there will tend to be an optimum current density range for maximum brightening, and this has been found to be the case for the bright deposits from aminoacetic acid.

The effect of pH is also likely to be indirect. The acidity of the bulk of the solution will affect the pH of the cathode layer, and this in turn will affect the stability of any reagent present in the solution, (especially if that reagent is colloidal, or a complex ion) which might otherwise be adsorbed. Thus in nickel plating, it is an established fact that the evolution of hydrogen raises the pH of the cathode layer, and encourages the formation of colloidal Ni(CH)₂ which is adsorbed on the cathode.

There is also evidence that pH may directly affect the adsorption of other substances, and in this respect, composition and concentration may also play a part. An indirect piece of evidence may be adduced as to the effect of pH, from the fact that very few commercial plating solutions are noticeably acidic, (and the few that are evolve hydrogen, thus decreasing the pH of the cathode layer). Thus it seems probable that the effect of pH is indirect, and affects the stability of the adsorbed reagents.
The effect of stirring is likely to be either a direct one of increasing the supply of depositing ion, or addition agent, to the cathode, or an indirect effect of increasing the pH of the cathode layer.

Finally, the adsorption theory is also capable of explaining the fact that, in a few cases, polarisation decreases with increasing brightness of the deposit. Thus Shreir and Smith (22) have shown that in acid copper sulphate solutions, thiourea has the effect of brightening the deposit, while, at the same time decreasing the polarisation. This may be explained by assuming that the hydrogen ions present are adsorbed, and then the thiourea molecules displace these ions, and the equilibrium rates of adsorption and desorption for the thiourea are more favourable to the production of bright deposits, and hence the polarisation is decreased, since the activation energies required are less.

Conclusions.

1. From a consideration of the experimental results reported, it seems that the mechanism of electrodeposition and its attendant polarisation phenomena, and the production of bright deposits of silver from non-cyanide solutions, are most fully explained by the adsorption theory.

2. The adsorption theory provides a more complete explanation of the observed phenomena than does either the
complex ion, or the interference theory.

3. Simple silver nitrate solutions give coarse deposits because there is some component of the solution (probably hydrogen ions) which is strongly adsorbed on certain parts of the cathode, and therefore, deposition is prevented on those parts.

4. The production of bright deposits appears to be the problem of attaining, and maintaining, an appropriate high equilibrium rate of adsorption and desorption, of one or more addition agents. This equilibrium is attained by balancing the various operating factors (concentration, current density, agitation; etc.) against each other.

5. In the achievement of such deposits, it is inevitable that the polarisation will increase, since an excess of energy will be required to activate the adsorption processes. Thus, polarisation potentials are more a secondary effect, indicative of the magnitude of the adsorption processes, than a direct measure of the brightness of the deposit.

6. Before the cathode polarisation phenomena reported can be put on a more quantitative basis, a much more detailed knowledge of the adsorption processes between metals and solutions will be required.
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