THE

GALVANO - PLASTIC METHOD

by

H. SUNDBERG, Civil Engineer, with a short introduction
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INTRODUCTION

In the summary concerning copper plate engraving, correction and repair, which appeared in the Hydrographic Review Vol. I, N° 2, 1924, the galvano-plastic method of working is, as a rule, touched upon but cursorily. The galvano-plastic process is however of great use in the reproduction department of a Hydrographic Office, especially as concerns the question of keeping chart plates up to date. The available literature referring to the galvano-plastic process seems but slightly adapted to the special needs of Hydrographic service. Any information desired has to be picked out piecemeal, from the periodicals on the subject, *etc.* During recent years, when continuous work was being carried out by the Swedish Hydrographic Office in order to develop the details in question of the work, this lack in the literature has been very noticeable.

In 1922, arrangements were made for the establishment of an entirely modern galvano-plastic department within the offices of the Hydrographic Office. It then became obvious that systematic investigation and experiments must be carried out in order to endeavour to obtain further data of the galvano-plastic working methods.

The program of these investigations included the following main points :

1.   A general investigation of the progress of precipitation, and the factors which influence it.

2.   Galvano-plastic precipitation of "alto" and "basso" plates.

3.   Galvano-plastic precipitation for correction of the plates of nautical charts.

4.   Experiments for finding a more rapid method of precipitation for the correction of nautical charts.

These investigations, which were carried out during the latter part of 1923, and throughout the whole of 1924, were entrusted to Mr. H. SUNDBERG, Civil Engineer.

Since they have now been completed and have given good results, it seems quite natural that the advantages gained thereby should be published in an adequate form, so as to add, to some extent, to the improvement of this detail in the production of nautical charts.

The accounts, as well as the recipes, given in the following article by Mr. SUNDBERG, are of course unreservedly presented for use, should occasion arise, by any Hydrographic Service which may be interested in the matter.   At the same time, I desire to add, that the Royal Swedish Hydrographic Office will be pleased to supply any further information that may be desired.

THE GALVANO-PLASTIC METHOD

GENERAL AND THEORETICAL CONSIDERATIONS ON THE COURSE OF THE
    PRECIPITATION.

Electrolytic copper is generally produced nowadays in an acid copper sulphate solution, according to different and, to a certain extent, varying recipes.   In order however, to understand the course of the process itself, as well as to allow of the influence of the different factors to be estimated, it may be of interest to allude to some theoretical data which have been found during various investigations.

CONDITIONS OF THE BATH.

Electrolytic copper is obtained in the simplest way by the use of the JACOBI cell method which still exists in some places to the present day in an almost unchanged form.   A porous clay cylinder is placed in

a copper sulphate solution containing dilute sulphuric acid and a piece of amalgamated zinc. A piece of copper, immersed in the bath, is used as a cathode. The principal constituents of the copper bath are ions of copper, hydrogen and sulphate, whereas no copper ions, but a great number of hydrogen and zinc ions are present in the acid solution inside the clay diaphragm. A potential difference of some tenths of a volt appears over the surface between the copper and the solution. The copper is thus found to be positively charged, and the degree of tension against the bath is determined by means of the Nernst formula, i.e. by the normal potential [1] corresponding to the slight solution tension of the metal as well as by the amount of active copper ions. The influence exerted by the last mentioned factor on the tension may however be taken at only a few hundredths of a volt, when the ion concentration is changed by 10. A certain potential difference has also been established between the zinc and the cylinder, important numerically on account of the high electrolytic solution tension of zinc. The zinc is negatively charged however, as it shows an inclination to send out positive ions with great force [2]. Instead, the hydrogen ions, which are positvely charged, strive to precipitate themselves on the negative zinc surface [3]. This self-dissolvation of the zinc, by the production of hydrogen, is prevented by the amalgam surface, as hydrogen can only be precipitated on mercury at a relatively high voltage. If on the other hand, the pieces of zinc and copper are connected by means of a good conductor, a current is excited, the active electromotive force of which consists exactly of the potential differences of the electrodes. Zinc is forced out into the solution in the form of ions, while an equal number of copper ions are simultaneously precipitated on the cathode.

A corresponding lack of copper ions is produced, however, in the solution as copper is deposited. Even hydrogen and zinc ions

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(1) For copper in a solution of di-valent copper ions the followings equation is valid $e = 0.34 + \dfrac{0.00198}{T\ 2}$ T log C, where e is the potential difference in volts, the absolute temp., and C the concentration of the ions. Further, the copper solution contains a very small amount of uni-valent copper ions for which the following holds good : $e = 0.52 + 0.000198$ T log C. The amount of the two ions is thereby determined by a certain equilibrium.

(2) Between zinc and a solution of zinc ions $e = 0.77 + \dfrac{0.000198}{2}$ T log C volts.

(3) An analogous behaviour appears when iron is dissolved in dilute sulphuric acid. The active electromotive force is then $e = 0.43 + \dfrac{0.000198}{2}$ T log. C.

$Fe + 0.000198$ T log $C_H - 3$ volts, where 3 is the overvoltage, acting against the precipitation of hydrogen. According to the theory for local elements, the dissolving rate is proportional to e, and to the conductivity of the solution. Thus, the speed is increased to the greatest extent by augmenting the concentration of the hydrogen ions (the acid content).

3.—

are gradually forced out through the diaphragm into the copper sulphate solution. The percentage of copper sulphate may then be maintained by adding either copper sulphate, copper hydrate or copper carbonate. The acid, which has diffused into the copper sulphate solution, is certainly exhausted in the last case, but due consideration has to be taken of the danger arising from the production of gas bubbles on the cathode. Sooner or later, however, the diffusing zinc salt spoils the solution. These difficulties, as well as limited methods of application and regulation, have caused this method to be more or less abandoned nowadays. Electrolysis with an external supply of current is now used instead and, in this connection, a closer investigation of the course of the precipitation will now be entered upon.

Taking the case when two plates of copper are immersed in an acid solution of copper sulphate. Between each piece of copper and the liquid a difference of tension of some tenths of a volt prevails, already, before any external electric current is applied. If one of the metal plates, the anode, is connected to the positive pole, and the other electrode, the cathode, is connected to the negative pole of a battery, a current passes through the system. The copper ions, present in the solution on the one hand with a certain tension, try to hinder the emission of any new copper ions from the anode, but they are simultaneously striving to precipitate copper on the cathode with an equal force. In reality the equilibrium of the ions on the surface nearest to the electrodes is somewhat affected during the passing of the current. A certain counter-EMF (polarisation) is produced. Apart from this slight polarisation no higher external tension on the electrodes should be necessary than that required in order to counteract the internal resistance of the bath. (*).

The amount of current necessary for the precipitation of a certain amount of copper may be taken, as 1 amp. in 1 hour is able to preci-pitate 1.186 grammes of copper as a maximum. To work economically with the smallest possible amount of energy for the electrolysis, the tension must be diminished, *i.e.* the internal resistance of the bath has to be lessened. This is brought about by increasing the number and velocity of the transmitting medium — *i.e.* the ions. The total percentage of copper sulphate might therefore be increased, but it has not proved advantageous to go too far in this direction. In the first instance, in the case of a concentrated solution we risk the precipitation of the salt

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(*) In a tank of uniform transverse section and fitted with two parallel electrodes filling up the section the resistance of the liquid is $= \dfrac{\text{electrode area}}{\text{electrode distance}} \times$ specific resistance of the solu-ion.

by evaporation, by inceasing the concentration of the acid, or by lower-
ing the temperature, secondly, too many uni-valent copper ions—secon-
darily forming metallic copper and *di-valent* ions ($2\ Cu^+ = Cu + Cu^{++}$)—
are produced at the electrodes if the solution is insufficiently stirred and
if too low a current is employed.

The most effective method will be to increase instead the number
of the most rapid ions of the solution — the hydrogen ions. This is also
desirable for two other reasons. By increasing the acidity—the hydrogen
ions—up to a certain degree dependent on the density of the current and
on the temperature as well as on the stirring, the quality of the preci-
pitate is improved. Further, some acid must be present in order to
avoid hydrolysis, *i.e.* the forming of hydrate of cuprous oxide
($Cu_2 SO_4 + H_2O = Cu_2O + H_2SO_4$). Too many hydrogen ions should not
however be present in the bath as, at an increased intensity of the
current, this might cause some hydrogen to fall out on the cathode,
rendering the precipitate spongy and useless.

Finally, the speed of the migrating ions may be augmented by
increasing the temperature of the solution, and it has also proved true
that the copper precipitate becomes improved by this procedure (within
limits of $+ 15°$ and $+ 14°\ C$).

A disadvantageous disturbance of the equilibrium between the *uni*
and *di-valent* copper ions sets in, however, simultaneously with an increase
of temperature : which will necessitate a great increase in the number
of the uni-valent copper ions. Part of the current will then be used
solely for the reduction of di-valent ions to uni-valent ions, with the
result that no copper precipitation, corresponding to this current, will
appear. It must further be kept in mind that, by increasing the
temperature ([1]) *i.e.* a decrease of the electromotive force ; polarisation,
which hinders the hydrogen from precipitating on the cathode, is brought
about.

The conditions required for obtaining pure electrolytic copper from
acid solutions may thus be said to be the maintenance of certain ion
concentrations and potential differences at the electrodes. The different
influencing factors must naturally stand, therefore, in a certain relation
to each other. Precautions must be taken, in the shape of additional

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([1]) The current efficiency should normally amount to 100 per cent.
  I.   The current efficiency of the anode in % = decrease in weight of the anode × 100 :
($1.186 \times$ amp. × hours).
  II. The current efficiency of the cathode in %c = increase in weight of the cathode × 110:
($1.186 \times$ amp. × hours).

stirring, to prevent any too great accumulation of copper ions at the anode, or too great a decrease in the concentration of these ions as well as any excessive increase of the hydrogen ions at the cathode. Even the raising of the temperature has the same effect as an intentional stirring, inasmuch as thereby the diffusion becomes more pronounced.

The Quality of Electrolytic copper.

Ordinary electrolytic copper slowly precipitated from pure solutions, however, possesses the disadvantage of becoming too soft. Its Brinell hardness scarcely appears to amount to more than 60. However a considerably harder material may be obtained simply by increasing the density of the current (*i.e.* the intensity of current applied per surface unit). An effective stirring is then necessary however, as otherwise the hydrogen ions are apt to accumulate, and the copper ions would disappear too rapidly at the cathode. During normal production of copper by electrolysis, small so called "germs" are supposed to be formed on the original surface of the cathode. During a slow precipitation, *i.e.* at a low current intensity, larger V-shaped crystals grow out later from these starting points. If, on the other hand, the precipitation takes place during a high density of the current, fresh germs are continually formed, and the crystals do not have sufficient time to develop. The precipitate however becomes incoherent and powdery at too high a density of current. The germs have then not even been afforded the opportunity of growing together.

A pronounced parallel to crystallisation in general seems to occur here. If the progress be slow, large crystal grains result; by quick progress small grains are obtained, likewise, in a mechanical disturbance, small crystals are produced.

In addition to the stirring process, there is still another means of preventing the formation of large grains at fairly low densities of the current. Certain foreign substances are added, which have been proved to exercise a very good influence on the character of the metal. Amongst these attention must especially be drawn to those of an extremely fine dispersion (colloidal form), which possess the quality of being able to follow the current to the cathode. The most general as well as the most effective of these substances, which has proved useful in the practical application of electrolysis, is *gelatine* in exceedingly small quantities. On the other hand too much colloidal substance gives a brittle, useless precipitate.

It does not seem unlikely that a slight decrease in hardness will appear in electrolytic copper after some time. Similar changes in other electrolytically precipitated metals, for instance iron, have been ascribed to the escape of hydrogen or to structural transformations into ranges of greater stability. The fact that such plates are inclined to warp, often seems in a practical application to involve great inconveniences. This difficulty is overcome by annealing, but as is the case in rolled metals, the material thereby looses its original hardness.

So far, it has been taken for granted that copper is really precipitated onto the surface of the cathode. The quality of the precipitate as well as its adhesion to the electrodes is dependent however on the bedding. A good result will only be obtained when the original cathode possesses regular conductivity, when it is free from grease, oxide layers, and so forth. The precipitate will otherwise become uneven, porous and papilliferous, with an unsatisfactory adhesion. Concerning the surface of emanation, two different cases must here be taken into consideration.

1. As the precipitate, after attaining the desired thickness, should be detachable from the electrode (the matrix), the latter is covered with a thin film of a suitable conducting material which prevents any actual metallic amalgamation of the original surface with the precipitate. Graphite is often used for this, or the primary surface may be silver plated by the contact method, and treated with iodine.

2. If a complete adhesion between the original surface and the precipitate be desired, this may be obtained after careful dipping. A thorough cleaning, followed by rapid etching in strong acids seems to give the best result. The electrolytic metal may then even primarily continue to build up a substance possessing the same structure as the original material.


INFLUENCE OF COMPOSITION OF PLATING SOLUTIONS
AND EFFECT OF CURRENT DENSITY ON THE GRAIN SIZE
OF ELECTROLYTIC COPPER
(According to Sieverts & Wippelman).

(Pfanhauser bath.)   I 250 gr. $CuSO_4$ 5 aq/ 7.5 gr. H_2SO_4 per litre
II 350 gr. $CuSO_4$ 5 aq/ 6.9 gr. H_2SO_4 per litre
III 250 gr. $CuSO_4$ 5 aq/ 34.5 gr. H_2SO_4 per litre

Experimental Temperature : about 25° C.

Stirring : 500 — 550 revs. per. min. by a Witt stirrer.

CURRENT DENSITY
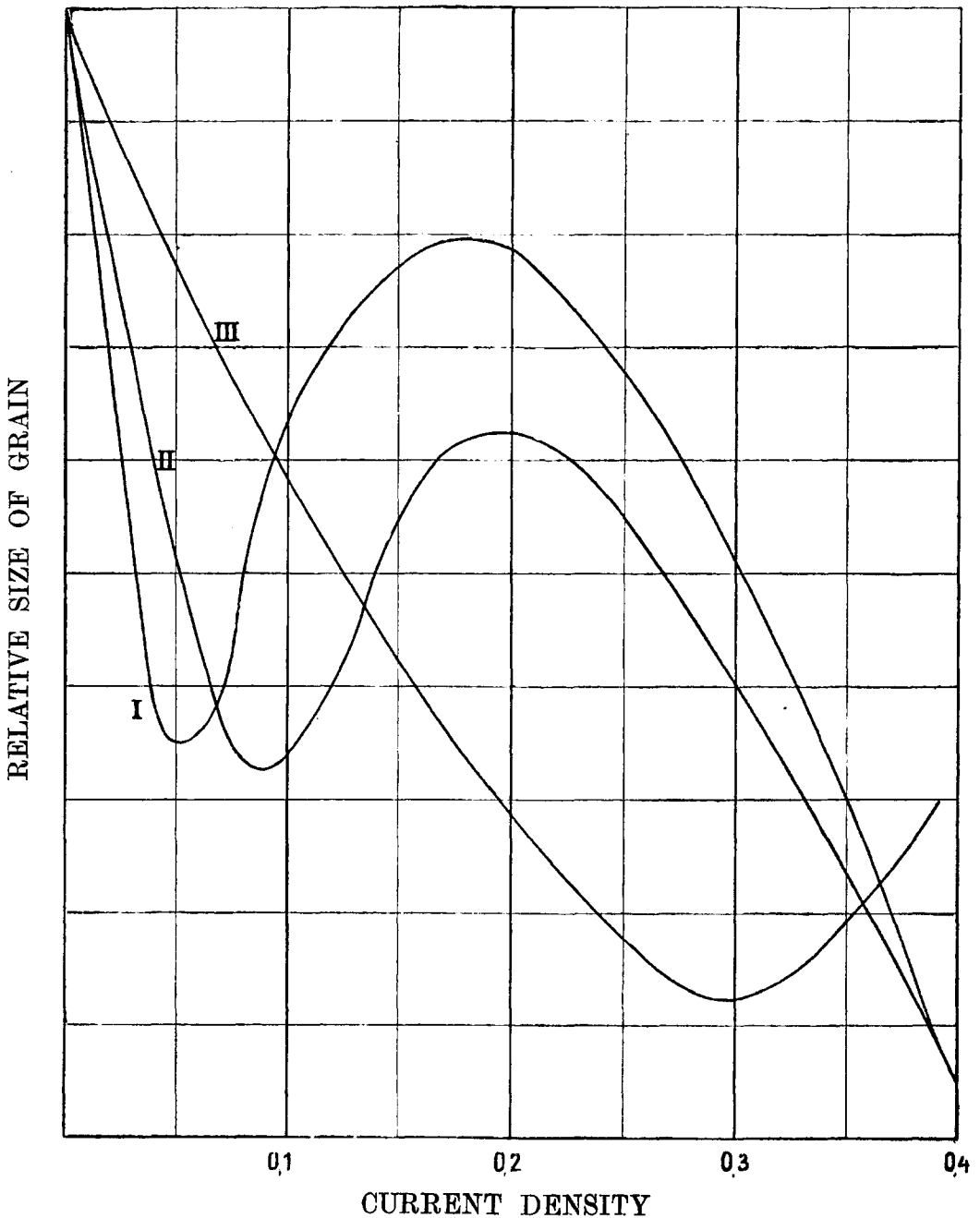
(*Fig. 1.*)

This solution has been found to be very good for rapid galva-no-plastic process. Its spec. gravity = 1.147 (19.5°)

spec. resistance = 0.16 ohm (a cube of 1cm³)

temp. coefficient = 0.0096.

The growth of the precipitate internally as well as externally, in other words the distribution of the metal, is determined by the conditions of the electrolyte and by those of the cathode. The following factors are of importance in this : the shape of and distance between the electrodes, the discharging potential at the cathode, the composition and conductivity of the bath, as well as conditions of stirring and diffusion. The uniform distribution over a given surface is increased by decreasing the distance between the electrodes, by increasing the cathodic potential and decreasing the specific resistance of the bath. In practice, however the electrodes must not be placed too near to one another. In the case of plane electrodes where an even thick deposit is aimed at, too great a current density at the edges should be limited by means of screening off. Very often the forming of holes as well as the growing of "buds" and "trees," which is inconvenient especially at high densities of the current, may be attributed to impurities in the bath. It is noticed that a bath which has become impure after having been used for a long time, and gives an irregular and bad precipitate, will give quite a satisfactory result after filtration. From this it follows that a pure anodic material is desirable. If the electrodes are placed one above the other, a possible shower of particles from the anode directly onto the cathode may be avoided by covering the anode with some material.

Summing up, the necessary factors for obtaining a homogeneous and resistant electrolytic copper are :

a) suitable shape and quality of the electrodes

b) a correct composition of the solution.

c) a certain density of the current

d) a suitable temperature.

e) sufficient stirring.

f) an addition to the solution of certain elements, in order to raise the quality of the precipitated copper as occasion arises.

It must not be taken for granted for instance that a certain solution may be used advantageously at many different densities of current and so on. Instead, it must be kept in mind that in the presence of one —or several— of the given conditions, the others must, as a rule, be adapted to them.

As a detailed mathematical treatment here of the influence of all these factors would be too lengthy, only the following curves for the density of current and the size of grain are given at two different concentrations of acid and sulphate (Fig. 1). In addition, some of the best conditions for an eventual addition of gelatine, applicable in the practise of plate-engraving, will be given later.

THE PRODUCTION OF COPPER ENGRAVING PLATES

In the use of the galvanoplastic method of producing engraving plates, more or less complicated processes show a possibility of satisfying even far reaching demands. Mechanically a recent American invention seems to offers a superior material. Copper and nickel are precipitated in alternate layers on the same plate. But as long as the number of impressions, required from each plate, is moderate, there is an easier way of obtaining a quite satisfactory result. For cartographic purposes plain copper engraving plates, with the engraving surface coated with iron or chromium, will probably prove most suitable. There is then a possibility of effecting the necessary alterations on the plate simply by removing the protecting metal surface by means of some acid. Experiments made on ordinary engraving plates show, in fact, that an iron coated surface on the top of a simple metal foundation is quite serviceable up to ten thousand impressions, and a chromium coated surface for even more. When producing a moderate quantity of nautical charts in localities where no corrosion need be feared, the ordinary method of iron plating is preferable both for economical and hygienic reasons.

The method employed at the Swedish Hydrographic Office for producing primary copper plates is direct engraving on copper. The material of the plates consists as a rule of hard rolled copper but occasionally, particularly lately, electrolytic copper has been used for this purpose with equally good results.

With a thickness of the plates of 2.55 mm, the mechanical qualities are quite satisfactory. These plates have not shown any disposition to warp worth mentioning and the stiffness leaves nothing to be desired.

A very good and exact relief plate of copper with a thickness of only 1.5 mm, will be obtained by an electrolytic copper precipitation on the primary plate which has been silver plated in advance by the contact method and slightly treated with iodine. When this plate, in its turn, has been silver plated and treated with iodine, the precipitation of the new "basso" plate may take place.

By using suitable current densities and gelatine additions in the bath, copper is produced in such a form that its hardness as well as its other mechanical qualities are quite equal to those of rolled copper. The elasticity is good, the Brinell hardness amounts to that of rolled copper (about 80) and in comparing the structure of the two materials we find, even, that the electrolytic copper (fig. 2) exceeds that of the rolled copper (fig. 3) in point of fineness of the grains.

The electrolytic method of producing engraving plates at the Swedish
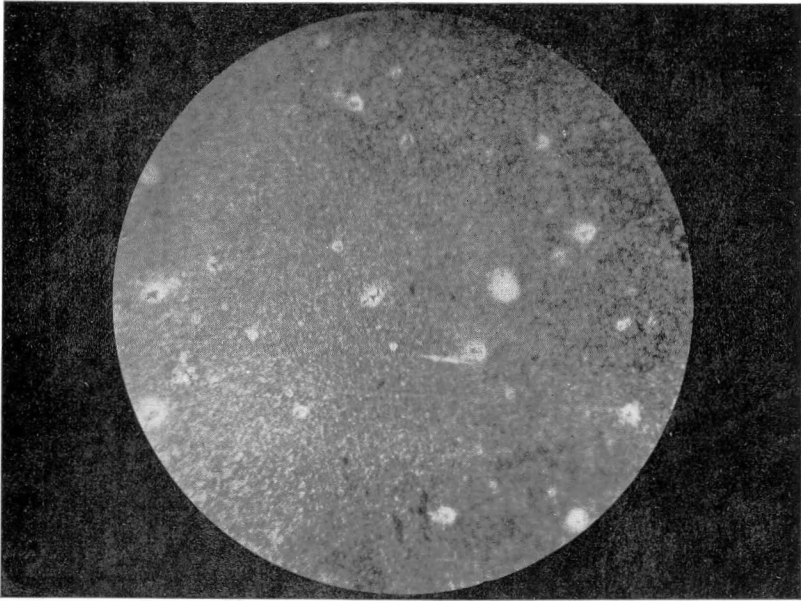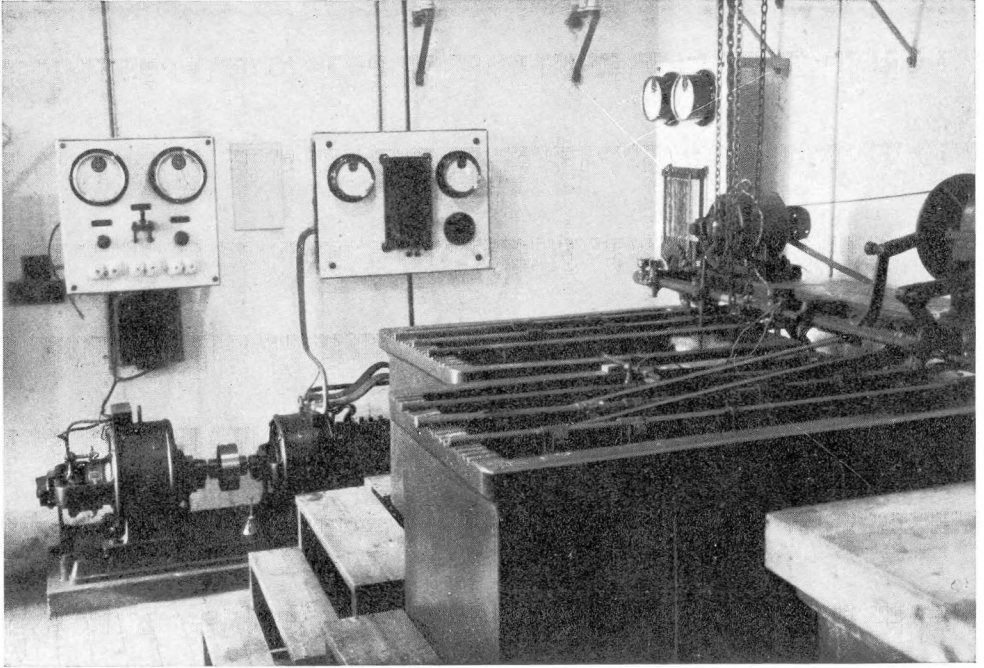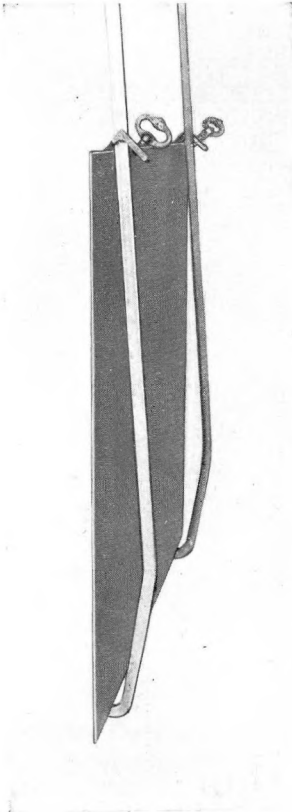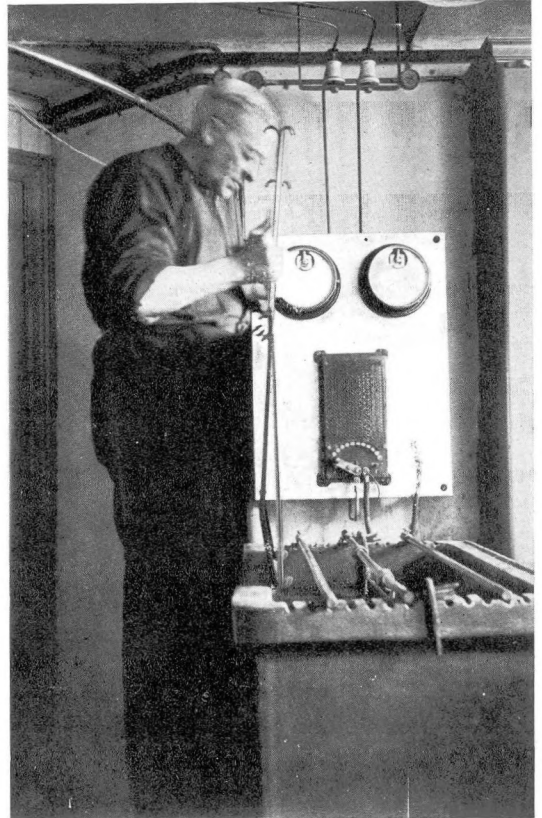
Fig. 2

PLANE SECTION
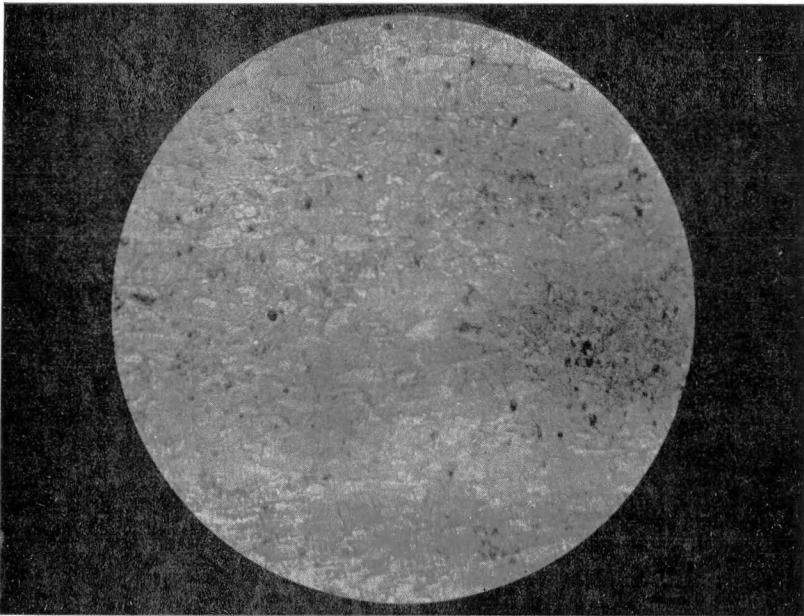
Fig. 3

PLANE SECTION

Fig. 4.

Fig. 5.

Fig. 6.

Hydrographic Office takes place in the electrolysis room, illustrated in fig. 4. The generating group of electrical devices, visible on the left of the figure, transforms a current of a tension of 440 volts into a low tension current, suitable for the precipitation of copper. This current may be regulated by means of a resistance placed in series with the field of the generator. According to a notice, stamped on the the generator group, the current of the low tension circuit amounts to 5 volts.

In order to obtain a specially low tension as well as current intensity—necessary at times— a larger storage battery would have been desirable. The installation costs for such a battery however being high, the management thereof troublesome and the current economy small, the Swedish Hydrographic Office therefore, in producing plates, always works directly on the transformer. The current density required for this is then simply brought about by immersing an extra anode plate, forming a supplementary cathode. In this way the working proves much more economical than if a storage battery were used.

The precipitation takes place in large clay cells of a rectangular section. The solution is heated by means of leadcoated, electric immersion heaters and the cells may be kept at the constant temperature desired by means of an arrangement of thermostat regulators. A motor driven stirring machine, consisting of hard rubber-covered copper rods, which alternately sink into the solution, supplies the necessary stirring.

Under normal circumstances a "basso" plate is produced in about 75 hours, but, if necessary, the current densities may be tripled and the precipitation is then carried out in about 24 hours. An ordinary "alto" plate requires, in analogous circumstances, 45 or 15 hours. No nightwork is necessary and the precipitation may be done intermittently.

Steel plating is done in a special "iron electrolyser". The application of the current and the suspension is effected by means of two strangely shaped hooks, by which the man in figs. 5 and 6 holds an engraving plate. The final high polishing is easily done. The plate is rubbed at the same time with a mixture of oil and turpentine, which protects it against corrosion. It is now quite ready to be rubbed with printers ink at the printers.

COMPOSITION AND TREATMENT OF THE BATH.

Fuller details re the production of plates are given below.

Directions for Producing Copper Engraving Plates

Solution : 220 — 280 gr. sulphate of copper (pure) }
                7 —   30 gr. sulphuric acid (conc.)   } per litre.

For the precipitation the vitriol is dissolved in warm, distilled water and the sulphuric acid is then gradually added while constantly stirring. Low vitriol and high acid concentrations are suitable for a low current density (1.3 — 2.5 amp per dm²), without any intentional stirring of the solution and at ordinary room temperature. Normally it is of advantage to work with vitriol percentage of 240 — 280 gr. per lit., a moderate amount of sulphuric acid up to 20 gr. per lit., at a current density of 2.5 amp per dm² or higher. Stirring is then always required. A high content of sulphuric acid is of advantage to the quality of the copper even at high current densities—provided sufficient and even stirring and temperature can be maintained.

The composition should be checked analytically at intervals, depending on the amount of use to which the bath has been put. The solution is generally found to have become too acid, and some copper carbonate has therefore to be added, the quantity depending on the results of the analysis. (e.g. The analysis gave a gr. vitriol per lit., then $250 - a \times 0.46$ gr. basic carbonate of copper ($2 \, Cu \, CO_3 \, Cu \, (OH)_2$) has to be added.). The copper carbonate is stirred together with a few litres of the solution to a thin paste which is then added to the solution while constantly stirring. After a few hours the liquid is filtered in order to remove any solid particles. Should the acidity prove insufficient, the necessary quantity of sulphuric acid must be added. Evaporation of water from the solution occurs incessantly, and is especially rapid at high temperature. The loss may be compensated by adding distilled water so as to maintain the normal height of the surface.

The copper acquires excellent qualities, even with a moderate current density and stirring, if 1 or 2 mg. of gelatine per litre are added whenever a new plate is to be precipitated. For this purpose the solid gelatine is dissolved in smaller quantities of lukewarm water and the liquid is poured through a piece of cloth direct into the bath.

In addition, the bath must be kept free of all foreign substances and must not, of course, come into contact with any iron object *etc.* Should the solution become defiled so as to have a muddy appearance, due to coagulation of the gelatine or for any other reason, it must certainly be filtered.

TEMPERATURE OF THE BATH.

A bath temperature of 25° to 28° *C.* is maintained during the precipitation, by means of an immersion heater (for solutions containing

a high percentage or vitriol and acid). Should the temperature become too low, vitriol is precipitated into the solution of the anode. This should be prevented of course (*). The higher the temperature, the lower the tension for a given density of current, for the resistance of the bath itself decreases by about 1 per cent, for each temperature increase of one degree C. (starting from a resistance value at 20° C.) Consequently, for a generator group it is possible to utilise, at high temperatures, the maximum intensity of the current. At too high a temperature, however, evaporation is augmented, the protecting wax softens (melting point 55° — 65°), the current efficiency becomes less and the hardness is again reduced (from 40° C. upwards). For baths rich in vitriol, the conclusion is actually reached that the temperature must not rise above the point where a precipitation of vitriol on the anode is excluded. The higher densities of current allow a higher temperature than the lower densities with reference to current efficiency, but they require it also in order to prevent any falling out of salt at the anode, where the accumulation of sulphate ions becomes great. The constancy of the temperature is most conveniently maintained by means of a thermo-regulator.

PLACING OF THE ELECTRODES AND MATERIAL OF THE ANODES.

The electrodes are generally placed as close to one another as comfort and mechanical arrangements permit. The anode plate should consist of pure electrolytic copper.

THE PRODUCTION OF A COPPER "GALVANO"

The process includes the following procedures :—

1. The production of an "alto" plate.
    a) Silver plating of the engraved original.
    b) Covering of the edges and back of the original with wax.
    c) Immersion of the original into the copper solution.
    d) Separation from the original of the ready precipitated copper.

2. The production of a "basso" plate (matrix).
    a)
    b) } as 1.
    c)
    d)

(*) Moderate concentrations (*e.g.* 250 grs. vitriol, 8 grs. sulphuric acid per litre) allow temperatures as low as 15° C.

DESCRIPTION OF THE DIFFERENT PROCESSES OF THE WORK.
PRODUCTION OF AN "ALTO" PLATE

Two strong copper hooks are soldered to the original plate made by the engraver. The plate is brushed over with a solution of hydrate of sodium (of about 10 %) mixed with some whiting and rinsed with water. The cleaning is continued with some cyanide of potassium (35 gr. *KCN* per litre) as well as with whiting and the plate is rinsed clean with water. It is then immediately silver plated by the contact method.

The liquid used in silver plating is produced in the following manner: 20 grammes nitrate of silver is dissolved in 100 cm³ of distilled water. A concentrated solution of cyanide of potassium is then added, until the precipitation of silver cyanide, formed at the beginning, has entirely disappeared.

A certain quantity of this solution is stirred with whiting to a fine paste which is spread, by means of a wad, on the copper plate which must be entirely free from grease and oxides. The surface is then immediately coated with a thin layer of silver.

After having been rinsed with water, the surface is then treated with a dilute solution of iodine. A few drops of iodine solution (1 part of iodine to 100 parts of alcohol) to one litre of water is quite sufficient.

The silver coated plate is now dried, either in warm air or else very carefully with clean filtering paper; the paper should not be rubbed on the prepared surface of the plate but only pressed against it. Great care should be taken not to touch the plate with the fingers when doing this. As soon as the silver coated copper plate, treated with iodine, is perfectly dry its edges and back are covered with wax. Ordinary bees' wax is quite suitable.

For economy's sake the wax may be mixed with up to 50 per cent of solid paraffin. The silver plated surface treated with iodine prevents the "galvano" from growing in close attachment to the original plate.

To remove the silver plating a solution of 10 grammes of iodine in 100 cm³ of 95 per cent alcohol may be used. In order to prevent the troublesome protrusion of the edges, these are covered with a suitable frame (called a current line screen) consisting for instance of a strip of waxed paper protruding 1 cm. (and if necessary coated with graphite on the inside). When the inside of the paper strip is graphite-coated, the precipitate will be of an even thickness, including the edges, and the risk of detrimental border growths is almost removed. The copper which has been used for the paper strip may be used during the partial correction process.

ESTIMATION OF THE PRECIPITATE.   CURRENT DENSITY.

If the precipitation has had to be carried out with a current density of only 1 amp. per dm², 74 hours would be required in order to obtain a precipitate of 1 mm thickness. If, however, the density of the current is raised, then the time for producing a plate may be shortened to a corresponding degree. Thus the precipitate becomes 1 millimeter thick after 10 hours at 7.5 amp per dm². The solution however is powerfully, heated by the current at high densities of the latter. The normal current density used is 2.5 amp. per dm² and the tension required is found to be about 3 volts at a distance of 17.5 cms between the anode and the cathode, but only 2.6 volts at a distance of 14 cms between the electrodes. (Temperature in this case about 28° C). The current intensity may be regulated partly by the magnetic resistance of the generator group, and partly by a balance resistance to be found at the cell, and lastly — the most economical — with necessarily greater alterations, by immersing a supplementary cathode in the same bath. For this latter additional cathode an extra "copper anode" is used, involving a welcome addition of copper to the original anode. During the first five minutes a lower density of the current is applied (about half of the current intensity) in order to avoid too firm an adhesion to the original surface.

The solution is stirred uniformly by a stirring machine the rods of which are lifted regularly up and down at a normal speed of about 10 beats per minute. If by any chance it should prove desirable to avoid the stirring process, then the copper vitriol percentage must be altered to 220 gr. per litre, and the current intensity should be lowered to half of that usually employed. The most suitable current density without any stirring is therefore only 1.3 amp. per dm².

Now and then the cathode has to be lifted up in order to see that no white spots appear at the beginning. Should this occur, the plate is lifted out and cleaned. Also, during the latter stages of the precipitation it must be seen to that no irregularities are allowed to form. Any crystals which may grow are removed. In the meantime it must be observed that no vitriol crystals or the like are allowed to settle on the surface of the anode.

When the precipitated copper layer has attained the desired thickness, the plate is lifted out and the wax edges are removed. It happens but very seldom that the edges of the plate have to be worked down with a milling cutter or a file until the division line between the original and the "galvano" may be seen.

As for primary plates, if treated with iodine it is easy to separate

them one from another. If necessary, wedges of some hard wood are used for this.

The new copper plate is an "alto" (relief) plate.

In order to obtain a "basso" plate for engravings, this must also be silver coated, and immersed in the copper solution as a cathode. All operations performed with the plate are identical to those for the production of the "alto" plate.

The engraving plates however are made thicker than the "alto" plates; their production also takes a correspondingly longer time (about 80 hours at a current density of 2.5 amp per dm^2 for obtaining a normal [2 ½ mm] thickness).

The edges of the plate are filed and trimmed. The back may be either polished by hand or else ground smooth with a special machine.

STEEL PLATING OF THE COPPER "GALVANO"

In order to give the copper engraving plate greater resistance the surface is covered with a thin layer of electrolytic iron.

The steel plating is effected in a cold solution of the following composition .

> 120 kgs. of iron vitriol
> 75 kgs. of ammonium chloride
> 1.000 litres of water.

The plate, which must be entirely free from grease, is immersed in the solution, hanging on two long iron hooks, whilst the current is passing. A current density of about 2.5 amp per dm^2 is maintained during the first minute, and 0.3 amp per dm^2 during the following 5 minutes.

After the steel plating has been completed, the plate is taken out of the bath, is well rinsed, and then polished with a moist mixture of emery flour and precipitated chalk. After having been dried quickly, the surface is immediately rubbed over with a mixture of machine oil and turpentine as a protection against corrosion.

REMOVAL OF THE IRON LAYER FROM THE SURFACE OF THE PLATE.

In order to remove the steel coating, a solution of 8 per cent sulphuric acid is used. This will dissolve the iron in 1 hour, but will not touch the copper. The dissolution may be carried out in a shorter time (about ½ hour) if the plate be occasionally taken out and brushed clean. If the plate has been immersed too long, the copper may also be somewhat attacked. This is dangerous in the case of electrolytically corrected plates of rolled copper, because electrolytic copper is affected perceptibly deeper than rolled copper.

If through carelessness during the removal of the iron casing some older, electrolytically corrected parts of the copper surface of the plate should become etched, they must be carefully polished. Thus it has happened during printing that these etched portions have appeared on the first charts produced, but they have disappeared however when the steel coated surface of the plate has become sufficiently worn by abrasion of the fairly hard cloth. To remove the iron with nitric acid would of course be a mistake as the copper would be attacked at the same time as the iron.

CORRECTION OF NAUTICAL CHARTS.

According to an old method, still exclusively practised at certain Hydrographic Offices, the parts intended for correction are hammered up from the back of the "basso" plate, whilst the front is resting against a level iron surface. Any new engraving that may be needed is then applied after polishing. In the case of somewhat larger corrections, the electrolytical procedure, more reliable in the long run, is now used at the Swedish Hydrographic Office. Experience has shown that cracking of the plates is out of the question. Besides this, the electrolytic method of depositing is advisable also for filling up troublesome old holes at the back of the plates caused by hammering-up.

The precipitation itself might be executed most quickly according to Bailey's impinging method. The solution is forced at great speed through a pipe in which a conducting piece of copper is inserted. The plate is applied as the second electrode (cathode at the filling up of copper, anode at the removal of the same); and the electrolyte is connected with a continuous current circuit. To be entirely effective, however, this method requires constant supervision. At the Swedish Hydrographic Office another arrangement has therefore been chosen, and a method of precipitation has been worked out with special regard to the provisos that the electrolysis itself can take place without having to be watched and that the correct engraving, as well as the surface of the plate, should not in any way be spoiled or altered.

Electrolytical correction is executed by means of smaller baths applied to parts of the horizontally placed plate. The principle is thus the same as that employed at the Danish Hydrographic Office (according to a description in the Hydrographic Review Vol. 1, N° 2, 1924, p. 28). The procedure itself has, however, been greatly changed in Sweden, for reasons of time-saving and convenience.

At the same time due consideration has been given to the circum-

stance that the hardness of the copper should not be allowed to fall below that of the bottom layer (that of the cold rolled plate). Figs. 7 and 8 show an example of the structure of electrolytic coppers, obtained in this way, with Brinell hardnesses of 80 and 100 respectively.

The procedure is comparatively simple. The area of a "basso" plate, in which engraving is to be filled up, is covered with asphalte varnish and surrounded with wax. The thin layer of varnish facilitates the observation of the engraving and makes it possibles to erase the parts to be filled up with copper. Round the whole a border of plastic clay is applied, as shown in Fig. 9. At the top, and parallel to the plate, an anode of copper is attached ; the cathode consists of the plate itself. The cell formed in this manner is dipped and rinsed with water and an acid copper sulphate solution is poured on. The electrolysis is effected by means of an external supply of current from an accumulator battery with a current efficiency of 1.2 and 2.4 volts. The other arrangement used for a partial precipitation is seen in Fig- 9. The correct intensity of the current is regulated on a switch board by means of a sliding resistance and an ammeter. The rate of precipitation is controlled by means of a voltmeter.

The greater part of the precipitation takes place at a low current density, without any stirring, and may therefore be left without super-vision even by night. During those seasons when the temperature of the room may be expected to sink so low that good precipitation may be endangered, the plates may be electrically heated from underneath. Accordingly, the upper part of the precipitation table consists of a large metal covered shallow box, in which is inserted a resistance loop of nichrome wire.

It is also possible, however, at the Swedish Hydrographic Office to work very quickly when precipitating without any great alterations. By using a solution with a higher percentage of vitriol and by a stronger air blast, the time for the electrolytic action may be lowered to *one* hour. Notwithstanding this, it is not necessary to watch the procedure very carefully. The air necessary for ventilation is obtained from a centrifugal fan (seen at the back of fig. 10) which is directly motor driven. The air is supplied through tubes of ebonite and its speed is regulated by the inlet cocks.
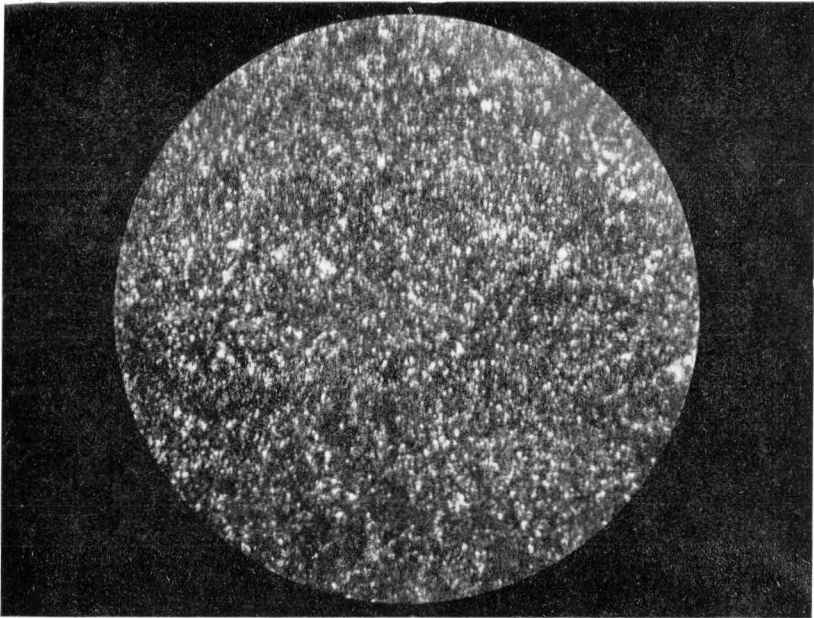
DETAILED DIRECTIONS FOR
PARTIAL PRECIPITATION OF COPPER ON ENGRAVED PLATES.

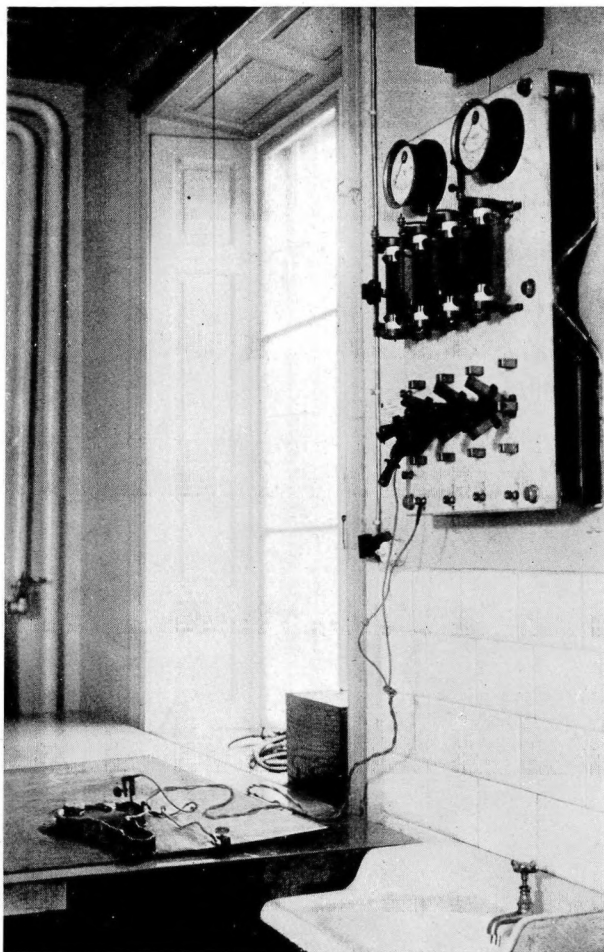The working operations necessary for engraved copper plates are :—

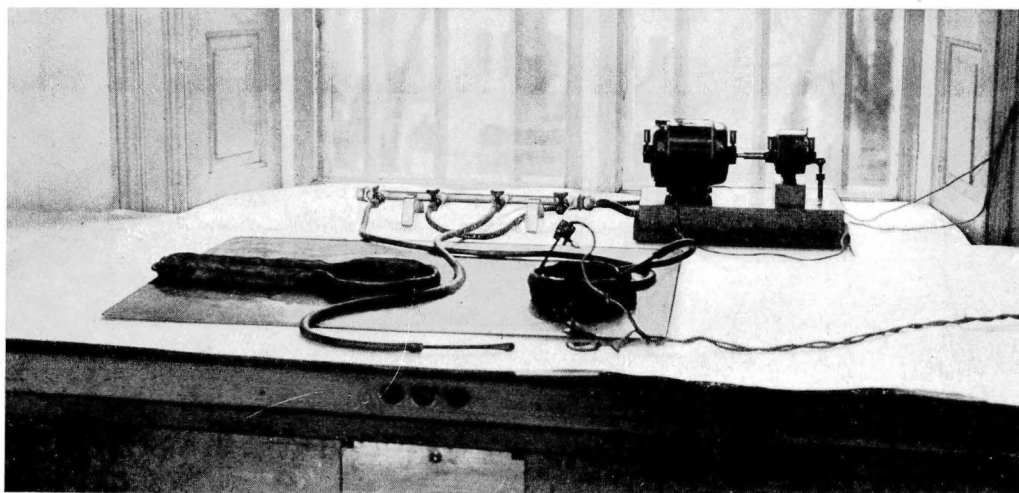*a*) Removal of the iron layer from the "engraving surface" of the plate.
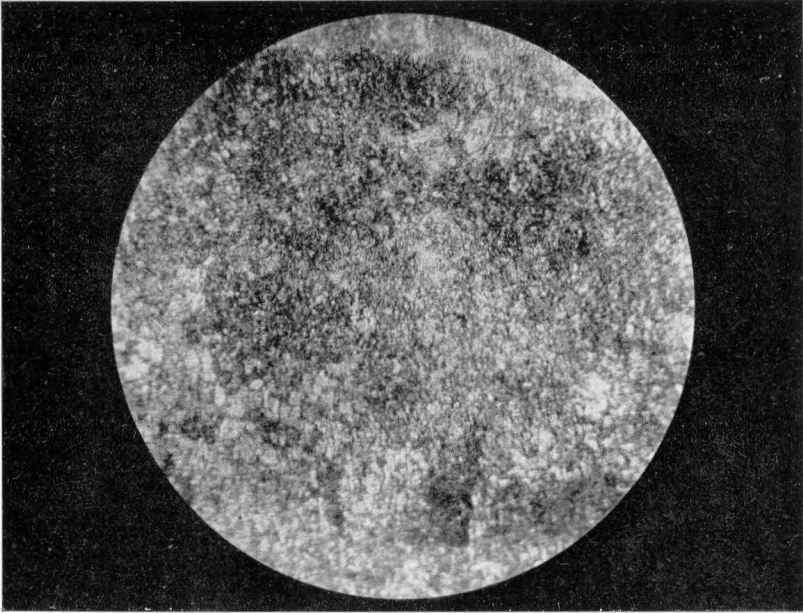
Fig. 7.

PLANE SECTION

Fig. 8.

PLANE SECTION

Fig. 9.

Fig. 10.

b) Application of a protecting layer of wax or varnish on that part of the surface which, during the work, must be protected against direct contact with the etching medium or the solution.

c) The building up of boundary cells around the places to be corrected.

d) Cleaning and etching.

e) Copper precipitation.

f) Polishing.

g) Engraving as necessary.

h) Steel plating.

The iron coating on the engraved plate is removed by dissolving it in a solution of 8 to 10 per cent sulphuric acid, as given in " Directions for producing copper engraving plates."

On, and around the part of the surface which is to be corrected asphalte varnish ("Black Japan" or "fernissa") is painted. When this varnish is dry, some melted wax is applied around the places for correction. The faulty parts which preferably should only be covered with wax, are scratched off with a graver and are hedged round at a suitable distance by walls of mixed plastic material such as clay, wax, glass, ebony, wax-saturated wood, celluloid and the like. The use of plastic clay only is most convenient, but it happens occasionally, with an inferior quality, that so many impurities are dissolved into the solution as to exert a detrimental influence on the copper precipitate. The latter will then become gritty or brittle, with inferior adhesion. With a good quality of plastic clay, it has been found that only a minor part is dissolved into the solution, with good effect, inasmuch as the precipitate becomes more even and hard thereby.

After the building up of the walls the erased parts are etched with some suitable acid mixture consisting, for instance, of 200 grammes of nitric acid, 100 grammes of sulphuric acid, 2 grammes of common salt or else of nitric acid alone. The etching medium is applied by means of a suitable glass syringe or pipette, with an india-rubber bulb, and is quickly removed. A subsequent rinsing with water is immediately effected in the same way. In the case of work covering greater areas, it may however be more advisable to pour on a greater quantity of water. This is quickly removed by turning over the plate and by the removal of the "sluice gate" of a previously arranged drainage.

PRECIPITATION.

To avoid oxidation of the erased surface the rinsing and replenishing of the copper solution after the etching should be done as quickly as possible after the immersion of the anode.

ANODE MATERIAL ; PLACING OF THE ANODE.

The anode material consists of pure electrolytic copper in the shape of sheets (or wire), which is attached to the cell walls parallel to the plate, and above the area to be corrected. The distance between the electrodes is of no great importance (1 cm).

CURRENT DENSITY OF THE BATH.

A. Under normal circumstances an acid copper sulphate solution is used, containing about 220 grammes of vitriol and about 25 grammes of acid per litre. Without any stirring, and almost without supervision, quite a satisfactory precipitate is obtained, as a rule, in about 16 hours with a current density of 0.013 amp. per cm². Now and then the work should be inspected to guard against the appearance of spots or protruding parts.

TEMPERATURE.

The precipitation is now allowed to proceed without any supervision during the night, but care must be taken, in every case, that the temperature does not fall too low. The diffusion will be lessened in too cold a solution, which might even cause a crystallisation of copper sulphate on the anode. The consequence will then be that more and more sulphuric acid will be formed whilst the copper percentage of the solution will decrease to an equal and unpermissible degree. This might easily cause the formation of hydrogen to begin on the cathode together with the copper. The precipitate thus becomes spongy and useless. Likewise, of course, the precipitate will become uneven and bad if vitriol crystals happen to form on the cathode. An insufficient amount of sulphuric acid gives a poor precipitate (cuprous oxide is then formed) even at an ordinary temperature. Equally risky is too high a percentage of sulphuric acid — especially when no stirring takes place — because as mentioned before, hydrogen may form on the cathode giving a spongy precipitate. For this reason the temperature is never kept below 15°. At too high a temperature on the other hand (above 30° *C*), the plastic clay becomes soft and a great quantity of impurities are dissolved.

All the solutions must be kept pure and the fluid must be filtered when necessary. Turbidity must be avoided.

RAPID GALVANOPLASTIC METHOD.

B. I. In a case of urgency recourse may be had to a rapid galvanoplastic method. If certain precautions be taken, a good result may be attained even after 2 or 3 hours. The solution used   this method

might suitably contain 250 gr. of sulphate of copper and 7.5 gr. of sulphuric acid per litre. An effective stirring, by an influx of air for instance, is necessary all the time. A current density of 0.05 to 0,09 amp. per cm^2 is applied.

The anode is wrapped up in cloth of a close texture to prevent any loose particles from falling down from it onto the cathode.

If the current intensity should show a tendency to fall and the tension to rise. this is a sign of some error in one place or another, and it is necessary that the anode and the cathode, as well as the stirring, should be looked to at once.

II. In extremely urgent cases the ultra-rapid galvanoplastic method should be chosen, and a more acid solution should be used; 250-280 gr. of sulphate of copper, 25-35 gr. of sulphuric acid per litre. The current density may be kept at 0.25 to 0.30 amp. per cm^2 provided a vigorous stirring is kept up. In the case of smaller quantities this is easily effected by air ventilation, if the nozzle is placed close to the surface of the cathode in question. For extensive and greater quantities an equally effective movement, brought about by the suitable placing of several nozzles, should be arranged. The electro-depositing may then be effected in one hour.

Cracks in the varnish and wax may cause great warty or lumpy formations, and must be avoided (*). It may be mentioned that quick, or rapid solutions are not suitable for slow precipitation because, at low densities of the current, solutions of a high copper concentration are apt to form cuprous salts and the precipitate will be of poor quality.

When the precipitate has grown sufficiently, the copper solution is removed by means of "draining off", or with a pipette, siphon, or some such means. The plate is rinsed clean, wiped, and may now be polished with a file or a special milling cutter. By covering the plate with waxed paper, it is easy to control the polishing so that it is executed without any risks to the adjacent parts and that it is performed on the same plane as the rest of the surface of the plate.

After re-engraving as necessary, the engraved side of the plate is again steel plated.

Occasional, and less extensive, cavities at the back of old plates corrected by hammering up may advantageously be filled with electrolytic deposits, according to the methods indicated above. In the case of a large number of cavities it will prove, however, more convenient to wax the whole plate, except the cavities, and to execute the precipi-

(*) Further, it must not be forgotten that the chances of an irregular deposit increase at high current density, especially if the primary cathode surface is sharp edged.

tation in the large tanks intended for the production of the plates them-
selves. The current density applied may then be fairly high but the
total precipitation surface is generally so small that an additional cathode
("anode plate") is attached or, preferably and if possible, a simultaneous
precipitation of "alto" and "basso" plates is made in order to enable
a generating set to work economically. It is of course unnecessary — at
least in the case of a large supply of current — to allow a great part
of the current to be wasted in heating the balance resistances.

By reversing the direction of the current in the partial cells, copper
may be electrolytically removed from the plate. The scraping down of
the "alto" engraving with a special steel tool, however, appears to be
a quicker and simpler way of proceeding.

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Concerning the methods mentioned above, it ought, of course, to
be remembered that they are specially adapted to the needs of the
Swedish Hydrographic Office, and according to what is desirable there.
Naturally circumstances may be different at other Hydrographic Offices
and the methods and details can then be varied accordingly.

Stockholm, May 1925.